Development of luminescent europium-based phosphor films

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Table of Contents

Acknowledgements.....	i
Table of Contents.....	iii
Summary.....	viii
List of Figures.....	xiii
List of Tables.....	xix
Chapter 1 Introduction.....	1
1.1 Motivation.....	1
1.2 Objectives.....	4
1.3 Major contribution of the thesis.....	6
1.4 Organization of the thesis.....	10
Chapter 2 Literature review.....	11
2.1 Introduction.....	11
2.2 The oxide-based and sulfide-based phosphor materials.....	11
2.3 The choice of Y_2O_3 and Eu^{3+}	12
2.4 Current research and trends: Increasing the emission efficiency of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films.....	13
2.5 The choice of ZnO and Eu^{3+}	19
2.6 Current research and trends: Energy transfer process from the ZnO to the Eu^{3+} ions.....	20
2.7 The choice of sol-gel process for the preparation of phosphor films.....	22
2.8 Chapter summary.....	24
Chapter 3 Theory of luminescence and thin film preparations, and principle of characterization equipment.....	25
3.1 Introduction.....	25
3.2 Basic concept of luminescence.....	25
3.3 The correlation between optical transition and spectra.....	27
3.4 Luminescence mechanism and LASER.....	28
3.4.1 Photoluminescence.....	29
3.4.2 LASER.....	31
3.5 The tuning of material's bandgap.....	34

3.6	Phosphor materials.....	35
3.6.1	Host material.....	36
3.6.2	Dopant / luminescent center / activator.....	37
3.6.3	Co-dopant.....	38
3.7	Lanthanide rare earth element – the optical center.....	40
3.8	Electronic states of dopant.....	43
3.8.1	Interactions of lanthanide ion in crystal.....	44
3.8.2	Electronic configuration ($ns\ np\ nd\ nf$ configuration).....	46
3.8.3	Coulomb interaction and exchange interaction (L and S).....	47
3.8.4	Spin orbit interaction (J).....	50
3.8.5	Crystal field.....	51
3.9	Introduction to radiative relaxation and non-radiative relaxation.....	53
3.9.1	Radiative relaxation.....	54
3.9.2	Non-radiative relaxation.....	55
3.9.2.1	Multi-phonon emission.....	55
3.9.2.2	Concentration quenching.....	57
3.10	Energy transfer.....	59
3.10.1	Radiative energy transfer.....	60
3.10.2	Non-radiative energy transfer.....	60
3.11	Fundamentals of thin film preparations.....	64
3.11.1	Sol-gel chemistry and processing steps for $Y_2O_3:Eu^{3+}$ -based phosphor films.....	64
3.11.2	Filtered cathodic vacuum arc (FCVA) deposition.....	69
3.11.3	Radio-frequency (RF) magnetron sputtering.....	71
3.12	Characterization equipment.....	73
3.12.1	Spectrofluorometer system (SPEX Fluorolog-3).....	74
3.12.2	Photoluminescence system.....	75
3.12.3	X-ray diffractometer (Siemens D5005).....	77
3.12.4	Fourier Transform Infrared Spectrometer (Perkin Elmer Spectrum 2000).....	78
3.12.5	Surface profile measuring system (Sloan Dektak 3).....	80
3.12.6	Four-point probe measurement (Cascade Microtech. Inc. CPS-06 Contact Probe Station).....	81

3.12.7	Scanning Probe Microscope (Digital Instruments Dimension™ 3000).....	82
3.12.8	Ultraviolet-visible (UV-Vis) spectrophotometer (Hewlett Packard 8453).....	84
3.13	Chapter summary.....	85
Chapter 4	Development of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films by sol-gel.....	86
4.1	Introduction.....	86
4.2	Preparation of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films with yttrium (III) isopropoxide...	86
4.2.1	Sample preparation procedure with yttrium (III) isopropoxide.....	87
4.2.2	Results and discussion.....	89
4.2.2.1	PL excitation and PL emission spectrum.....	89
4.2.2.2	The effect of annealing temperature in RTP.....	92
4.2.2.3	The effect of annealing environment in RTP.....	96
4.2.2.4	The effect of Eu^{3+} dopant concentration.....	97
4.2.2.5	The effect of annealing time in RTP.....	99
4.3	Preparation of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films with yttrium 2-methoxyethoxide..	101
4.3.1	Comparison between yttrium (III) isopropoxide and yttrium 2-methoxyethoxide.....	102
4.3.2	Sample preparation procedure with yttrium 2-methoxyethoxide..	104
4.3.3	Results and discussion.....	106
4.3.3.1	The effect of annealing temperature in RTP.....	106
4.3.3.2	The effect of post-annealing treatment.....	110
4.4	Chapter summary.....	116
Chapter 5	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films with co-dopants.....	117
5.1	Introduction.....	117
5.2	Sample preparation procedure of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films with co-dopants.....	118
5.3	Results and discussion.....	119
5.4	Chapter summary.....	127
Chapter 6	Efficient radiative energy transfer in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure.....	128

6.1	Introduction.....	128
6.2	Preparation of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure.....	130
6.2.1	Sample preparation procedure of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure.....	130
6.2.2	Results and discussion.....	132
6.2.2.1	The effect of Cd dopants to the PL of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure.....	132
6.2.2.2	The effect of Eu^{3+} dopant concentration.....	136
6.3	Preparation of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure.....	137
6.3.1	Sample preparation procedure of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure.....	137
6.3.2	Results and discussion.....	139
6.3.2.1	Ultra-violet (UV) random lasing of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure	139
6.3.2.2	Ultra-violet (UV) random laser pumped red emission of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure	140
6.4	Schematic diagram of radiative energy transfer in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ and the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure.....	144
6.5	Chapter summary.....	146
Chapter 7	Deposition of indium tin oxide (ITO) films.....	148
7.1	Introduction.....	148
7.2	Sample preparation procedure of ITO films.....	149
7.3	Results and discussion.....	150
7.3.1	The effect of deposition pressure.....	150
7.3.2	The effect of substrate temperature.....	151
7.3.3	The effect of oxygen flow.....	153
7.3.4	The effect of post-annealing treatment.....	155
7.4	Chapter summary.....	161
Chapter 8	Conclusion and Recommendations.....	162
8.1	Conclusion.....	162
8.2	Recommendations for further research.....	166
Author's Publications.....		169
Bibliography.....		170

Appendices.....	190
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Summary

Phosphor material is a light-emitting material that shows great potential in many photonic applications such as electronic display devices, optoelectronic devices, and fluorescent lamps. Yttrium oxide doped with europium ions ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ material) is a well-known red-emitting phosphor material with the peak wavelength at about 613nm (5D_0 - 7F_2 emission transition). However, the emission efficiency of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films is still low. Therefore, there is a demand to increase the efficiency of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. The low efficiency of phosphor films is associated with the process conditions, the composition of materials, and the morphology of films. The first objective of this work is to develop high efficiency $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films by optimizing the process conditions and by using the co-dopants, namely Mg^{2+} and Al^{3+} .

Recently, zinc oxide doped with europium ions ($\text{ZnO}:\text{Eu}^{3+}$ material) has attracted considerable interest for future photonic applications. The widespread use of the $\text{ZnO}:\text{Eu}^{3+}$ material in practical applications relies on the energy transfer process from the ZnO to the Eu^{3+} ions. The energy transfer process in the $\text{ZnO}:\text{Eu}^{3+}$ materials is usually mediated by the defect states. However, the efficiency of energy transfer process is still low and the mechanism is not well understood. Another problem related to the practical applications of $\text{ZnO}:\text{Eu}^{3+}$ material is that the defect states in the $\text{ZnO}:\text{Eu}^{3+}$ material that are involved in the energy transfer process are hard to control and reproduce. Therefore, the second objective of this work is to develop ZnO-based material systems which show efficient radiative energy transfer process from the ZnO films to the Eu^{3+} ions without the involvement of the defect states.

This work began with the development of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films by using the sol-gel process. The sol-gel process has three main advantages compared to other thin film preparation methods. These advantages include excellent material stoichiometry, inexpensive raw materials and equipment, and the flexibility to control the composition of materials. The development of efficient $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films by using the sol-gel process involved the optimization of several important process parameters such as concentration of Eu^{3+} dopants, annealing temperature, annealing environment, and annealing duration. The optimum concentration of Eu^{3+} dopant is found to be 12mole% Eu^{3+} (or $\text{Y}_{1.76}\text{Eu}_{0.24}\text{O}_3$). The optimum annealing temperature has been received at 750°C. It has been found that annealing in the rapid thermal processor (RTP) and in vacuum environment is more efficient than that in oxygen and nitrogen atmosphere to eliminate H_2O impurities and hence yields the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films with higher photoluminescent (PL) intensity at wavelength of about 613nm (5D_0 - 7F_2 emission transition). The H_2O impurities have been effectively eliminated after longer annealing time both in the RTP and in the furnace. Furthermore, two sol-gel precursors, namely yttrium 2-methoxyethoxide and yttrium (III) isopropoxide, were used in the fabrication of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. It has been found that the yttrium 2-methoxyethoxide is better than the yttrium (III) isopropoxide in terms of higher stability against moisture sensitivity and the ease of handling during the preparation.

Subsequently, the sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films were incorporated with the Mg^{2+} and Al^{3+} co-dopants in order to enhance the emission efficiency. The effect of Mg^{2+} and Al^{3+} co-dopants on the PL intensity of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films were investigated. Both the Mg^{2+} and Al^{3+} co-dopants have been found to further enhance the PL intensity of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films at wavelength of about 613nm (5D_0 - 7F_2 emission transition) at the optimum concentration of 7mole% Mg^{2+} and 2mole% Al^{3+} ,

respectively. The enhancement of PL intensity by the Mg^{2+} and Al^{3+} co-dopants is explained in terms of the creation of defect states near the $\text{Y}(4d+5s)$ conduction band, which overlap with the charge-transfer state (CTS) of Eu^{3+} ions. The overlap leads to CTS broadening and consequently induces higher absorption and hence the increase of the PL intensity. From the experiment results, a schematic energy band diagram of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films has been constructed.

Having achieved the first objective, the work continued to realize the second objective. In the second part of this work, the author developed the ZnO-based material systems which show efficient radiative energy transfer process from the ZnO films to the Eu^{3+} ions without the involvement of the defect states. The $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films (ZnO films with varied concentration of cadmium (Cd) dopants) and the ZnO films were used in two different experiments. In one experiment, the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films were deposited on top of the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films and this resulted in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure. By varying the concentration of Cd dopants, the peak wavelength of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films was tuned from 381nm (x value is 0mole%) to 394nm (x value is 8mole%) so that the emission spectrum of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films overlapped with the absorption spectrum of Eu^{3+} ions peaked at 394nm ($^7F_0-^5L_6$ absorption transition). The peak wavelength shifts because the bandgap of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films takes an intermediate value between the bandgap of the ZnO and CdO, which is influenced by the concentration of Cd dopants (i.e. the x value of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films). When the peak wavelength of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films shifts towards the absorption wavelength of Eu^{3+} ions at 394nm, this results in larger spectral overlap and hence an increase of the PL intensity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films at about 611nm ($^5D_0-^7F_2$ emission transition). This is because the larger spectral overlap leads to more efficient radiative energy transfer process from the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films to the Eu^{3+} ions of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films.

In another experiment, the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films were deposited on top of the ZnO films to form the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure. The ultra-violet (UV) random lasing spectrum in the wavelength range of about 385–397nm is produced from the polycrystalline ZnO films with an optical excitation (Nd:YAG laser) at room temperature. In this experiment, the UV random lasing spectrum of ZnO films was tuned to overlap with the absorption spectrum of Eu^{3+} ions peaked at 394nm (${}^7F_0\text{--}{}^5L_6$ absorption transition) by increasing the pump power of Nd:YAG laser. It has been found that increasing the pump power of Nd:YAG laser results in larger spectral overlap between the UV random lasing spectrum of ZnO films and the absorption spectrum of Eu^{3+} ions. The large spectral overlap leads to very efficient radiative energy transfer from the ZnO films to the Eu^{3+} ions of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. Hence, the UV random laser pumped red emission centered at about 611nm (${}^5D_0\text{--}{}^7F_2$ emission transition) has been observed. A schematic energy diagram has been constructed to explain the radiative energy transfer process in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure and the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure.

As an additional work, the indium tin oxide (ITO) films were also developed by using radio-frequency (RF) magnetron sputtering. The process parameters such as substrate temperature, oxygen gas flow rate, post-annealing temperature, and post-annealing ambient for forming the ITO films were optimized. The ITO film post-annealed at 500°C in vacuum has a low resistivity of about $3.49 \times 10^{-4} \Omega\text{cm}$. Comparison of preferred crystal growth orientation in the X-ray diffraction (XRD) characterization supports the model of oxygen diffusion from air into the ITO films during post-annealing. The diffusion of oxygen atoms from air results in (400) preferred crystal growth orientation. Moreover, the atomic force microscope (AFM) images reveal that the ITO films post-annealed in vacuum have larger grain size compared to those post-annealed in air. The

resistivity of ITO films post-annealed in vacuum is lower because of reduced grain boundary scattering.

List of Figures

Figure 3-1:	Electromagnetic spectra. The expanded visible wavelength range shows the wavelength corresponds to each color emission.....	25
Figure 3-2:	Schematic electronic states and the corresponding emission spectrum of an isolated atom or ion.....	28
Figure 3-3:	Schematic illustration of photoluminescence for (a) dopant and (b) host material	29
Figure 3-4:	Formation of a closed-loop path for light through recurrent scatterings in ZnO powders. The filled circles represent the ZnO powders.....	33
Figure 3-5:	The lanthanide and actinide rare earth elements in periodic table.	41
Figure 3-6:	Spectra splitting of lanthanide ions due to the Coulomb, spin-orbit, and crystal field interactions in decreasing interaction strength.....	45
Figure 3-7:	Schematic diagram for partially spectra splitting of Eu^{3+} ion due to the Coulomb, spin-orbit, and crystal field interactions in decreasing interaction strength.....	46
Figure 3-8:	Schematic representative of orbital energy according to principle quantum number (n) and orbital quantum number (l).....	46
Figure 3-9:	(a) The orbital angular momentum (L) and (b) spin angular momentum (S) exhibits quantization.....	48
Figure 3-10:	Illustration of the vector L and S precess about vector J	51
Figure 3-11:	(a) The shape of $3d$ orbital and ligand positions (the open and close circle represents the ligands with octahedral and tetrahedral symmetry, respectively) (b) The splitting of the degenerate $3d$ orbital under octahedral symmetry.....	52
Figure 3-12:	“Stokes shift”– the shift of wavelength between the absorption and the emission spectra.....	54
Figure 3-13:	Multi-phonon emission through phonon bridging after excitation	56
Figure 3-14:	Schemes of concentration quenching in which the energy migration from dopants (open circles) to quenching center (close triangle) and finally non-radiative relaxation occurs (top). Concentration quenching is represented by the resonance energy state scheme (bottom).....	58

Figure 3-15:	Schematic representative of the Coulombic interaction between dopant D* and dopant A.....	61
Figure 3-16:	Schematic representative of the exchange interaction between dopant D* and dopant A	62
Figure 3-17:	Phonon-assisted energy transfer.....	63
Figure 3-18:	The typical preparation steps of Y ₂ O ₃ :Eu ³⁺ -based phosphor films in the sol-gel process.....	65
Figure 3-19:	Spin coating process, from sol dispensing (deposition) until the formation of gel films (evaporation).....	68
Figure 3-20:	Schematic diagram of FCVA system	70
Figure 3-21:	Schematic diagram of the cathodic arc spot with the generation of electron, atom, ion, plasma, and macroparticle after a mechanical striker hits the target surface.....	70
Figure 3-22:	Schematic diagram shows the sputtering process.....	72
Figure 3-23:	Schematic diagram of spectrofluorometer.....	74
Figure 3-24:	Schematic diagram of photoluminescence system.....	76
Figure 3-25:	Schematic diagram of X-ray diffractometer.....	77
Figure 3-26:	Schematic diagram of Fourier Transform Infrared Spectrometer..	79
Figure 3-27:	Block diagram of surface profile measuring system.....	80
Figure 3-28:	Schematic diagram of four-point probe measurement unit.....	81
Figure 3-29:	Schematic diagram of tapping mode atomic force microscope....	83
Figure 3-30:	Optical system of UV-Vis spectrophotometer.....	84
Figure 4-1:	Preparation of Y ₂ O ₃ :Eu ³⁺ phosphor films by the sol-gel process with yttrium (III) isopropoxide precursor.....	87
Figure 4-2:	Rapid thermal annealing profile.....	88
Figure 4-3:	PL excitation spectrum of Y ₂ O ₃ :12%Eu ³⁺ phosphor films from 200nm to 300nm (λ _{emi.} =613nm).....	89
Figure 4-4:	PL excitation spectrum of Y ₂ O ₃ :12%Eu ³⁺ phosphor films from 350nm to 500nm (λ _{emi.} =613nm).....	90

Figure 4-5:	(a) PL emission spectrum of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor film from 550nm to 730nm ($\lambda_{\text{ext.}}=246\text{nm}$) (b) The energy diagram shows the excitation and emission transition in the electronic states of Eu^{3+} dopants (Solid arrows denote radiative transition whereas dashed arrows denote non-radiative transition after excitation)...	91
Figure 4-6:	PL intensity of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films at 613nm as a function of annealing temperature in RTP.....	93
Figure 4-7:	XRD patterns of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of annealing temperature in RTP.....	94
Figure 4-8:	FTIR spectra of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of annealing temperature in RTP.....	95
Figure 4-9:	PL emission spectra of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of annealing environment in RTP ($\lambda_{\text{ext.}} = 246\text{nm}$). Inset shows the FTIR spectra of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films annealed at different environments.....	96
Figure 4-10:	PL intensity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films as a function of Eu^{3+} dopant concentration at 750°C	97
Figure 4-11:	PL intensity of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of annealing time in RTP.....	100
Figure 4-12:	PL emission spectra of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of annealing time in RTP ($\lambda_{\text{ext.}} = 246\text{nm}$). Inset shows the FTIR spectra of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films annealed at different annealing times.....	100
Figure 4-13:	Comparison of the molecular structure between (a) yttrium (III) isopropoxide and (b) yttrium 2-methoxyethoxide (--- line represents the donation of unshared pair of electrons (lone pair) from the O atom to the Y atom).....	102
Figure 4-14:	Preparation of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films by the sol-gel process with yttrium 2-methoxyethoxide precursor	104
Figure 4-15:	XRD patterns of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films annealed at different annealing temperatures in RTP.....	106
Figure 4-16:	XRD patterns of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films annealed at 750°C , 950°C , 1150°C , and 1250°C in furnace.....	107
Figure 4-17:	PL spectra corresponds to the change of crystal structures from 750°C to 1250°C ($\lambda_{\text{ext.}} = 254\text{nm}$).....	107
Figure 4-18:	Illustration of two Y^{3+} crystallographic sites in cubic Y_2O_3	108

Figure 4-19:	PL intensity ratio at 590nm to 613nm ($R=I(^5D_0-^7F_1)/I(^5D_0-^7F_2)$) corresponds to the change of crystal structures from 750°C to 1250°C.....	109
Figure 4-20:	PL emission spectra of $Y_2O_3:12\%Eu^{3+}$ phosphor films as a function of post-annealing time ($\lambda_{ext.} = 254nm$).....	110
Figure 4-21:	FTIR spectra of $Y_2O_3:12\%Eu^{3+}$ phosphor films as a function of post-annealing time.....	111
Figure 4-22:	XRD patterns of $Y_2O_3:12\%Eu^{3+}$ phosphor films as a function of post-annealing time.....	112
Figure 4-23:	The full-width half-maximum (FWHM) of (222) peak decreases with the increase of post-annealing time at 750°C.....	113
Figure 4-24:	Average grain size of $Y_2O_3:12\%Eu^{3+}$ phosphor films increases with post-annealing time at 750°C. The grain size is obtained by manually measuring the grains of AFM image.....	114
Figure 4-25:	AFM images of $Y_2O_3:12\%Eu^{3+}$ phosphor films as a function of post-annealing time at 750°C: (a) No post-annealing (b) post-annealing 1 hour (c) post-annealing 5 hours (d) post-annealing 11 hours (e) post-annealing 20 hours.....	115
Figure 5-1:	Preparation of Mg^{2+} and Al^{3+} co-doped $Y_2O_3:Eu^{3+}$ phosphor films by a sol-gel process with yttrium (III) isopropoxide precursor.....	118
Figure 5-2:	PL emission spectrum of $Y_2O_3:Eu^{3+}$ phosphor films ($\lambda_{ext.}=246nm$). Inset shows the corresponding PL excitation spectrum of $Y_2O_3:Eu^{3+}$ phosphor films.....	119
Figure 5-3:	PL emission spectra as a function of Mg^{2+} co-dopant concentration in $Y_2O_3:12\%Eu^{3+}$ phosphor films ($\lambda_{ext.}=246nm$).....	120
Figure 5-4:	PL emission spectra as a function of Al^{3+} co-dopant concentration in $Y_2O_3:12\%Eu^{3+}$ phosphor films ($\lambda_{ext.} = 246nm$).....	121
Figure 5-5:	XRD patterns of Mg^{2+} co-doped $Y_2O_3:12\%Eu^{3+}$ phosphor films at various co-dopant concentrations.....	122
Figure 5-6:	XRD patterns of Al^{3+} co-doped $Y_2O_3:12\%Eu^{3+}$ phosphor films at various co-dopant concentrations.....	123
Figure 5-7:	Phase diagram of $MgO-Y_2O_3$	123
Figure 5-8:	Phase diagram of $Y_2O_3-Al_2O_3$	124
Figure 5-9:	PL excitation spectra of $Y_2O_3:12\%Eu^{3+}$ phosphor films as a function of Mg^{2+} co-dopant concentration ($\lambda_{emi.} = 613nm$).....	125

Figure 5-10:	PL excitation spectra of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of Al^{3+} co-dopant concentration ($\lambda_{\text{emi.}} = 613\text{nm}$).....	125
Figure 5-11:	Proposed mechanism due to co-dopants. Defect states created by the co-dopants cause the broadening of CTS. The light grey box denotes the broadening of CTS caused by the co-dopants.....	127
Figure 6-1:	Preparation of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure by the sol-gel process.....	130
Figure 6-2:	The overlapping spectra between the PL emission spectra of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films (solid line, $\lambda_{\text{ext.}}=355\text{nm}$) and the absorption spectrum of Eu^{3+} ions (dash dot line).....	132
Figure 6-3:	Interpolation of bandgap of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films prepared in this experiment as a function of Cd dopant concentration. The inset shows the bandgap of ZnO and CdO. The closed squares represent the bandgap of ZnO films obtained in this experiment. The open circle at the other endpoint represents the bandgap of CdO films taken from Ref. 6-2 & Ref. 6-3. The gradient of both dot-dot line is the same.....	133
Figure 6-4:	The relation between the spectral overlap and the red emission intensity at 611nm of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure as a function of Cd dopant concentration. The ${}^7F_0-{}^5L_6$ absorption transition of Eu^{3+} peaks at 394nm is used for the estimation of spectral overlap.....	135
Figure 6-5:	PL emission spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure at 611nm ($\lambda_{\text{ext.}}=355\text{nm}$).....	135
Figure 6-6:	PL emission spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ with different concentration of Eu^{3+} ions deposited on top of the $\text{Zn}_{0.92}\text{Cd}_{0.08}\text{O}$ films ($\lambda_{\text{ext.}}=355\text{nm}$). The inset shows the concentration quenching at 12mole% Eu^{3+} ions.....	136
Figure 6-7:	Preparation steps of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure.....	138
Figure 6-8:	The light-light characteristics of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure in UV wavelength range. The inset shows the UV random lasing spectra of the structure at different pump powers ($\lambda_{\text{ext.}}=355\text{nm}$ with Nd:YAG laser).....	139
Figure 6-9:	The overlapping spectra at three different pump powers at 0.4 MW/cm^2 , 5.5 MW/cm^2 , and 8.0 MW/cm^2 . Dash dot line represents the absorption spectrum of Eu^{3+} ions. Solid lines represent the emission spectra of ZnO films. (The magnification of the ZnO emission spectra is indicated in the bracket) ($\lambda_{\text{ext.}}=355\text{nm}$ with Nd:YAG laser).....	140

Figure 6-10:	The relation between the spectral overlap and the UV random laser pumped red emission intensity at 611nm of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure as a function of Nd:YAG laser pump power. The ${}^7F_0-{}^5L_6$ absorption transition of Eu^{3+} peaks at 394nm is used for the estimation of spectral overlap	142
Figure 6-11:	The UV random laser pumped red emission spectra of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure at three different pump powers at (a)0.4 MW/cm ² , (b)5.5 MW/cm ² , and (c)8.0 MW/cm ² ($\lambda_{\text{ext.}}=355\text{nm}$ with Nd:YAG laser)	143
Figure 6-12:	An unified schematic diagram of radiative energy transfer process. E_g is the original bandgap of the ZnO films. E_g' is the new bandgap after doping with 8mole% Cd dopants (for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure) or pumped with high power Nd:YAG laser (for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure).....	145
Figure 7-1:	Preparation and optimization process flow of ITO films.....	149
Figure 7-2:	Deposition rate of ITO films as a function of Ar deposition pressure.....	150
Figure 7-3:	Influence of substrate temperature to the resistivity of ITO films.	151
Figure 7-4:	XRD patterns of ITO films as a function of substrate temperature.....	152
Figure 7-5:	Influence of oxygen gas flow rate to the resistivity of ITO films..	153
Figure 7-6:	XRD patterns of as-deposited ITO films as a function of oxygen gas flow rate	154
Figure 7-7:	AFM images of ITO films: (a) reference sample (as-deposited 300°C) (b) post-annealing at 400°C in air (c) post-annealing at 500°C in air (d) post-annealing at 400°C in vacuum (e) post-annealing at 500°C in vacuum.....	156
Figure 7-8:	Influence of post-annealing temperature and ambient to the resistivity of ITO films. 300°C is the as-deposited ITO film which serves as a reference sample.....	157
Figure 7-9:	(a) XRD patterns of ITO films post-annealed in air from temperature 350 °C to 500°C (b) XRD patterns of ITO films post-annealed in vacuum from temperature 350°C to 500°C. In both figures, 300°C is the as-deposited ITO film which serves as a reference sample.....	159
Figure 7-10:	Influence of post-annealing temperature and ambient to the transmittance of ITO films. 300°C is the as-deposited ITO film which serves as reference sample.....	160

List of Tables

Table 3-1:	Some examples of luminescence based on excitation modes....	26
Table 3-2:	The configuration and the number of optically active electron of trivalent lanthanide ions.....	43
Table 3-3:	The symbol L is the total orbital angular momentum quantum number corresponds to orbital angular momentum quantum number (l).....	49
Table 7-1:	Comparison of grain size and surface roughness of ITO films post-annealed in vacuum and air. The grain size was obtained by manually measuring the grains of AFM image. The Root-Mean-Square (RMS) surface roughness is an automated statistical measurement by the computer.....	157

Chapter 1 Introduction

1.1 Motivation

Luminescent material is a solid that converts particular types of energy into an electromagnetic radiation or light. The luminescent material is also called phosphor material. The phosphor material consists of host material and dopant [1-1]. In general, the phosphor materials can either be in the form of thin films or powders. Depending on the applications, the phosphor materials in the form of thin films or powders can be used. The phosphor materials play an important role in our daily life. For example, the phosphor materials are used in many photonic applications, such as electronic display devices [1-2], optoelectronic devices [1-3], fluorescent lamps [1-4] and so on. For practical applications, the phosphor materials should have high emission efficiency and consume less power [1-5]. Yttrium oxide doped with europium ions ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$) is a well-known red-emitting phosphor material with the peak emission wavelength at about 613nm (5D_0 - 7F_2 emission transition). The Y_2O_3 has been identified as a promising host material because it has low phonon energy that can reduce non-radiative transition probability [1-1]. Furthermore, the Y_2O_3 has trivalent substitution site for the dopants from lanthanide rare earth series [1-1]. Hence, the Y_2O_3 was selected as the host material in this work. The review about the choice of Y_2O_3 host materials and Eu^{3+} dopants will be discussed in details in section 2.3. However, the emission efficiency of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films is still low. In general, the low efficiency of phosphor films is associated with the process conditions, the composition of materials, and the morphology of films [1-6],[1-7]. Hence, considerable efforts have been devoted to increase the efficiency of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films in the last few years [1-8]-[1-15].

Generally, three different approaches have been used to increase the emission efficiency of phosphor films, namely by developing the process conditions, varying the composition of materials, and modifying the morphology of films. The literature review of these approaches will be given in section 2.4. Among the three approaches, developing the process conditions and varying the composition of materials are very important and challenging. In this work, the author therefore focused more on these two approaches. Developing the process conditions is necessary for each preparation method because only the phosphor films prepared in optimum process conditions can achieve highest efficiency. The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films have been prepared by using the deposition method such as pulsed laser deposition [1-16]-[1-19], sputtering [1-20], electron beam evaporation [1-21], metal-organic chemical vapor deposition (MOCVD) [1-22], electrodeposition [1-23], and sol-gel [1-24]-[1-27]. The sol-gel process is distinguished from some of the vacuum-based deposition methods mentioned above (e.g. sputtering, electron beam evaporation, and pulsed laser deposition) by its excellent material stoichiometry, inexpensive raw materials and equipment, and the flexibility to control material composition [1-24],[1-28]-[1-31]. Therefore, the sol-gel process was chosen to prepare the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films in this work. The choice of sol-gel process will be discussed in details in section 2.7.

The second approach, namely varying the composition of materials, by adding co-dopants into the phosphor films is based on the thought that the interaction between the dopants and the co-dopants may induce new spectroscopic phenomenon that may increase the emission efficiency of phosphor materials. The co-dopants are the additional elements added into the phosphor materials [1-1]. The co-dopants can usually be broadly classified into two types, namely lanthanide rare earth ions (lanthanide co-dopants) and non-lanthanide rare earth ions (non-lanthanide co-dopants). The

mechanism related to lanthanide co-dopants is the energy transfer from the co-dopants to the dopants [1-32]-[1-36]. Contrary to the lanthanide co-dopants, the roles of non-lanthanide co-dopants are not well established. For example, the most studied non-lanthanide co-dopant in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films is Li^+ . It has been reported that the incorporation of Li^+ co-dopant into the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films may induce changes of crystallinity and surface roughness [1-8],[1-10]. However, Nissamudeen *et al.* explains that the Li^+ co-dopant may help to reduce the processing temperature of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films [1-11]. This shows that the roles of non-lanthanide co-dopants warrant further investigations. In this work, the author therefore investigated the roles of two non-lanthanide co-dopants (Mg^{2+} and Al^{3+}) in increasing the emission efficiency of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. In summary, the first objective of this work is to develop high efficiency $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films by optimizing the process conditions of sol-gel process and by using the Mg^{2+} and Al^{3+} co-dopants.

Recently, zinc oxide doped with europium ions ($\text{ZnO}:\text{Eu}^{3+}$) material has attracted considerable interest for future photonic applications. The wide applications of $\text{ZnO}:\text{Eu}^{3+}$ material in future relies on the efficient energy transfer from the ZnO to the Eu^{3+} ions, in which the red emission from the Eu^{3+} ions is expected. However, the energy transfer from the ZnO to the Eu^{3+} ions is still not efficient [1-37]-[1-41]. The inefficient energy transfer is generally explained due to the very short lifetime of the excitons in ZnO [1-38],[1-42],[1-43],[1-45],[1-46]. Therefore, the energy transfer process mediated by the defect states is always used to explain the observation of red emission from the Eu^{3+} ions [1-37],[1-38],[1-42]-[1-44]. It has been proposed that the defect states in ZnO can temporarily store the excitation energy [1-37],[1-38],[1-42]-[1-44], which will then facilitate the energy transfer from the ZnO to the Eu^{3+} ions. Furthermore, the radiative energy transfer and non-radiative energy transfer have also

been proposed [1-43],[1-47],[1-48]. Another problem is that the defect states involved in the energy transfer process are practically hard to control and reproduce, and the origin of the defect states is still not clear. Therefore, the second objective of this work is to develop ZnO-based material systems that can show efficient radiative energy transfer from the ZnO films to the Eu^{3+} ions without the involvement of the defect states. The details of the approaches will be described in section 1.2 below.

With all these considerations, the thesis entitled “Development of luminescent Europium-based phosphor films” has therefore been proposed.

1.2 Objectives

As stated above, there are two objectives in this work. The first objective is to develop high efficiency $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films by optimizing the process conditions of sol-gel process and by using the Mg^{2+} and Al^{3+} co-dopants. The second objective is to develop ZnO-based material systems which can show efficient radiative energy transfer from the ZnO films to the Eu^{3+} ions without the involvement of the defect states. To achieve these two objectives, the author has divided the work into 4 sub-sections as follows:

1. To develop $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films by using the sol-gel process: The Eu^{3+} ions which generate red emission were doped into the Y_2O_3 host materials by using the sol-gel process. The process parameters of sol-gel process such as concentration of Eu^{3+} dopants, annealing temperature, annealing environment, and annealing duration have been optimized at this stage in order to prepare high efficiency $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films.
2. To develop high efficiency $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films by using the Mg^{2+} and Al^{3+} co-dopants: The effect of Mg^{2+} and Al^{3+} co-dopants to the photoluminescent (PL)

property of the sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films has been studied. The mechanism that leads to the increased PL intensity at 613nm (5D_0 - 7F_2 emission transition) has been investigated.

3. To develop $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure: The sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films were deposited on top of the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films (ZnO films with varied concentration of cadmium (Cd) dopants). By incorporating the Cd dopants, the emission wavelength of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films has been tuned to shift towards the absorption wavelength of Eu^{3+} ions at 394nm (7F_0 - 5L_6 absorption transition). This is to increase the spectral overlap which leads to an efficient radiative energy transfer. The mechanism that leads to the increased PL intensity from the Eu^{3+} ions of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films at about 611nm (5D_0 - 7F_2 emission transition) has been proposed.

4. To develop $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure: The sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films were deposited on top of the ZnO films. The ultra-violet (UV) random lasing spectrum of ZnO films has been tuned to overlap with the absorption wavelength of Eu^{3+} ions at 394nm (7F_0 - 5L_6 absorption transition) by increasing the pump power of Nd:YAG laser. This is to increase the spectral overlap which leads to very efficient radiative energy transfer. The mechanism that leads to the UV random laser pumped red emission from the Eu^{3+} ions of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films at about 611nm (5D_0 - 7F_2 emission transition) has been proposed.

In addition, the indium tin oxide (ITO) films that are widely used as a transparent electrode material in many photonic devices have also been developed.

1.3 Major contribution of the thesis

The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films have been developed by the sol-gel process. The sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films have potential to be used as phosphor materials for photonic applications. The red emission of the samples has been clearly observed by naked eye in a bright room under UV excitation. The major contributions of this work are summarized as follows:

- i. To achieve the first objective of this work, a series of experiments were conducted to optimize the process conditions for preparing the high efficiency $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. The sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films show the most intense 613nm red emission (5D_0 - 7F_2 emission transition) after rapid thermal processing (RTP) at temperature of 750°C. Annealing temperature beyond 750°C causes the orange emission of the films due to the change of the crystal structures. The study on RTP annealing environment shows that the vacuum environment is better than in oxygen and nitrogen atmosphere. This is attributed to the efficient elimination of OH impurities among the three RTP annealing ambients (vacuum, oxygen, and nitrogen). The optimum Eu^{3+} dopant concentration is 12mole% (or $\text{Y}_{1.76}\text{Eu}_{0.24}\text{O}_3$). This maybe related to the homogeneous mixing of precursors in the sol-gel process. The author has also shown that the post-annealing treatment after RTP annealing can considerably enhance the PL intensity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. This is attributed to the grain growth after prolonged post-annealing treatment and the elimination of OH impurities. The results will be presented in chapter 4. The results of this work have been published in Paper-I and Paper-II (please see the details in page 9).
- ii. Consistent with the first objective of this work, the incorporation of Mg^{2+} and Al^{3+} co-dopants into the sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films has led to the increase of PL intensity at 613nm (5D_0 - 7F_2 emission transition). A model leading to the increase of PL intensity has been proposed according to the schematic energy band diagram with

co-dopants. This model has been explained in terms of the increase of absorption. The absorption from the ground state to the charge-transfer state (CTS) increases because of the overlap between the defect states created by the co-dopants with the CTS of Eu^{3+} ions near the $\text{Y}(4d+5s)$ conduction band. The results will be presented in chapter 5. The results of this work have been published in Paper-III (please see the details in page 9).

iii. To achieve the second objective, the author has developed the ZnO-based material systems which could show efficient radiative energy transfer process from the ZnO films to the Eu^{3+} ions without the involvement of the defect states. The $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films and the ZnO films were used in two different experiments. In one experiment, the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films were deposited on top of the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films and this structure was denoted as $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure. The peak wavelength of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films has been tuned from 381nm (x value is 0mole%) towards the absorption wavelength of Eu^{3+} ions at 394nm (${}^7F_0-{}^5L_6$ absorption transition) by increasing the concentration of Cd dopants. The PL intensity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films at about 611nm (${}^5D_0-{}^7F_2$ emission transition) has been observed to increase when the peak wavelength of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films shifts towards the absorption wavelength of Eu^{3+} ions, which causes larger spectral overlap. The larger spectral overlap leads to more efficient radiative energy transfer. The results will be presented in chapter 6. The results of this work have been published in Paper-IV (please see the details in page 9).

iv. Furthermore, in another experiment, the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films were deposited on top of the ZnO films and this structure was denoted as $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure. The UV random lasing spectrum of ZnO films has been tuned to overlap with the absorption wavelength of Eu^{3+} ions at 394nm (${}^7F_0-{}^5L_6$ absorption transition) by controlling the pump power of Nd:YAG laser. At room temperature, a strong UV random laser pumped red emission centered at about 611nm (${}^5D_0-{}^7F_2$ emission transition) has been observed in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure. Note that the UV random

laser pumped red emission could be observed by naked eye. It is because the strong spectral overlap between the emission spectrum and the absorption spectrum of the two films leads to very efficient radiative energy transfer from the ZnO films to the Eu^{3+} ions. The results will be presented in chapter 6. The results of this work have been published in Paper-V (please see the details in page 9).

v. In addition to the works related to $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films and ZnO-based material systems ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure) described above, the indium tin oxide (ITO) films that have been widely used as a transparent electrode material in many photonic devices have also been developed in this work by using the radio-frequency (RF) sputtering deposition. The author has developed the ITO films through a systematic study on several process parameters such as substrate temperature, oxygen gas flow rate, post-annealing temperature, and post-annealing ambient. Atomic force microscope (AFM) images show that the ITO films post-annealed in vacuum have lower resistivity compared to the ITO films post-annealed in air. It is because the ITO films post-annealed in vacuum have larger grain size reduces the grain boundary scatterings. The author has also related the model of oxygen diffusion with the X-ray diffraction (XRD) results. The diffusion of oxygen atoms from air results in (400) preferred crystal growth orientation. The results will be presented in chapter 7. The results of this work have been published in Paper-VI (please see the details in page 9).

The results of this work have been reported in 6 publications below.

[Paper-I] M.K.Chong, K.Pita, and C.H.Kam, "Photoluminescence of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ thin film phosphors by sol-gel deposition and rapid thermal annealing," *Journal of Physics and Chemistry of Solids*, vol. 66, pp. 213-217, Jan 2005.

[Paper-II] M.K.Chong, K.Pita, and C.H.Kam, "Thermal annealing effect on $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films prepared by yttrium 2-methoxyethoxide sol-gel precursor," *Materials Chemistry and Physics*, vol. 100, pp.329-332, Dec 2006.

[Paper-III] M.K.Chong, K.Pita, and C.H.Kam, "Photoluminescence of sol-gel-derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ thin-film phosphors with Mg^{2+} and Al^{3+} co-doping," *Applied Physics A: Materials Science & Processing*, vol. 79, pp. 433-437, Aug 2004.

[Paper-IV] M. K. Chong, Q. V. Vu, and K. Pita, "Red emission through radiative energy transfer from wavelength-tunable $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ layers to $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films," *Electrochemical and Solid State Letters*, vol. 13, pp. J50-J52, Feb 2010.

[Paper-V] M.K.Chong, A.P.Abiyasa, K.Pita, and S.F.Yu, "Visible red random lasing in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ polycrystalline thin films by energy transfer from ZnO films to Eu^{3+} ," *Applied Physics Letters*, vol. 93, pp. 151105-151105, Oct 2008.

[Paper-VI] M.K.Chong, K.Pita, and S.T.H.Silalahi, "Correlation between diffraction patterns and surface morphology to the model of oxygen diffusion into ITO films," *Materials Chemistry and Physics*, vol. 115, pp. 154-157, May 2009.

1.4 Organization of the thesis

The organization of this dissertation is as follows. Chapter 1 mainly outlines the motivation, objectives, major contributions, and the organization of the thesis. This chapter discloses the spirit of this work. In chapter 2, the author reviews the current research and trends in increasing the emission efficiency of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films and energy transfer process from the ZnO to the Eu^{3+} ions. Chapter 3 is related to the theory of luminescence, theory of thin films preparation, and the working principle of characterization equipment. This will prepare the reader to understand the explanation and the argument in the section of results and discussion. The development work of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films and ZnO-based material systems are reported in the later three chapters. The development works of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films with the sol-gel process are reported in chapter 4. The effect of Mg^{2+} and Al^{3+} co-dopants to the sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films is reported in chapter 5. Chapter 6 presents the results of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ and the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure. The red emission has been observed in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure. The UV random laser pumped red emission has been observed in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure. The ITO films are an important constituent layer in many photonic devices. The development works of ITO films are deferred to chapter 7. The conclusion of this work and outlook for future works are finally summarized in chapter 8.

Chapter 2 Literature Review

2.1 Introduction

In this chapter, the literature review of oxide-based and sulfide-based phosphor materials will be firstly presented. The literature review of these phosphor materials will lead the author to explain why the yttrium oxide (Y_2O_3) and the europium ion (Eu^{3+}) was respectively chosen as the host material and the dopant in this work. Subsequently, the literature related to the approaches used to increase the emission efficiency of yttrium oxide doped with europium ions ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$) phosphor films are reviewed. This is related to the first objective of this work. This will be followed by the literature related to the energy transfer process from the zinc oxide (ZnO) to the Eu^{3+} ions, which is related to the second objective of this work. The choice of thin films preparation methods is presented in the last section.

2.2 The oxide-based and sulfide-based phosphor materials

In this section, the author reviews the oxide-based and sulfide-based phosphor materials and justifies the use of the oxide-based phosphor materials in this work. The introduction of phosphor material is deferred to section 3.6 in chapter 3. Generally, the phosphor materials can be loosely grouped into 2 categories in terms of chemical composition, namely oxide-based and sulfide-based phosphor materials. In recent years, considerable research interest has been focused on the oxide-based phosphor materials. Through this effort, a vast number of binary and ternary oxide-based phosphor materials have been developed. Some examples of oxide-based host materials are Y_2O_3 [2-1],[2-2], Y_2SiO_5 [2-3]-[2-5], Zn_2SiO_4 [2-6],[2-7], Y_2GeO_5 [2-8], Zn_2GeO_4 [2-9], and many others in Ref. 2-10. Of course, there are some good justifications why the oxide-based phosphor materials are attracting much attention. First and foremost, the oxides have

higher chemical inertness than sulfide-based phosphor materials [2-5],[2-11],[2-12]. This is important since the phosphor materials are usually exposed to moisture during operation. Secondly, the oxides are more thermally stable than the sulfide-based phosphor materials. For applications in some electronic display devices such as cathode-ray tubes (CRTs) and field emission displays (FEDs), the electron beam bombardment is imperative. The sulfides are unstable under electron beam bombardment which leads to the degradation of field emitters because of the corrosive gases [2-13],[2-14]. In addition, the oxides can be fabricated in the presence of moisture whereas the sulfide-based host materials such as ZnS, SrS, CaS, SrGa₂S₄, and CaGa₂S₄ are unstable in water [2-12],[2-15]-[2-17]. This is why commercial production must be done in vacuum conditions if the sulfide-based phosphor materials are used. Finally, the oxide-based host materials are abundant [2-18]. In fact, most of the natural mineral crystals are oxides.

2.3 The choice of Y₂O₃ and Eu³⁺

The author just gave justifications why the oxides are better than sulfide-based phosphor materials in section 2.2. Among various oxide-based host materials, the Y₂O₃ is an appealing candidate because of its excellent physical properties. Y₂O₃:Eu³⁺ is one of the promising oxide-based red-emitting phosphor materials [2-19],[2-20]. It comes as no surprise that Y₂O₃ has been chosen as the host material in this work. Below are some reasons why the Y₂O₃ is chosen. Firstly, Y₂O₃ has low phonon energy. The highest phonon energy is about 600cm⁻¹ and the most effective phonon is between 430cm⁻¹ and 550cm⁻¹ [2-19],[2-21],[2-22]. The low phonon energy makes the radiative relaxation more possible and thus enables higher emission efficiency. Secondly, elemental yttrium can only exist at trivalent oxidation state and has similar ionic radius with the lanthanide rare earth ions. Thus the cation sites of the Y₂O₃ host material can be conveniently

substituted by dopants without violating the requirement of charge neutrality and matching of valency. Thirdly, Y_2O_3 is a binary oxide. The structural simplicity ensures easy substitution of dopants for the cation sites. The bandgap of Y_2O_3 is about 5.8eV [2-22],[2-23]. The large bandgap has eliminated the possibility of photon re-absorption. The Y_2O_3 should not have any thermal stability constraint because the Y_2O_3 has melting temperature of about 2401°C [2-23] and stability up to 2325°C [2-24]. Therefore, Y_2O_3 has been chosen as the host material in this work. The Eu^{3+} ion has been constantly used as a red-emitting dopant in phosphor materials because of the very intense red emission at the wavelength of about 613nm (5D_0 - 7F_2 emission transition). The combination of the Y_2O_3 host material and the Eu^{3+} dopants forms the red-emitting $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films in this work.

2.4 Current research and trends: Increasing the emission efficiency of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films

In this section, the author reviews the early attempts that have been dedicated to increase the emission efficiency of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. Developing the process conditions, varying the composition of materials, and modifying the morphology of films are the common approaches that have been used to increase the efficiency of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. A recent approach that is poised to increase the efficiency of phosphor powders by using nanophosphors is also included in this section. Each approach is explicitly explained below.

1) Developing the process conditions: The best phosphor material cannot show high efficiency if it is not prepared under optimum process conditions. Therefore, there have been tremendous efforts devoted to the optimization of process conditions for various fabrication methods. Each fabrication method has its critical process parameters. The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films have been prepared by using the deposition method such as

pulsed laser deposition [2-1],[2-20],[2-23],[2-25]-[2-27], sputtering [2-28], electron beam evaporation [2-29], metal-organic chemical vapor deposition (MOCVD) [2-30], electrodeposition [2-31], and sol-gel [2-2],[2-32]-[2-34]. The process parameters that are critical to produce high efficiency $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films such as annealing temperature [2-2],[2-29]-[2-34], Eu^{3+} dopant concentration [2-31],[2-32],[2-34], annealing time [2-27], post-annealing time [2-26], substrate temperature [2-23],[2-26],[2-29], and oxygen pressure [2-23],[2-26] have been studied. Compared to the sol-gel process, most of the deposition methods mentioned above require expensive and complicated equipment setup. More importantly, the problem of composition non-stoichiometry may prevail in some of these deposition methods. In the sol-gel process, highly stoichiometry materials are obtained through mixing of precursor solution at molecular level. Other advantages of the sol-gel process include relatively inexpensive raw materials and equipment and the flexibility to control the composition of materials. The advantages of sol-gel process will be described in details in section 2.7 below. To the best of author's knowledge, there are only few studies concern with the preparation of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films by using the sol-gel process. From the literature, different precursors have been used by different research groups to prepare the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. For example, Rao prepares the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films by using yttrium nitrate, oxalic acid (as drying control chemical additive), and acetylacetone (as chelating agent) [2-2]. Pang *et al.* prepares the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films by using yttrium oxide powders, europium oxide powders, citric acid (as chelating agent), and polyethylene glycol (as cross-linking agent) [2-32]. To explore the possibility for cathodoluminescent (CL) applications, Cho *et al.* prepares the sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films by using yttrium nitrate, europium nitrate, lithium carbonate (as flux), 2-methoxyethanol, and citric acid (as chelating agent) [2-33]. Cho *et al.* also uses the citric acid and formaldehyde (drying control chemical additive) to prepare the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$

phosphor films in another report [2-34]. As already pointed out, many researchers use chelating agents in the sol-gel process. In this work, however, the author developed the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films without the need of additional chelating agents or complicated chemical modification processes. The author only used the precursor and solvent. The author used two sol-gel precursors (yttrium (III) isopropoxide and yttrium 2-methoxyethoxide) to develop the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. It was a challenge to develop a process to prepare the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films with high emission efficiency. The critical process parameters such as Eu^{3+} dopant concentration, annealing temperature, annealing environment, and annealing duration had to be optimized, and the humidity level (15% relative humidity) during preparation had to be carefully controlled. The sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films with high emission efficiency have been successfully prepared. The results will be discussed in chapter 4.

2) Varying the composition of materials: Other than developing the process conditions that has just been described above, another approach used to increase the emission efficiency of phosphor films is to incorporate co-dopant into the phosphor materials. Co-doping is a process of adding co-dopant into the phosphor materials. Co-dopant is deliberately added ion that is usually help to improve the efficiency of phosphor materials. The roles of co-dopant will be explained in section 3.6.3. The co-doping approach is based on the thought that the interaction between the dopant and the co-dopant may induce new spectroscopic phenomenon and is therefore most likely to make a breakthrough in developing high efficiency phosphor materials. The co-dopants can usually be broadly classified into two types, namely lanthanide rare earth ions (lanthanide co-dopants) and non-lanthanide rare earth ions (non-lanthanide co-dopants). The mechanism related to the lanthanide co-dopants is the energy transfer from the co-dopants to the dopants. The details of energy transfer process will be discussed in

section 3.10. Briefly, the energy from co-dopants is transferred to the dopants during energy transfer and this results in the increase of luminescent intensity of the dopants at particular wavelength. For example, energy transfer from co-dopant Tb^{3+} to dopant Eu^{3+} has been observed in $\text{Y}_2\text{O}_3:\text{Eu},\text{Tb}$ materials [2-35],[2-36] and $\text{LiTb}_{1-x}\text{Eu}_x\text{P}_4\text{O}_{12}$ materials [2-37]. Similar mechanism has been found in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ materials with Sm^{3+} [2-38] and Bi^{3+} [2-39]-[2-41] as co-dopants. Furthermore, energy transfer have been observed from Yb^{3+} co-dopant to Eu^{3+} dopant in oxyfluoroborate glass [2-42] and from Tm^{3+} co-dopant to Eu^{3+} dopant in YVO_4 crystal [2-43]. Contrary to the lanthanide co-dopants, the roles of non-lanthanide co-dopants vary from host material to host material. This will be explained in more details in section 3.6.3. For example, the most studied non-lanthanide co-dopant in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films is Li^+ . It is well known that the Li^+ co-dopants frequently enhance the emission efficiency of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor materials. The incorporation of Li^+ co-dopant into the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films induces changes of crystallinity and surface roughness [2-44],[2-45]. It has been explained that the rougher surface scatters more light from the phosphor films [2-44],[2-45]. Other than the surface morphology, the Li^+ co-dopant also helps to reduce the processing temperature of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films with Li^+ co-dopant show early crystallization compared to the samples without Li^+ co-dopant [2-46]. Jeong *et al.* speculates that the incorporation of Li^+ co-dopant into the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films might create oxygen vacancies, which acts as a sensitizer for the efficient energy transfer [2-47]. Every co-dopant has been speculated to play different roles in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor materials. For instance, findings by Sakuma *et al.* has shown that the Zn^{2+} co-dopant increases the CL efficiency [2-48]. This maybe associated with the reduction of charge-up on the film surface with electron-beam bombardment [2-49]. Sychev *et al.* investigates the influence of Zn^{2+} co-dopant to the morphology and luminescence properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. It has been reported that the Zn^{2+}

co-dopant improves the uniformity of the films [2-50]. Tanaka *et al.* explains that the Zn^{2+} co-dopant promotes the incorporation of Eu^{3+} dopant into the Y_2O_3 host material [2-51]. Another example is Gd^{3+} co-dopant. The Gd^{3+} co-dopant has been found to increase the photoluminescent (PL) intensity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ materials. However, the reasons given by different researchers are not the same. For example, Bae *et al.* explains that the Gd^{3+} co-dopant might affect the crystallinity and surface roughness of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films [2-52]. Li *et al.*, however, explains that the Gd^{3+} co-dopant with smaller electronegativity than Y^{3+} may help to facilitate the charge transfer from O^{2-} to Eu^{3+} ions [2-53]. It is important to note that not all the co-dopants are useful to increase the emission efficiency of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor materials. For example, the La^{3+} co-dopant deteriorates the crystallinity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor materials [2-48]. With the B^{3+} co-dopant, the PL of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor materials decreases because of the Y_3BO_6 impurity phase [2-54]. Therefore, the investigation on the luminescence mechanism of different non-lanthanide co-dopants to the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films is much needed. From the literature review, the role of Mg^{2+} and Al^{3+} co-dopants (non-lanthanide co-dopants) in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films has not been explored. In this work, the author aimed to study the roles of Mg^{2+} and Al^{3+} co-dopants in the sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. It has been found that the role of Mg^{2+} and Al^{3+} co-dopants in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films is different from the other co-dopants studied so far. The results will be discussed in chapter 5.

In addition to the work associated with the process conditions and the composition of materials, the author is also aware that there are other approaches that have been used to increase the emission efficiency of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor materials. The two approaches will be explained below. Note that the two approaches were not included in this work.

3) Modifying the morphology of films: Modifying the morphology of films is accomplished by either roughening the surface of phosphor films or substrate. The common objective of these approaches is to liberate more light from the phosphor films. It has been reported that the light extraction efficiency can be improved by using 580nm-diameter polystyrene nanospheres [2-55] and SiO₂ nanorod arrays [2-56],[2-57]. Moreover, it has been found that the SiN_x nanoarrays with higher refractive index contrast can achieve higher light extraction efficiency than SiO₂ nanoarrays in Y₂O₃:Eu³⁺ phosphor films [2-58]. Furthermore, the arrangement of the SiN_x nanoarrays has also been explored. The light extraction efficiency of the SiN_x nanorods air hole with triangular arrangement is approximately 1.33 times higher than the square arrangement [2-59]. Different substrates can also influence the light extraction efficiency. The light extraction efficiency of Li-doped Y₂O₃:Eu³⁺ phosphor films deposited on sapphire substrate is higher compared with the films deposited on silicon substrate [2-60]. In another study, it has been found that the incorporation of Gd₂O₃:Eu³⁺ buffer layer on top of silicon substrate prior to the depositions of Y₂O₃:Eu³⁺ phosphor films might help to improve the crystallinity and surface roughness [2-61]. Basically, the growth pattern of the phosphor films essentially follows the morphology of substrate. If the morphology of substrate is made rough, the phosphor films will also have rough surface and this will increase the light extraction efficiency.

4) The emerging nanophosphors: The investigation on the optical properties of nanosized materials has recently attracted much attention due to the advance of nanoscience and nanotechnology. Along with the nano-fabrication research trend, a growing interest in the development of nanophosphors has been seen in recent years. Particularly, some work has been reported on Y₂O₃:Eu³⁺ nanophosphors [2-35],[2-36],[2-62]-[2-64]. This again justifies why the Y₂O₃:Eu³⁺ phosphor films has been

chosen in this work. A recent review paper related to the synthesis methods of nanophosphors is available in Ref. 2-65. Like the definition of nanomaterials, the nanophosphors can be defined as the powder phosphors with particle size less than 100nm. Nanophosphor is actually a miniature phosphor powder consisting of host material and dopant. According to the results reported in Ref. 2-66 to 2-68, the nanophosphors have higher emission efficiency than the micron-sized phosphor powders (bulk phosphor powders) because the nanophosphors have higher surface-to-volume ratio, higher packing density, and allow deeper penetration of electron bombardment. All these factors are related to the amount of dopants that can be located on the surface of nanophosphors. The larger the amount of dopants located on or near the surface of nanophosphors, the more efficient is the excitation process, which results in more dopants being excited and thus, more light is produced in the nanophosphors compared to the bulk phosphor powders. The bulk phosphor powders have to be further powderized to obtain the desired fine powders in the preparation of commercial phosphor powders, which is usually accomplished by gentle grinding or milling [2-69]. This shows that the size of the phosphor powders is important.

2.5 The choice of ZnO and Eu^{3+}

The author has just reviewed the approaches used to increase the emission efficiency of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films, which is the first objective of this work. Before the author reviews the literature related to the energy transfer process from the ZnO to the Eu^{3+} (the second objective of this work), the justification why the ZnO and the Eu^{3+} were chosen in this work will be firstly explained. Particularly, some interesting properties of ZnO are briefly discussed here. ZnO is a promising II-VI semiconductor for a variety of optoelectronic applications. ZnO has the direct bandgap of about 3.3eV and large exciton binding energy (~60meV) at room temperature [2-70]-[2-72], which give ZnO

an efficient emission. Being an oxide-based material, ZnO is also chemically stable [2-73]. Two emission bands at the ultra-violet (UV) and green wavelength region are usually found in ZnO. In general, the UV emission band observed at around 380 nm is due to the recombination of excitons. The emission band observed at around 500-530nm is due to the defect-related emission of oxygen vacancies [2-73],[2-74]. With all the interesting optical properties mentioned above, it is not surprising to know that there has been growing interest and attention in zinc oxide doped with europium ions (ZnO:Eu^{3+}) for photonic applications.

2.6 Current research and trends: Energy transfer process from the ZnO to the Eu^{3+} ions

In this section, the author reviews the literature related to the energy transfer process from the ZnO to the Eu^{3+} ions. This will lead the author to justify why the $\text{Y}_2\text{O}_3\text{:Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure (the $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ phosphor films deposited on top of the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films) and the $\text{Y}_2\text{O}_3\text{:Eu}^{3+}/\text{ZnO}$ structure (the $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ phosphor films deposited on top of the ZnO films) were prepared in this work.

1) Energy transfer from the ZnO to the Eu^{3+} ions: As mentioned in section 2.5, there has been growing interest in the ZnO:Eu^{3+} materials for future photonic applications. Undoubtedly, the main reason that the Eu^{3+} ion is incorporated into the ZnO is to harvest the red emission from the ZnO:Eu^{3+} materials for practical applications. It is desirable that the energy is transferred efficiently from the ZnO to the Eu^{3+} ions so that the intense red emission can be obtained. So far, however, it has been reported that the energy transfer from the ZnO to the Eu^{3+} ions is still not efficient [2-75],[2-76]. In some cases, the energy transfer from the ZnO to the Eu^{3+} ions is even not observed [2-76]-[2-79]. The inefficient energy transfer from the ZnO to the Eu^{3+} ions is generally explained due to the short lifetime of the excitons in ZnO (the lifetime of excitons in ZnO is

shorter than the energy transfer rate from the ZnO to the Eu^{3+} ions) [2-73],[2-74],[2-76],[2-80],[2-81]. Therefore, in most of the work, to facilitate the energy transfer, the defect states in ZnO have been used to temporarily store the excitation energy [2-73]-[2-76],[2-82] thereby increasing the lifetime. Zeng *et al.*, for example, shows that the increase of the density of trap centers (the defect states), charge-carrier trapping rate, and energy transfer rate will enhance the energy transfer from the ZnO to the Eu^{3+} ions [2-76]. Other than Zeng *et al.*, Du *et al.* has proposed that the excited electrons of ZnO are trapped at the defect states [2-73]. The Eu^{3+} ions at the defect states are excited and finally decay radiatively to give characteristics emission at 580nm (5D_0 - 7F_0 emission transition), 591nm (5D_0 - 7F_1 emission transition), and 613nm (5D_0 - 7F_2 emission transition). There is no clear explanation, however, how the Eu^{3+} ions are excited. Furthermore, Zhang *et al.* has observed non-radiative energy transfer from the ZnO to the Eu^{3+} ions in which the $\text{ZnO}:\text{Eu}^{3+}$ nanopowders exhibit red emission with a complete quenching of ZnO defect emission [2-70]. In other studies, the radiative energy transfer and non-radiative energy transfer have also been proposed [2-74],[2-83],[2-84]. For example, Yu *et al.* disperses the ZnO quantum dots in the $\text{SiO}_2:\text{Eu}^{3+}$ matrix [2-83] and the author proposes that the UV emission is produced when the excited electrons at defect states recombine with the holes in the valence band of ZnO quantum dots. Part of the UV emission is transferred to the Eu^{3+} ions to cause excitation and the excited Eu^{3+} finally generates red emission. This indicates the existence of a radiative energy transfer process. At the same time, Yu *et al.* also showed that the red emission intensity of Eu^{3+} ions increases with increasing concentration of ZnO quantum dots. They propose that this could be due to the enhanced energy transfer between the ZnO quantum dots and the Eu^{3+} ions when the distance between the ZnO quantum dots and the Eu^{3+} ions is shorter, which indicates the existence of the non-radiative energy transfer process. All in all, the energy transfer from the ZnO to the Eu^{3+} ions involves defect states. It is

understandable that the defect states involved in the energy transfer process are practically difficult to control and reproduce. Furthermore, the origin of the defect states involved in the energy transfer process is still not clear. It has been speculated that the defect states result from the surface of ZnO nanosheets [2-76], substitution of Zn^{2+} by Eu^{3+} ions [2-73], and interstitial zinc [2-82]. Therefore, there is a need to develop ZnO-based material systems that can produce efficient energy transfer from the ZnO to the Eu^{3+} ions without the involvement of the defect states. In addition, to the best of the author's knowledge, all the ZnO-based material systems mentioned above are not in the form of thin films. Since many optoelectronic devices for photonic applications require thin film materials, it is desirable to develop ZnO-based material systems with efficient energy transfer to the Eu^{3+} ions in the form of thin films. Based on the above, the author deposited the sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films on top of the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films (denoted as the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure) and the ZnO films (denoted as the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure). The aim is to develop and show efficient radiative energy transfer from the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films and the ZnO films to the Eu^{3+} ions of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films without the involvement of the defect states. The red spontaneous emission peaks at about 611nm (${}^5D_0-{}^7F_2$ emission transition) have been observed in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure. A strong UV random laser pumped red emission at 611nm has been observed in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure. The results will be discussed in chapter 6.

2.7 The choice of sol-gel process for the preparation of phosphor films

In this section, the author reviews the thin film preparation methods that have been used to prepare phosphor films and provide the answer why the sol-gel process was chosen in this work. As mentioned in section 2.4, the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films have been prepared by using the deposition method such as pulsed laser deposition [2-1],[2-20],[2-

23],[2-25]-[2-27], sputtering [2-28], electron beam evaporation [2-29], metal-organic chemical vapor deposition (MOCVD) [2-30], electrodeposition [2-31], and sol-gel [2-2]-[2-32]-[2-34]. Other than the sol-gel process, most of the deposition methods mentioned above such as pulsed laser deposition, sputtering, and electron beam evaporation are vacuum-based deposition methods which require expensive vacuum deposition system or complicated equipment setup [2-85]. Furthermore, some of these vacuum-based deposition methods such as sputtering, electron beam evaporation, and pulsed laser deposition may generally produce non-stoichiometric materials. The sol-gel process may emerge as an alternative preparation method to replace these vacuum-based deposition methods. The sol-gel process can be used to prepare material in various configurations such as films, monoliths, and fibers [2-86]. The sol-gel derived films have been used as planar waveguide films, optical coatings, fluorescent films, electrochromic films, chemical sensing films, and magnetic films [2-87]. In the past, the sol-gel process has been used to prepare the phosphor films [2-3],[2-17] and the phosphor powders [2-88],[2-89]. The details of sol-gel chemistry are deferred to section 3.11.1. The advantages of the sol-gel process derive from the following three salient features:

1. Excellent material stoichiometry: Sol is prepared through mixing of precursors and solvent at molecular level. Hydrolysis and condensation reactions begin after mixing of the precursors with solvent and water. Since the chemical mixing occurs at molecular level, highly homogeneous and stoichiometric films are almost assured [2-2],[2-22],[2-85],[2-90].
2. Low cost: The vacuum-based instrument requires expensive accessories and complicated equipment setup [2-85]. Conversely, the sol-gel process eliminates the need of vacuum environment and hence the cost required to purchase equipment and accessories is relatively lower.

3. Flexibility to control the composition of materials: As explained above, the sol is obtained after the mixing of precursors and solvent at molecular level. This method provides great flexibility to incorporate various types of dopants or co-dopants, which is difficult to achieve by using other thin films preparation methods. Furthermore, the concentration of dopant and co-dopant in the films can be conveniently controlled.

With the three combined merits mentioned above, it is clear that why the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films and the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films were prepared by using the sol-gel process in this work.

2.8 Chapter summary

The author has provided the literature review of oxide-based and sulfide-based phosphor materials and justified why the Y_2O_3 was chosen in this work. The author has also reviewed the current approaches that have been used to increase the emission efficiency of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films (the first objective of this work), namely by developing the process conditions, varying the composition of materials, and modifying the morphology of films. Two approaches were adopted in this work, which include optimizing the process conditions of the sol-gel process and varying the composition of materials by using the Mg^{2+} and Al^{3+} co-dopants. In the later part, the author has also reviewed the literature relevant to the energy transfer process from the ZnO to the Eu^{3+} ions. Based on the literature review, the author prepared the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure and the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure. The objective is to realize efficient radiative energy transfer process from the ZnO -based material systems to the Eu^{3+} ions without the involvement of the defect states.

Chapter 3 Theory of luminescence and thin film preparations, and principle of characterization equipment

3.1 Introduction

This chapter consists of three parts. In the first part, the author outlines the luminescence and some topics related to phosphor materials. In the second part, the theory of thin film preparation methods, which includes sol-gel for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films, filtered cathodic vacuum arc (FCVA) deposition for zinc oxide (ZnO) films, and radio-frequency (RF) magnetron sputtering for indium tin oxide (ITO) films employed in this work are described. Finally in the last part, the working principle of the characterization equipment used in this work and precaution taken when using the equipment are elucidated.

3.2 Basic concept of luminescence

Figure 3-1: Electromagnetic spectra. The expanded visible wavelength range shows the wavelength corresponds to each color emission [3-1]

Humans are exposed to various types of electromagnetic radiation such as transmission signal of radio and television, light of fluorescent tube, and ultra-violet (UV) radiation

from the sun in daily life. Figure 3-1 shows the classifications of the electromagnetic spectra according to the frequency and wavelength range. Needless to say, the luminescent materials (phosphor materials) entail the spectrum of electromagnetic radiation falling in the visible wavelength range from 400nm to 700nm. Luminescence is the emission of electromagnetic radiation in the visible wavelength range. It occurs when the excited electrons return from excited state to ground state [3-2]. A material will not generate any emission if no excitation energy is applied to and absorbed by the material. In general, luminescence is classified according to various excitation modes as shown in Table 3-1.

Table 3-1: Some examples of luminescence based on excitation modes [3-1]

Luminescence classification	Excitation source which generates luminescence
Photoluminescence	visible light or ultra-violet radiation
Cathodoluminescence	cathode-rays
Electroluminescence	electric field
Thermoluminescence	the raise of temperature
Radioluminescence	energetic radiation or particles
Triboluminescence	mechanical disturbance
Sonoluminescence	sound waves passing through a liquid
Chemiluminescence	chemical energy
Bioluminescence	biological mechanism

Each excitation mode has its own unique excitation and emission characteristics [3-3]. For example, *photo*luminescence (PL) occurs after excitation by electromagnetic radiation, which typically occurs at short wavelength. *Cathodo*luminescence (CL) takes place when a material is excited by energetic electron beam, and so forth. Generally, the first part of the term always denotes the excitation mode whereas the second part (luminescence) means generation of light.

3.3 The correlation between optical transition and spectra

As previously been described in section 1.1, phosphor material consists of host material and dopant. The aim of this section is to distinguish the type of optical transitions that occur in phosphor materials, either at the host material or at the dopant. With reference to the shape of absorption or emission spectrum, the type of optical transition whether from the host material or from the dopant can be easily determined.

In general, the absorption or emission spectrum of the host material is relatively broad because the optical transitions involve energy bands (conduction band and valence band). This type of optical transition is known as band-to-band transition. When a dopant ion is involved, depending on the electronic configuration, the absorption or emission spectrum of a dopant can be either broad or sharp. As will be explained in section 3.6.2, the dopant can either be a transition metal ion or a lanthanide rare earth ion. If the dopant is a transition metal ion, its absorption or emission spectrum is usually broad. The optical transition between electronic states formed by the electrons in the $3d$ orbital of a transition metal ion is called the $d-d$ transition. The absorption or emission spectrum results from the $d-d$ transition are usually broad because of the interactions between the optical center ($3d$ optically active electrons at outer orbital) and the surroundings, as will be explained in section 3.8.5 later. On the other hand, the absorption or emission spectrum is usually sharp if the dopant is a lanthanide rare earth ion. This sharp absorption or emission spectrum results from the $f-f$ transition. The reasons that the lanthanide rare earth ion shows sharp absorption or emission spectrum are explained as follows. As generally known, an isolated atom or ion has its own discrete electronic states and electronic configuration. The discrete nature of electronic states implies that the optical transition should involve specific energy and hence specific wavelength [3-2]. Figure 3-2 shows the schematic electronic states and the

corresponding emission spectrum of an isolated atom or ion. In phosphor materials, the absorption or emission spectrum of trivalent lanthanide rare earth ions such as europium (III) (Eu^{3+}), erbium (III) (Tb^{3+}), and thulium (III) (Tm^{3+}) is relatively sharp compared with that of the transition metal ions because the optical center ($4f$ optically active electrons) is well shielded from the surroundings [3-3]. The origin of the f - f transition will be given in section 3.8.

Figure 3-2: Schematic electronic states and the corresponding emission spectrum of an isolated atom or ion

Furthermore, the optical transitions may involve defect states. It is because impurities may be present in materials and the impurities may induce defect states within the energy gap. Depending on the condition, the defect state may be a discrete electronic state or a band state [3-4]-[3-7].

3.4 Luminescence mechanism and LASER

The author just presented the difference between absorption and emission spectra relevant to the dopant and the host material in section 3.3. In this section, the author will outline the mechanism of luminescence (photoluminescence) and the LASER. This is because both processes are related to the author's work.

3.4.1 Photoluminescence

In a broad sense, luminescence is defined as a phenomenon in which the excitation energy is released in the form of emitting photons when the excited electrons return radiatively from excited state to ground state after a material is excited by some energy from an external source, as shown before in Table 3-1. Because photoluminescence (PL) is very common and has been widely used in many practical applications, PL is therefore chosen to describe the general mechanism of the luminescence process. The photon is the excitation source for PL and the photons used for PL excitation are typically high energy photons. The author firstly explains the case for dopant and this will be followed by the case for host material in the phosphor materials. As will be explained in section 3.6.1, the host materials can either insulator or semiconductor materials. In this section, the author treats the host material as a semiconductor material in order to explain the PL. The PL of the host material is shown in Figure 3-3(b) below.

Figure 3-3: Schematic illustration of photoluminescence for
(a) dopant and (b) host material

In the dopant, the electrons that are involved in the optical transition are called optically active electrons. The details of optically active electrons will be given in section 3.6.2

and section 3.7. Once a beam of incident photons is impinged upon the dopant, the optically active electrons are promoted from ground state to excited state. This is represented by excitation from ground state E_1 to excited E_3 or E_4 in Figure 3-3(a). In this case, the dopant is excited and the author will use the term “excited dopant” in chapter 4, chapter 5, and chapter 6. After the excitation, some excitation energy can be released non-radiatively as phonons. The details of non-radiative relaxation will be discussed in section 3.9.2. The non-radiative relaxation is represented by the transitions from excited state E_4 to E_2 and from excited state E_3 to E_2 in Figure 3-3(a). Subsequently, the excitation energy is released in the form of a photon when the excited dopant returns radiatively from excited state E_2 to ground state E_1 . The luminescence of dopant is the result of spontaneous emission. This is different from the stimulated emission that occurs in solid-state laser, as will be described in section 3.4.2.

Similarly, the schematic PL process of the host material (treated as a semiconductor material) is illustrated in Figure 3-3(b). Photon excitation takes place in the host material when a beam of incident photons with energy equal to or larger than the bandgap of host material is impinged upon the phosphor material. In the host material, the electrons are promoted from valence band to conduction band. This transition leads to the formation of electron-hole pairs. After excitation, some excitation energy is released non-radiatively and the excitation energy is released as phonons. When the electrons return radiatively from the bottom of the conduction band to the valence band, the electrons and holes recombine and the excess energy is released in the form of photons.

Hence, both the band-to-band transition and the f - f transition can be observed in the phosphor materials with high excitation photon energy. The focus of author’s work is

about the trivalent lanthanide rare earth europium ions (Eu^{3+}) in which the f - f transition is involved.

3.4.2 LASER

The acronym for LASER simply means Light Amplification by Stimulated Emission of Radiation. In this section, the author will briefly discuss the theory about two different laser systems, namely conventional laser and random laser. This is because the author will report the results of UV random laser pumped red emission from $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure (the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films deposited on top of the ZnO films) in chapter 6. A brief explanation about the conventional laser will lead the reader to understand the random laser of ZnO films better.

As described in section 3.4.1, luminescence is a spontaneous light emission process in which the emitted photons are in the random direction. Consider that an atom of a material is initially at excited state (E_2). The atom tends to decay to lower state (E_1) and the corresponding energy difference between E_2 and E_1 is released through spontaneous light emission. The frequency (ν) of the emitted photon is given by equation 3-1:

$$\nu = (E_2 - E_1) / h \quad (3-1)$$

where h is Plank's constant. Contrary to luminescence, the mechanism of the laser is based on the stimulated emission process. To explain stimulated emission, let us again suppose that an atom is initially at excited state (E_2). When one photon of frequency ν is incident on the material, the incident photon will stimulate the whole emission process by forcing the atom to undergo a transition from excited state (E_2) to lower state (E_1) [3-8]. In the laser, the incident photon and the stimulated photons are coherent (same phase) and monochromatic (same wavelength). The conditions for producing a laser include population inversion, laser gain, and phase condition (resonance condition). As

has been pointed out before, the incident photon needs to stimulate the transition from excited state (E_2) to lower state (E_1) in order to initiate the photon amplification process. To do this, the number of atoms at the excited state should be larger than the number of atoms at the lower state. This is indeed what happens in a laser system and this phenomenon is called population inversion. Other than the population inversion, the photon amplification process is also related to gain. The gain is a measure of how well the active medium amplifies photons by stimulated emission per unit distance [3-9]. Depending on the wavelength of the stimulated emission and the cavity length of a laser system, the light may interfere destructively or constructively. The reflected light will be out of phase with the other light if twice of the cavity length is not an integral multiple of the wavelength after it has made a round trip. Hence, the condition to achieve constructive interference must be fulfilled. This is called a phase condition or resonance [3-9],[3-10].

Recently, a different type of laser named as random laser has been demonstrated. The random laser is a non-conventional laser which uses multiple scattering effects to amplify the stimulated emission and to provide coherent feedback for lasing oscillation [3-11]. The mechanism of random lasing has been observed in ZnO films [3-12] and ZnO powders [3-13]. By using the ZnO powders as an example, the mechanism of random lasing can be briefly explained as follows.

Figure 3-4: Formation of a closed-loop path for light through recurrent scatterings in ZnO powders. The filled circles represent the ZnO powders [3-11]

Like the conventional laser, the random laser also requires both the active medium and the excitation source to create population inversion. In the random laser, the active medium is also a scattering material [3-14]. Hence, the ZnO powders in this example simultaneously play the role of an active medium and a scattering material. Upon optical excitation, the electrons are excited from the valence band to the conduction band of ZnO powders. The excited electrons subsequently relax to the bottom of conduction band before radiative relaxation [3-11]. The photons are emitted when the excited electrons of ZnO return from the bottom of conduction band to the valence band. Hence, a single broad spontaneous emission peak is observed at low excitation intensity [3-11],[3-13]. Since the ZnO powders are close to one another, the emitted photons may be scattered in random direction. Some emitted photons may be scattered back to the starting point after multiple scatterings. When this happens, a closed-loop path is formed. This is shown in Figure 3-4. The closed-loop path serves as a ring cavity in this case [3-11]. In the ZnO powders, several numbers of closed-loop path can be simultaneously formed (i.e. there are many such cavities in the ZnO powders). The probability of a photon scattered back to its starting point is different for each loop path. This means that different loop paths have different loss because the path length traveled

by the photon during scatterings is not the same. When the excitation intensity increases, the gain exceeds the loss first in the low-loss cavities. Therefore, the lasing oscillation take place in these cavities and the lasing frequencies are determined by the cavity resonances [3-11]. In the lasing emission spectrum, the closed-loop paths are reflected by the very narrow peaks (discrete lasing peaks) [3-11]. Other than ZnO powders [3-13], the ZnO films with coarse grain structure also display the random lasing mechanism [3-12]. In fact, the observation of UV random laser pumped red emission from the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure in this work is due to the UV random lasing of ZnO films underneath. The results will be discussed in chapter 6.

3.5 The tuning of material's bandgap

In this section, the author will discuss the tuning of material's bandgap when two materials are mixed. In this work, the author incorporated the cadmium (Cd) dopants into the ZnO films. The bandgap of the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ film can be tuned and take an intermediate value between the bandgap of ZnO ($\sim 3.4\text{eV}$) [3-15] and the bandgap of cadmium oxide (CdO) ($\sim 2.3\text{eV}$) [3-16],[3-17]. The peak wavelength of the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films was tuned from 381nm (x value is 0mole%) towards the absorption wavelength of Eu^{3+} ions at 394nm (${}^7F_0-{}^5L_6$ absorption transition) by increasing the concentration of Cd dopants. The main objective was to increase the spectral overlap between the emission spectrum of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films and the absorption spectrum of Eu^{3+} dopants. This result of this study will be reported in chapter 6.

Bandgap engineering is related to the tuning of material's bandgap. The tuning of material's bandgap can usually be achieved either by alloying, by forming superlattice, by applying strain, or by increasing the temperature [3-18]-[3-20]. Among the four methods, only the alloying method is described in this section because it was used in

this work. The alloying method is related to the combination of two constituent materials, one with a wider bandgap and another with a narrower bandgap, to form an alloy (the new compound). When the new compound is made of two constituent materials, it is expected that the bandgap of the new compound will take an intermediate value between the bandgap of the constituent materials [3-21]-[3-22]. A well-known example is the silicon (Si) and germanium (Ge) semiconductor. As shown in equation 3-2, the bandgap of $\text{Si}_x\text{Ge}_{1-x}$ can be estimated by using the linear interpolation when x varies from $0 \leq x \leq 0.15$ [3-23].

$$E_g(\text{Si}_x\text{Ge}_{1-x}) = 0.66 + 1.34x \text{ (eV)} \quad (3-2)$$

where x is the concentration of Si. The resulting dependence may deviate from the linear behavior and can be described by equation 3-3 when x varies from $0.16 \leq x \leq 1.00$ [3-23].

$$E_g(\text{Si}_x\text{Ge}_{1-x}) = 0.852 - 0.032x + 0.300x^2 \text{ (eV)} \quad (3-3)$$

Furthermore, the lattice constant of one material can expand or contract when the impurity atoms are incorporated into the material since the size of the impurity atoms is usually either larger or smaller. This type of interaction will, therefore, perturb the band edge of a material. Si and Ge are completely miscible over entire compositional range. Hence the Si-Ge alloys has a linearly interpolated lattice constant given by Vegard's rule [3-24]:

$$a(\text{Si}_x\text{Ge}_{1-x}) = a_{\text{Ge}} + x(a_{\text{Si}} - a_{\text{Ge}}) \quad (3-4)$$

where a is the lattice constant and x is the concentration of Si.

3.6 Phosphor materials

In this section, the author gives some fundamental background about the phosphor materials since this work concerns the development of phosphor films. Phosphor materials have found wide applications in many consumer products such as electronic display devices [3-25], optoelectronic devices [3-26], fluorescent lamps [3-27] and so

on. Basically, the phosphor material is a luminescent material that typically consists of an inert host material with a several percentage of deliberately added dopants. The dopants are actually substitutional impurity atoms which randomly occupy the cation sites of the host material [3-28],[3-29]. Almost in all cases, the emission results from the dopants [3-29]. The technical term of dopant, luminescent center, and activator is interchangeable. However, only the term “dopant” is used in this thesis to represent the Eu^{3+} dopant of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. In some circumstances, co-dopants are also incorporated into the phosphor materials. The co-dopants are the additional elements added into the phosphor materials for particular reasons. Various roles of co-dopants will be given in section 3.6.3. The substitution of dopants or co-dopants in the host material may be accomplished through solid solution substitution. Taking the phosphor materials used in this work as an example, red emission is observed when the lanthanide rare earth europium ions (Eu^{3+}) are doped into the yttrium oxide (Y_2O_3). In this example, Y_2O_3 is the host material whereas Eu^{3+} is the dopants. The abbreviation for phosphor material is generally denoted as $(\text{Y}_{1-x}\text{Eu}_x)_2\text{O}_3$ in which x indicates the proportion of Eu^{3+} ions that substitute for Y^{3+} ions [3-30]. The requirement and function of host material, dopant, and co-dopant are described below.

3.6.1 Host material

The host material constitutes the major composition of a phosphor material. This is the reason why the material properties of a phosphor material are largely determined by the host material [3-31]. In general, the host material has two distinct roles: as a passive matrix to allow for the substitution of dopants and as an active matrix to exert an influence to the spectroscopic behavior of dopants [3-32]. The general requirements of host materials are explained as follows. The host materials should be optically passive so that the electronic transition occurs mainly in the dopants. The host materials should

have bandgap energy larger than photons emitted by the dopants in order to avoid photon re-absorption. This implies that the host materials should have bandgap of at least $\sim 3\text{eV}$ to cater for the blue emission in the visible wavelength range. The host materials should be able to be doped with dopants without introducing much defects. In $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor materials, for instance, the ionic radius of Y^{3+} ($0.89\text{\AA}$) and Eu^{3+} ($0.95\text{\AA}$) are of little difference ($\pm 6.7\%$). The host materials with good crystallinity are usually obtained after high temperature annealing. Hence the host materials should have high thermal stability. Because some phosphor materials are exposed to harsh environment, the host materials should be chemically stable in order to maintain the service performance. Almost all the host materials are either insulator or semiconductor materials because only these materials can fulfill the stringent requirement mentioned above [3-33],[3-34].

3.6.2 Dopant / luminescent center / activator

In general, the dopants can either be transition metal ions or lanthanide rare earth ions. The preferable requirements of dopants are basically as follows: (a) the dopants are optically active, (b) the dopants have substantial energy gap between excited state and ground state, and (c) the dopants have proper valence state with the cations of host material. In general, the dopants are the substitutional defects in the host materials because the dopants replace the cations of the host materials. In order to form solid solution, the maximum acceptable lattice mismatch between the dopants and the cations of host materials is about $\pm 15\%$ [3-35]. This is because the greater the dissimilarity in the ionic radius or valency, the more the defects will be introduced [3-33],[3-34]. The consequence will be that non-radiative relaxation will be more probable. The lanthanide rare earth ions are frequently found to form good solid solution with the host material due to the similarity of ionic size and matching of valency.

As will be pointed out in section 3.7, the lanthanide rare earth series consists of 15 lanthanide rare earth elements from Lanthanum (La) to Lutetium (Lu), plus Scandium (Sc) and Yttrium (Y). If the dopants are lanthanide rare earth ions, the emission color is dependent on the type of dopants being doped into the host material. The incorporated lanthanide rare earth ions give characteristic emission which is represented by narrow emission spectra. It is because the optically active electrons in $4f$ orbital are shielded from the outer $5s$ and $5p$ orbital. Another candidate for dopants is transition metal ions. However, the host materials largely affect the emission spectrum of transition metal ions since the d orbital of transition metal ions are directly exposed to the surroundings. This is because different host materials impose different crystal field interactions to the dopants. The crystal field theory will be introduced in section 3.8.5.

3.6.3 Co-dopant

Apart from the dopant, there is one more component which is deliberately added into the phosphor material. This component is named as co-dopant. The incorporation of co-dopants into the phosphor materials has been an active research approach to improve the luminescent performance of phosphor materials. Nevertheless, there is a great deal of uncertainty about the roles of co-dopants and hence their exact roles remain unresolved. From the literature review, the proposed roles of co-dopants can be broadly discussed as follows:

1. Charge compensator: the most common role of the co-dopants is acting as a charge compensator. This is aimed to compensate imbalance charge between the host materials and the dopants so that the resulting phosphor materials have the least concentration of induced defects. As pointed out earlier in section 3.6.2, the dopants deliberately introduced into the host materials are actually the defects. The size and valency of the dopants should preferably match with the cations of

host material. Under certain circumstances, however, the requirement of matching of size and valency cannot be simultaneously fulfilled. Other ions must be introduced for charge compensation. This is the situation where the role of co-dopants as the charge compensator comes into play. An example of phosphor material with the co-dopant acts as the charge compensator is $\text{ZnS:Tm}^{3+}, \text{Li}^+$ [3-36],[3-37].

2. Sensitizer: the co-dopants are called sensitizer if the co-dopants transfer energy to the dopants [3-3],[3-30]. In the phosphor materials, the sensitizer can also be named as donor. The sensitizers convert primary excitation energy into secondary excitation energy that will be subsequently absorbed by the dopants (acceptors). For example, Ce^{3+} ion is a good sensitizer to Cr^{3+} ion [3-38] and Tb^{3+} ion [3-39]. The details of energy transfer process, namely radiative and non-radiative energy transfer process will be discussed in more details in section 3.10.
3. Flux materials: the inclusion of fluxes material is beneficial in assisting atomic diffusion between compounds during crystal growth. For example, LiF promotes better incorporation of Eu_2O_3 into Gd_2O_3 during sintering [3-40]. Better material crystallinity can be expected with the use of fluxes material because of the enhanced crystal growth. The co-dopants that act as fluxes material are Li^+ in $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}, \text{Li}^+$ [3-41]-[3-43] and $\text{Ga}_2\text{O}_3:\text{Dy}^{3+}, \text{Li}^+$ [3-44] as well as Gd^{3+} in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}, \text{Gd}^{3+}$ [3-45].
4. Reduction of processing temperature: consider that there are two constituent materials, one crystallizes at higher temperature and the other one crystallizes at a lower temperature are mixed in certain proportion. A new compound with a new processing temperature is produced. The new processing temperature usually occurs within the highest and the lowest temperature range of the two

constituent materials. Some host materials only crystallize after high temperature annealing. With the introduction of suitable co-dopants into the phosphor materials, the annealing temperature can be reduced. The phosphor materials that show this effect are $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}, \text{Ge}^{4+}$ [3-46] and $\text{BaAl}_2\text{S}_4:\text{Eu}^{2+}, \text{Mg}^{2+}$ [3-47].

3.7 Lanthanide rare earth element – the optical center

As discussed in section 3.6.2, the lanthanide rare earth ions act as the optical centers in phosphor materials. This section therefore outlines the lanthanide rare earth elements. The lanthanide rare earth ions represent an important class of optical materials because they form the so-called optically active centers in the phosphor materials. In principle, photons are generated through radiative relaxation from excited state to ground state. This is opposite to non-radiative relaxation in which no photons are emitted. For the lanthanide rare earth ions, the emission results from the transition between electronic states of the ions, which is called f - f transition. This has been discussed in section 3.3. The lanthanide rare earth elements are those elements in periodic table with atomic number from 57 (Lanthanum) to 71 (Lutetium). Scandium (Sc) and yttrium (Y) are also included because they are found in nature along with the lanthanide rare earth elements. This makes up the total number of 17 lanthanide rare earth elements as depicted in Figure 3-5 [3-48]. For simplicity, the author names lanthanide rare earth elements as lanthanide ions from this section onwards.

[illegible]

Figure 3-5: The lanthanide and actinide rare earth elements in periodic table [3-48]

As mentioned before, the photons are emitted through the radiative transition between the electronic states of a lanthanide ion. The interesting optical properties of lanthanide ions lie on the incompletely filled $4f$ orbital [3-3]. The $4f$ orbital of lanthanide ions is progressively filled when crossing the fifth period of periodic table from Cerium (Ce) to Lutetium (Lu) atom. The electron configuration of a lanthanide atom can be written as [3-4]:

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^n 5s^2 5p^6 6s^2 \quad (3-5)$$

where n is an integer from 2 to 14. The electronic configuration of trivalent lanthanide ions transforms into the configuration below (equation 3-6) when two electrons in $6s$ orbital and one electron in $4f$ orbital are stripped off. This normally occurs when the lanthanide atom substitutes for the trivalent cation site of host material. The new electronic configuration is written as [3-4]:

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{n-1} 5s^2 5p^6 \quad (3-6)$$

The electrons in $4f$ orbital are called optically active electrons because these electrons are those electrons involved in the optical transitions giving rise to photon emission. The optical transition involves $4f$ electrons is therefore named as f - f transition.

The electronic configuration of each lanthanide atom, lanthanide ion, and the number of optically active electrons are shown in Table 3-2. The electronic states of all trivalent lanthanide ions in lanthanum trichloride (LaCl_3) are given in Appendices. It is called “Dieke diagram”, named in honor of Professor Dieke and his associates who devised the diagram [3-5]. When the lanthanide ions are in trivalent state, the optically active electrons in $4f$ orbital are shielded by the outer $5s$ and $5p$ orbital. As a result, the optically active electrons are less affected by the crystal field induced by the host material and thus the gross electronic states of lanthanide ions do not vary greatly from one host material to another [3-3],[3-49]. As presented earlier in Figure 3-5, the rare earth elements consist of two series, namely the lanthanide series and the actinide series. It is intuitive to think that the elements of the actinide series should have similar optical property as the one in lanthanide series because of the partially filled $5f$ orbital. The actinide ions, however, do not find practical application as the optical center because of their high radioactivity and are only available in small quantity [3-50].

Table 3-2: The configuration and the number of optically active electron of trivalent lanthanide ions [3-4],[3-51]

Element	Configuration of lanthanide atom	Configuration of trivalent lanthanide ion	Number of optically active electron(s)
Cerium, Ce	[Xe] $4f^2 6s^2$	[Xe] $4f^1$	1
Praseodymium, Pr	[Xe] $4f^3 6s^2$	[Xe] $4f^2$	2
Neodymium, Nd	[Xe] $4f^4 6s^2$	[Xe] $4f^3$	3
Promethium, Pm	[Xe] $4f^5 6s^2$	[Xe] $4f^4$	4
Samarium, Sm	[Xe] $4f^6 6s^2$	[Xe] $4f^5$	5
Europium, Eu	[Xe] $4f^7 6s^2$	[Xe] $4f^6$	6
Gadolinium, Gd	[Xe] $4f^7 5d^1 6s^2$	[Xe] $4f^7$	7
Terbium, Tb	[Xe] $4f^9 6s^2$	[Xe] $4f^8$	8
Dysprosium, Dy	[Xe] $4f^{10} 6s^2$	[Xe] $4f^9$	9
Holmium, Ho	[Xe] $4f^{11} 6s^2$	[Xe] $4f^{10}$	10
Erbium, Er	[Xe] $4f^{12} 6s^2$	[Xe] $4f^{11}$	11
Thulium, Tm	[Xe] $4f^{13} 6s^2$	[Xe] $4f^{12}$	12
Ytterbium, Yb	[Xe] $4f^{14} 6s^2$	[Xe] $4f^{13}$	13
Lutetium, Lu	[Xe] $4f^{14} 5d^1 6s^2$	[Xe] $4f^{14}$	14

* [Xe] denotes the electronic configuration of Xenon

3.8 Electronic states of dopant

The usefulness of lanthanide ions as the optical centers has just been introduced in section 3.7. From the “Dieke diagram” shown in Appendices, it is observed that there are abundant fine electronic states for each lanthanide ion. The f - f transition refers to the transition within these electronic states. This section deals with the construction of these electronic states when a lanthanide ion is introduced into a host material. In general, there are four types of interactions involve in the construction of these electronic states. These interactions are (a) electron kinetics motion and the potential energy between electrons and nucleus, (b) Coulomb and exchange interaction between electrons, (c) spin-orbit interaction, and (d) crystal field [3-32]. The author will firstly outline these four interactions as a whole in section 3.8.1. Based on the introduction given in section

3.8.1, each interaction will be respectively described in section 3.8.2, 3.8.3, 3.8.4, and 3.8.5.

3.8.1 Interactions of lanthanide ion in crystal

Schrödinger equation forms the foundation of quantum theory. In the Schrödinger equation, Hamiltonian represents the total energy of a given system. The interpretation of Hamiltonian will be useful later when the author describes the total interactions of a lanthanide ion introduced into a host material. In general, free ion refers to the ion which experiences no perturbation from the direct surroundings. The interactions considered in a free lanthanide ion are only those that arise from the interactions between the optically active $4f$ electrons. The Hamiltonian of the free lanthanide ion arranged in the order of decreasing interaction strength can be written as [3-2]:

$$H_{free\ ion} = H_0 + H_{ee} + H_{SL} \quad (3-7)$$

where H_0 represents the electron kinetics motion and the potential energy between electrons and nucleus, H_{ee} represents the Coulomb and exchange interaction between electrons, and H_{SL} represents the spin-orbit interaction. Briefly, the effect of these interactions is that the H_0 leads to atomic electron configuration (ns , np , nd , nf), the H_{ee} splits the $4f^n$ configuration into LS terms, and the H_{SL} splits the LS term into the multiplet levels [3-32],[3-52]. Each interaction corresponds to spectra splitting scheme will be introduced in details in section 3.8.2, 3.8.3, and 3.8.4, respectively.

When a lanthanide ion is doped into a host material, the electronic states are subjected to perturbation from direct surroundings. Consequently, the interaction strength is considerably changed. The author mentioned in section 3.7 that the gross electronic states of lanthanide ions are almost unchanged because of the shielding effect of outer $5s$ and $5p$ orbital. Different host materials, however, do affect the splitting of electronic

states to certain extent [3-53]. The extent of crystal field perturbation to the lanthanide ions is depicted as fine spectra splitting in the “Dieke diagram” (see Appendices). The crystal field interaction (H_{CF}) splits the levels of free lanthanide ion with total angular momentum (J) into $(2J+1)$ distinct sublevels or component lines [3-54]. The new Hamiltonian (H_F) includes all the interactions from the free lanthanide ion plus the crystal field interaction (H_{CF}), as described by equation 3-8 [3-31].

$$H_F = H_{free\ ion} + H_{CF} \quad (3-8)$$

Combining equation 3-7 and equation 3-8, H_F therefore becomes:

$$H_F = H_0 + H_{ee} + H_{SL} + H_{CF} \quad (3-9)$$

The interaction in equation 3-9 is arranged in the order of decreasing interaction strength. The approximated magnitude for Coulomb interaction (H_{ee}) is about $10,000\text{cm}^{-1}$. This is much stronger than the magnitude of spin-orbit (H_{SL}) and the crystal field interaction (H_{CF}) which is about $1,000\text{cm}^{-1}$ and 100cm^{-1} , respectively [3-3],[3-4],[3-28],[3-32],[3-55]. An universal spectra splitting scheme of lanthanide ion is shown in Figure 3-6. By using the same spectra splitting scheme, the spectra splitting of Eu^{3+} ions is depicted in Figure 3-7.

Figure 3-6: Spectra splitting of lanthanide ions due to the Coulomb, spin-orbit, and crystal field interactions in decreasing interaction strength [3-55]

Figure 3-7: Schematic diagram for partially spectra splitting of Eu^{3+} ion due to the Coulomb, spin-orbit, and crystal field interactions in decreasing interaction strength [3-35]

3.8.2 Electronic configuration (ns np nd nf configuration)

Figure 3-8: Schematic representative of orbital energy according to principle quantum number (n) and orbital quantum number (l) [3-56]

According to Pauli Exclusion Principle, no two electrons in an atom can have the same set of quantum number [3-52]. This implies that every electron can only occupy particular quantum state. Each electron in an atom is assigned to four unique quantum numbers: the principal quantum number (n), the orbital quantum number (l), the

magnetic quantum number (m), and the spin quantum number (s). The orbitals of an atom are progressively filled starting from the orbital nearest to the nucleus according to the orbital energy level scheme as shown in Figure 3-8. The resulting electron configuration of Eu atom and Eu^{3+} ion, which is the element (dopant) of interest in this work, is respectively denoted in equation 3-10 and equation 3-11 [3-52],[3-57].

$$\text{Eu atom} \quad 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^7 5s^2 5p^6 6s^2 \quad (3-10)$$

$$\text{Eu}^{3+} \text{ ion} \quad 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^6 5s^2 5p^6 \quad (3-11)$$

3.8.3 Coulomb interaction and exchange interaction (L and S)

Electrons are constantly attracted to the nucleus when the electrons are rotating about the nucleus. The rotating electrons possess orbital angular momentum (L). At the same time, the electrons also spin about its own axis, which gives rise to the spin angular momentum (S). The magnitude of vector L and S is respectively given in equation 3-12 and equation 3-12. In the equations, l is the orbital quantum number and s is the spin quantum number of the electron, $\hbar$ is the Planck's constant divided by 2π . The quantization of orbital angular momentum (L) and spin angular momentum (S) is depicted in Figure 3-9(a) and Figure 3-9(b), respectively [3-56],[3-57].

$$L = \hbar\sqrt{l(l+1)} \quad (3-12)$$

$$S = \hbar\sqrt{s(s+1)} \quad (3-13)$$

Figure 3-9: (a) The orbital angular momentum ($\mathbf{L}$) and (b) spin angular momentum ($\mathbf{S}$) exhibits quantization [3-56],[3-57]

In a multi-electron atom, the orbital angular momentum ($\mathbf{L}$) of individual electron couples to form total orbital angular momentum ($\mathbf{L}'$) with magnitude:

$$L' = \hbar \sqrt{l'(l'+1)} \quad (3-14)$$

The possible values of l' for a multi-electron atom with N optically active electrons can be derived as follows:

$$l' = |l_1 \pm l_2 \pm l_N|_{\min}, |l_1 \pm l_2 \pm l_N|_{\min} + 1, \dots, |l_1 \pm l_2 \pm l_N|_{\max} \quad (3-15)$$

where l is the orbital quantum number of individual electron and the modulus in equation 3-15 indicates that only the positive value of l' is permitted.

In addition to orbital angular momentum ($\mathbf{L}$), the spin angular momentum ($\mathbf{S}$) of individual electron also couples to form total spin angular momentum ($\mathbf{S}'$) with magnitude:

$$S' = \hbar \sqrt{s'(s'+1)} \quad (3-16)$$

The method to obtain s' is much the same way the author obtains the l' in equation 3-15. Equation 3-17 shows the similar derivative to get s' where s is the spin quantum number of individual electron.

$$s' = \left| s_1 \pm s_2 \pm s_N \right|_{\min}, \left| s_1 \pm s_2 \pm s_N \right|_{\min} + 1, \dots, \left| s_1 \pm s_2 \pm s_N \right|_{\max} \quad (3-17)$$

In a multi-electron atom, the electrons are arranged very near to each other. As a result, the Coulomb interaction exists between the electrons. The term notation shown below is used to account for the Coulomb interaction and exchange interaction among electrons,

$$^{2S+1}L$$

where the symbol S is the total spin quantum number and the symbol L is the total orbital angular momentum quantum number. In this writing, L is equivalent to the possible values of l' as shown in equation 3-15 whereas S is equivalent to the possible values of s' as shown in equation 3-17. The symbol L and S which the author just described are the universal term. The reader should not be confused with the vector $\mathbf{L}$, $\mathbf{S}$, $\mathbf{L}'$, and $\mathbf{S}'$ in equation 3-12, 3-13, 3-14, and 3-16, respectively. The symbols used to describe the total orbital angular momentum quantum number (L) are shown in Table 3-3. Note that the uppercase designation (e.g. S , P , D , F ...) refers to the overall state of a multi-electron atom [3-1],[3-52],[3-58],[3-59].

Table 3-3: The symbol L is the total orbital angular momentum quantum number corresponds to orbital angular momentum quantum number (l) [3-58],[3-59]

l	0	1	2	3	4	5	6	7	8	9	...
L	S	P	D	F	G	H	I	K	L	M	...

3.8.4 Spin orbit interaction (J)

In this section, the author deals with the origin of total angular momentum (J). In the last section, it has been explained that the individual electron has orbital angular momentum (L) which couples together to give the total orbital angular momentum (L'). Similar treatment can also be applied to obtain the total spin angular momentum (S'). In a multi-electron atom, the vectors L' and S' exert magnetic forces to each other and they couple to form the total angular momentum (J). The interaction between vector L' and S' is called spin-orbit coupling. The total angular momentum (J) of a multi-electron atom is the sum of the vector L' and S' , as indicated in equation 3-18. The magnitude of vector J is given in equation 3-19.

$$\mathbf{J} = \mathbf{L}' + \mathbf{S}' \quad (3-18)$$

$$J = \hbar \sqrt{j(j+1)} \quad (3-19)$$

With reference to equation 3-15 and 3-17, the possible value of j' in equation 3-19 can be derived as shown in equation 3-20.

$$j = |s' - l'|, |s' - l'| + 1, \dots, |s' + l'| \quad (3-20)$$

Figure 3-10 illustrates how the vector L' and S' precess about the vector J . The total angular momentum quantum number (J) is written as a right hand subscript of the term notation ($^{2S+1}L_J$). The author arrives here on all the symbols used to describe the electronic states. Since the trivalent lanthanide ions usually have several optically active electrons in the $4f$ orbital, the lanthanide ions are considered as multi-electron atoms. Hence the electronic transition of lanthanide ions is universally represented by the term notation ($^{2S+1}L_J$) [3-52],[3-58],[3-60]. The energy states for all lanthanide ions are shown in the “Dieke diagram” in Appendices [3-61].

Figure 3-10: Illustration of the vector L and S precess about vector J [3-52]

3.8.5 Crystal field

The author briefly mentioned the crystal field in section 3.7. In this section, the theory of crystal field is discussed in more details. Although the effect of crystal field perturbation to the lanthanide ions is the weakest among different types of interaction as shown in equation 3-9, its effect to the spectroscopic spectra cannot be ignored. When an optical center is incorporated into different host materials, the spectroscopic spectra may vary from one host material to another due to different surroundings of the optical center. This is because different surroundings will give rise to different electric fields and this will influence the spectroscopic spectra of the optical center. This effect is usually called crystal field perturbation [3-3],[3-5],[3-53],[3-58]. The most elegant example of the crystal field perturbation is manganese (II) ions (Mn^{2+}) in different host materials. Here, the author takes the Mn^{2+} ions as an example to illustrate how the crystal field perturbation affects the spectroscopic spectra. Manganese atom (Mn) has an atomic number of 25 and the electronic configuration can be denoted as [3-52],[3-57]:

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2 \quad (3-21)$$

After the detachment of two electrons from outer $4s$ orbital, the electronic configuration of Mn^{2+} ions becomes [3-62]:

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 \quad (3-22)$$

The five optically active electrons in $3d$ orbital are not well shielded in the same way as $4f$ electrons. This makes the optically active electrons in $3d$ orbital to be strongly affected by the surrounding ligands. Ligand is an atom, ion, or molecule connected to the central atom. As a result, different crystal field strength is expected once the direct surroundings of Mn^{2+} ions are changed. The splitting of Mn^{2+} ions is therefore altered and the spectroscopic spectra are affected. For example, both the $Y_2O_3:Mn^{2+}$ [3-63] and $ZnS:Mn^{2+}$ phosphor materials [3-64] exhibit yellow emission whereas $Zn_2SiO_4:Mn^{2+}$ phosphor materials [3-65] give green emission. This phenomenon can be explained as follows. In a host material, the Mn^{2+} ion is the central ion with octahedral symmetry whereas the O^{2-} ion is the surrounding ligands. The $3d$ state has orbital quantum number of two and hence it is fivefold degenerate. The shape of the five $3d$ orbitals and its location against six O^{2-} ions are shown in Figure 3-11(a).

Figure 3-11: (a) The shape of $3d$ orbital and ligand positions (the open and close circle represents the ligands with octahedral and tetrahedral symmetry, respectively) (b) The splitting of the degenerate $3d$ orbital under octahedral symmetry [3-28],[3-66]

As depicted in Figure 3-11(a), the $3d_z^2$ and $3d_{x^2-y^2}$ orbital have lobes pointing towards the O^{2-} ligands. This implies that the electrons in central ion get closer to O^{2-} ligands and

thus experience larger splitting energy than the other three orbitals ($3d_{yz}$, $3d_{zx}$, and $3d_{xy}$). Consequently, the five $3d$ orbitals are no longer degenerate in energy. The octahedral crystal symmetry splits the fivefold degenerate $3d$ orbital into two sets, the e_g orbital (with $3d_z^2$ and $3d_{x^2-y^2}$ orbital) and t_{2g} orbital (with $3d_{yz}$, $3d_{zx}$, and $3d_{xy}$ orbital), as shown in Figure 3-11(b). The energy separation between the e_g orbital and the t_{2g} orbital is expressed as $10Dq$, in which Dq is the strength measurement of octahedral symmetry [3-28],[3-61],[3-66]. Because the value of Dq varies with different host materials, the crystal field strength can have a profound impact on the optical properties of dopant, especially the transition metal ions. For lanthanide ions, the crystal field causes the splitting of J degenerate electronic states. The extent of the crystal field effect to the lanthanide ions in lanthanum trichloride (LaCl_3) is indicated by the width of the electron states as shown in the “Dieke diagram” in Appendices [3-61].

3.9 Introduction to radiative relaxation and non-radiative relaxation

As already mentioned in section 3.2, an excitation source is required for luminescence to occur. After excitation, the absorbed energy will be released in order to restore the system to the equilibrium state. The energy-release process is called relaxation. In general, the absorbed energy may be released through radiative relaxation or non-radiative relaxation [3-3]. Radiative relaxation is a process that gives rise to emission. Competitor to the radiative relaxation is the non-radiative relaxation in which the relaxation occurs without the emission of photons. Because radiative relaxation and non-radiative relaxation are an inter-competitive process, the higher probability of non-radiative relaxation will cause the radiative relaxation to be less efficient. The process of radiative relaxation and non-radiative relaxation will be described in more details in the following sections.

3.9.1 Radiative relaxation

Radiative relaxation refers to an electronic transition process that emits photons when the excited electrons return from excited state to ground state. Obviously, the phosphor material should have higher radiative relaxation probability than the non-radiative relaxation probability [3-3]. By reducing the sources of non-radiative relaxation, the radiative transition can be enhanced [3-49]. In general, high radiative relaxation probability can be achieved by having a large energy separation between the excited state and the ground state. In addition, the host material should have low phonon energy. The need of low phonon energy in the host material will become clear when the author discusses the multi-phonon emission in section 3.9.2.1. During the relaxation processes, the emission wavelength usually shifts to lower energy in relative to the absorption energy because a portion of the absorbed energy is dissipated non-radiatively. This shift is called “Stokes shift”, as depicted in Figure 3-12 [3-2],[3-3].

Figure 3-12: “Stokes shift” – the shift of wavelength between the absorption and the emission spectra [3-3]

3.9.2 Non-radiative relaxation

In section 3.9, it has been mentioned that the non-radiative relaxation is the electronic transition which does not result in luminescence. The non-radiative relaxation competes with the radiative relaxation and hence the origin of the non-radiative relaxation must be understood in order to enhance the radiative relaxation. The non-radiative relaxation may be due to multi-phonon emission and defects, which can be related to the concentration quenching. This will be described in details below.

3.9.2.1 Multi-phonon emission

In a crystal lattice, the atoms are vibrating about their average position. The quantized lattice wave or quantized lattice vibration is called phonon [3-56]. With the phonons, the absorbed energy is dissipated as heat rather than emission of photons [3-3]. Depending on the energy separation between excited state and ground state as well as the phonon energy, the energy dissipation process can occur through single or multiple phonon relaxation. If the energy separation between excited state-ground state is small and the phonon energy is large, single phonon emission is enough to bridge the energy separation. Conversely, the multi-phonon emission takes place if the energy separation between excited state-ground state is larger than the maximum energy of a single phonon. The multi-phonon emission is named when several numbers of phonons are simultaneously emitted to bridge the energy separation between excited state-ground state [3-53]. The multi-phonon emission is illustrated in Figure 3-13.

Figure 3-13: Multi-phonon emission through phonon bridging after excitation [3-53]

The multi-phonon transition probability (W) can be described by equation 3-23 as follows [3-3],[3-5],[3-53],[3-67]:

$$W = B \exp(-\alpha \Delta E) \quad (3-23)$$

$$\Delta E = \sum p_i \hbar \omega \quad (3-24)$$

where B and α are the constant determined by the host material, ΔE is the energy separation, p_i is the number of effective phonon, and $\hbar \omega$ is the phonon energy. From the equations, it is clear that the probability of multi-phonon emission critically depends on the energy separation and phonon energy. Therefore, the multi-phonon emission has higher probability to occur if a phosphor material contains higher phonon energy. With high phonon energy, lesser number of phonons is required to bridge the energy separation simultaneously. The critical number of phonons is limited to five phonons. Above five phonons, the radiative relaxation will dominate [3-5]. This is the key reason why one must carefully choose the host material with low phonon energy because this will make the radiative relaxation more probable. Take the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor materials used in this work as an example. The dominant PL peak at about 613nm (5D_0 - 7F_2 emission transition) corresponds to the energy separation of about 2eV or wavenumber of $16,300\text{cm}^{-1}$. The highest phonon energy in Y_2O_3 is 600cm^{-1} [3-3]. For

the multi-phonon emission to be effective, approximately 27 phonons of Y_2O_3 are required to bridge the energy separation simultaneously. The number of phonon involved is far larger than the critical number of phonons (five phonons). Not only the phonon of host material is important, the chemical species or impurities such as OH^- ($\omega_{\text{max}} \sim 3500 \text{cm}^{-1}$) adsorbed in the phosphor material can account for the low luminescence. In the presence of chemical species with high phonon energy, there is higher probability that the high phonon energy will bridge the energy separation simultaneously. Hence, the energy is dissipated non-radiatively. This is the reason why the chemical species with high phonon energy should be eliminated from the phosphor material. Otherwise, these chemical species may provide an effective pathway for non-radiative relaxation, thereby reducing the radiative relaxation [3-32],[3-49].

3.9.2.2 Concentration quenching

Last section describes the non-radiative relaxation via multi-phonon emission that is closely related to the phonon energy of host material. In this section, the author will explain that the dopant concentration may also contribute to non-radiative relaxation. This phenomenon is called concentration quenching. It involves a change in luminescent intensity with increasing dopant concentration in a phosphor material. The emission intensity of phosphor material passes through a maximum and then decays [3-3]-[3-4]. In this work, this phenomenon is shown in the relation between PL intensity and Eu^{3+} concentration in Y_2O_3 . The results will be shown in section 4.2.2.4 of chapter 4. The concentration quenching process involves the non-radiative energy transfer among the same dopant species (Eu^{3+} dopants). The energy transfer between two dissimilar dopants will be considered later in section 3.10. Because the dopants are the source of luminescence, it is intuitive to assume that the emission intensity will increase with increasing dopant concentration. However, this is not the case for phosphor materials.

Every phosphor material has an optimum dopant concentration to achieve the highest luminescence. The emission intensity will be reduced sharply if the optimum dopant concentration is exceeded. This is related to the existence of luminescent quenching centers in the phosphor material. The luminescent quenching center is the place where the excitation energy is dissipated non-radiatively [3-3],[3-31],[3-68]. To understand the concentration quenching, consider the energy migration from dopants to dopants and finally to quenching center. The concentration quenching process is illustrated in Figure 3-14.

Figure 3-14: Schemes of concentration quenching in which the energy migration from dopants (open circles) to quenching center (close triangle) and finally non-radiative relaxation occurs [3-53] (top). Concentration quenching is represented by the resonance energy state scheme (bottom) [3-69]

The interaction strength between dopants is proportional to $1/r^6$, where r is the distance between two dopants [3-4],[3-70]. From this simple relation, it is clear that the interaction strength between dopants is large with increasing dopant concentration. Therefore, the transfer of energy from one dopant to another becomes easier as the dopant concentration increases. The energy can be transferred to the luminescent quenching centers in the phosphor material and finally the energy is dissipated non-radiatively. An example of luminescent quenching center is the defects in materials such as OH^- ($\omega_{\text{max}} \sim 3500 \text{ cm}^{-1}$).

3.10 Energy transfer

After absorption, the excited dopant must return to ground state from excited state. The excitation energy is released during the transition from the excited state to the ground state. As described before in section 3.9, the usual pathways are the radiation relaxation and non-radiative relaxation. Other than the radiation relaxation and non-radiative relaxation, another possibility to return to the ground state is by transfer of the excitation energy from the excited dopant to another dopant nearby. The energy transfer process may finally be followed by emission from the dopant which receives the energy being transferred. Generally, there are two types of energy transfer process, namely radiative energy transfer and non-radiative energy transfer.

To distinguish the two energy transfer processes, let us consider transfer of energy between two dopants, say from dopant D to dopant A at the conditions described below. Take note that dopant D and dopant A are of dissimilar species. The dopant D and the dopant A is separated from one another at certain distance. Initially, the dopant D has been excited and it is represented by D^* , in which the asterisk (*) denotes the excited condition. The alphabet “D” and “A” is normally used because these notations carry

certain meaning. The dopant that finally emits photons is called the acceptor (dopant “A”). The dopant that receives excitation energy and transfers the energy to the acceptor (dopant “A”) is called the donor (dopant “D”) [3-71].

3.10.1 Radiative energy transfer

The author begins with the radiative energy transfer process. In the radiative energy transfer, dopant D* emits photons and the emitted photons are subsequently absorbed by dopant A [3-71]. This process can still occur even though the distance between the dopant D* and the dopant A is large. Unlike non-radiative energy transfer, the radiative energy transfer does not require any interaction between the 2 dopants but it depends on the spectral overlap. There will be considerable amount of radiative energy transfer if the spectral overlap of an emission band from D* and an absorption band from A is large. The excited dopant A* may finally emit photons as its own characteristic radiation [3-56],[3-71]-[3-74]. In the author’s work, radiative energy transfer is observed in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ and the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure. Take the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure as an example. The emitted photons of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure at about 394nm is absorbed by the Eu^{3+} ions of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. Eventually, the excited Eu^{3+} emits red emission at about 611nm (5D_0 - 7F_2 emission transition) from the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure. The results will be reported in chapter 6.

3.10.2 Non-radiative energy transfer

In contrast, non-radiative energy transfer occurs without emission of photons from dopant D*. If the dopant D* is in the excited state and dopant A in the ground state, the energy from the dopant D* can still be transferred across to the dopant A provided that there exists a suitable interaction between the two dopants. Here, the interactions are

electrostatic interaction (Coulombic interaction) and exchange interaction [3-73]. The Coulombic interaction corresponds to the non-radiative energy transfer process in which the initially excited electron of the dopant D^* returns to the ground state, while simultaneously an electron of the dopant A is promoted to the excited state. This is illustrated in Figure 3-15.

Figure 3-15: Schematic representative of the Coulombic interaction between dopant D^* and dopant A [3-73]

Conversely, the exchange interaction corresponds to the non-radiative energy transfer process associated with an exchange of two electrons between dopant D^* and dopant A. The way the energy is transferred can be visualized as follows: an excited electron from the dopant D^* travels to the dopant A whereas one electron from the dopant A goes to the dopant D^* . This is illustrated in Figure 3-16.

Figure 3-16: Schematic representative of the exchange interaction between dopant D^* and dopant A [3-73]

In the non-radiative energy transfer, the distance between the two dopants should be small so that there will be either Coulomb interaction or exchange interaction presents between the two dopants. Hence, the probability of non-radiative energy transfer between the dopants decreases rapidly as the distance between the two dopants increases [3-71]. The dopant A will becomes excited after it receives energy from dopant D^* . Finally, the excited dopant A^* may emit photons as its own characteristic radiation [3-71].

To better understand the mechanism of non-radiative energy transfer between two dopants of dissimilar species (dopant D^* and dopant A) that are usually observed in the phosphor materials, let us consider Figure 3-17. After absorption of excitation energy, the dopant D is excited from ground state E_0 to excited state E_2 . Now, the dopant D is labeled as D^* . Because of small energy separation between the excited state E_2 and intermediate excited state E_1 , the dopant D^* undergoes non-radiative relaxation and some energy is dissipated as phonon. Following the emission of phonon, the dopant D^* returns non-radiatively from the intermediate excited state E_1 to ground state E_0 .

Figure 3-17: Phonon-assisted energy transfer [3-5]

As mentioned above, these are the two dopants of dissimilar species. The dopant D^* and dopant A is very close to one another. Note that the energy separation between E_1-E_0 of dopant D^* and $E_3'-E_0'$ of dopant A is not equal. In order to transfer the energy from the dopant D^* to the dopant A , the energy mismatch between excited state $E_3'-E_2'$ of dopant A is bridged by a phonon. The dopant A is finally excited from ground state E_0' to excited state E_2' after accepting the transferred energy from the dopant D^* . The process is completed through non-radiative energy transfer. Because of small energy separation between intermediate excited state $E_2'-E_1'$, the dopant A^* undergoes non-radiative relaxation and some energy is dissipated as phonon. The dopant A^* finally emits its characteristics radiation through the emitted photons from intermediate excited state E_1' to ground state E_0' . This kind of energy transfer is called phonon-assisted energy transfer. The phonon is required to bridge the energy mismatch because the dopants of dissimilar species usually have different energy separation in the electronic states.

Non-radiative energy transfer between the same dopant species can also take place. It is the non-radiative energy transfer mechanism leads to concentration quenching, as was discussed in section 3.9.9.2 and schematically shown in Figure 3-14.

3.11 Fundamentals of thin film preparations

So far, all sections above concern with the theory of luminescence and relevant spectroscopic interactions. This section is devoted to the overview of thin film preparation methods employed in this work. In this work, the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films were prepared by the sol-gel process, the zinc oxide (ZnO) films were prepared by filtered cathodic vacuum arc (FCVA) deposition, and the indium tin oxide (ITO) films were prepared by radio-frequency (RF) magnetron sputtering deposition. The principle of each technique is briefly described in this section.

3.11.1 Sol-gel chemistry and processing steps for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films

In this work, the author used Y_2O_3 as the host material. The justification of using the Y_2O_3 as the host material has been discussed in section 2.3. The choice of sol-gel process for the preparation of phosphor films has also been justified in section 2.7. Hence, this section serves to explain the preparation steps and chemical reactions of the sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films. Other than the information provided in this section, the author will also show the detailed preparation steps in chapter 4, chapter 5, and chapter 6 to represent the process flow of the particular experiment. In general, the sol-gel process can be classified into 4 major steps, namely chemical mixing, aging and gelation, deposition, and densification. The typical preparation steps of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films are shown in Figure 3-18.

Figure 3-18: The typical preparation steps of $Y_2O_3:Eu^{3+}$ -based phosphor films in the sol-gel process

Before the details of each preparation step are discussed in next paragraph, some background theories about the general sol-gel process will be briefly described here. The name “sol-gel” is given because sol-gel process is basically the chemical process transition from a “sol” to a “gel” through a series of hydrolysis, condensation, and polymerization reactions [3-75]. The sol is a colloidal suspension of solid particles in liquid media with dimension in the range of 1nm to 100nm whereas the gel is an interconnected and rigid polymeric network with submicron pores which are filled by the water and solvent [3-76],[3-77]. The gel is actually an intermediate state between solid and liquid. The alcohol, water, and precursor are the three major starting reagents of the sol-gel process. The alcohol is used as a mutual solvent for precursor and water. The primary role of water is to initiate the hydrolysis process. The precursor usually used in the sol-gel process is metal alkoxides. The general chemical formula for metal alkoxide is $M(OR)_x$, in which M represents metal cation, $(OR)_x$ is an alkoxy group attached to the metal cation, R is an alkyl group with general formula C_nH_{2n+1} (n is an integer), and x is the valence state of the metal cation. The yttrium alkoxide precursor

used in this experiment, namely yttrium (III) isopropoxide, will be represented by chemical formula $Y(OR)_3$ in the chemical reactions. In the $Y(OR)_3$, R is an alkyl group with formula C_3H_7 . The preparation steps of $Y_2O_3:Eu^{3+}$ -based phosphor films will be described below.

Step 1 - Chemical mixing: the chemical mixing process was performed in a custom-made plastics glove box flushed with dry nitrogen gas to maintain low relative humidity (RH) in the glove box. This was because the yttrium alkoxide precursor was sensitive to moisture. Initially, the yttrium alkoxide precursor was mixed with alcohol solvent. Suitable amount of water is subsequently added into the mixture to initiate hydrolysis process. Equation 3-25 shows the hydrolysis process upon addition of water to the mixture.

As described previously, the yttrium alkoxide precursor was sensitive to moisture and this would lead to rapid hydrolysis without the aid of catalyst. Generally, the rapid hydrolysis of metal alkoxide is related to the electronegativity of the metal atom. The metal-oxygen bond polarizes in the direction of $M^{\delta+}-O^{\delta-}$ because of the high electronegativity of oxygen atom. Consequently, the positively-charged metal cation ($M^{\delta+}$) is attacked by the oxygen atom of water [3-78],[3-79]. In equation 3-25, the alkoxo groups (-OR) of the yttrium alkoxide precursors were replaced by hydroxo groups (-OH) of the water. The hydrolysis process occurs simultaneously between many yttrium alkoxide molecules and water molecules. Following the hydrolysis process, condensation process takes place. There are two types of condensation process, namely water condensation (see equation 3-26) and alcohol condensation (see equation 3-27).

The Y-O-Y network is gradually formed by the elimination of water molecules (water condensation) and alcohol molecules (alcohol condensation). Further repetition of the Y-O-Y linkage during aging leads to the formation of polymeric three-dimensional structure [3-75]-[3-77].

Step 2 - Aging & gelation: the sol formed after chemical mixing is a low viscosity liquid. At this stage, the Y-O-Y bonds are still weak. Hence, the substitution of dopant (Eu^{3+}) or co-dopant (denoted by **D** in equation 3-29) into the Y-O-Y networks could be easily accomplished. The europium (III) nitrate ($\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) was used as the raw chemical for Eu^{3+} dopants. As shown in equation 3-28, the Eu^{3+} ions and the NO_3^- ions were separated apart after the europium (III) nitrate was dissolved in alcohol. After that, the chemicals were introduced into the Y_2O_3 sols. The Eu^{3+} ions would substitute into the weak Y-O-Y network. The author names this chemical step as dopant substitution. Because the co-dopant (Mg^{2+} and Al^{3+}) were also used in this work, the substitution mechanism of co-dopant was similar to the mechanism of dopant substitution. This was because the chemical of co-dopant was introduced into the Y_2O_3 sol together with Eu^{3+} dopant. This reaction is shown in equation 3-29. In equation 3-29, the **D** represents the co-dopants. Aging time generally refers to the time used to stir the sol before deposition. With the increase of aging time, the Y-O-Y polymeric structure becomes stronger.

Step 3 – Deposition: the films deposition was performed after over a certain period of aging time. In general, the thin films could be prepared from the sols through spin coating or dip coating technique. However, only the spin coating technique was employed in this work. The spin coating can be divided into several stages: deposition, spin, and evaporation. This is illustrated in Figure 3-19. At the deposition stage, excess amount of sol was dispensed onto the substrate. Subsequently, the substrate was spun with suitable rotation speed and spinning time. Driven by the centrifugal force of the spinning process, the dispensed sol flowed radially outward to the perimeter of substrate in the spin stage. The solvent and water molecule gradually evaporated from the pores during spinning. At the end of the spinning process, a gel film was formed on the substrate. At this stage, solvent and water molecules were still entrapped inside the pores of the gel films. Therefore, densification process was required. This will be explained in next step.

Figure 3-19: Spin coating process, from sol dispensing (deposition) until the formation of gel films (evaporation) [3-77]

Step 4 – Densification: because the chemically bound water and some other residual organic molecules were still entrapped inside the pores of the gel films, densification must be carried out in order to eliminate these residual molecules. The residual organic molecules could be eliminated in the form of carbon dioxide gas (CO_2) or water vapour (H_2O) during annealing. The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films were finally obtained after annealing at certain temperature. In the author's work, the annealing temperature of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films was optimized. The results will be reported in chapter 4.

3.11.2 Filtered cathodic vacuum arc (FCVA) deposition

In this work, the ZnO films in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure were prepared by using the filtered cathodic vacuum arc (FCVA) deposition. The results will be presented in chapter 6. The principle of FCVA deposition is briefly described in this section. Since this was a collaboration work, the ZnO films that show UV random lasing were contributed by another research group. The detailed fabrication and optimization processes for the preparation of ZnO films by FCVA deposition can be found in chapter 6. The schematic diagram of a FCVA system is illustrated in Figure 3-20. The main components of a FCVA system include a cathodic vacuum arc source, a plasma-filtering duct, and a deposition chamber.

Figure 3-20: Schematic diagram of FCVA system [3-80],[3-81]

In general, the FCVA technique refers to the combination of cathodic vacuum arc deposition with the magnetic filters. The cathodic vacuum arc is a deposition technique in which the plasma is produced from the metal target (cathode) when a mechanical trigger strikes the cathode. This leads to the formation of cathodic arc spot, as shown in Figure 3-21. Plasma is a partially ionized gas containing an equal number of positive and negative charges, as well as none ionized gas particles [3-82]. The electrons, metal atoms, metal ions and micron-sized droplets (macroparticles) of the metal target are also produced other than the plasma [3-80],[3-81].

Figure 3-21: Schematic diagram of the cathodic arc spot with the generation of electron, atom, ion, plasma, and macroparticle after a mechanical striker hits the target surface [3-80]

As shown in Figure 3-20, the plasma-filtering duct has a 90° bend with respect to the axis of the cathodic vacuum arc source. It is used to filter out the macroparticles from the plasma and this is accomplished by using the magnetic field generated from the magnetic filters surrounding the plasma-filtering duct. The macroparticles can be separated from the plasma because the macroparticles have larger mass-to-charge ratio compared with the ions and electrons. Because of the inertia, the macroparticles that move in a straight trajectory will hit the wall of the plasma-filtering duct and thus being separated. The motion of electrons bound to the magnetic field lines of the plasma-filtering duct. The ions will pass through the plasma-filtering duct and heading to the substrate by following the magnetic field lines. This is guided by the electric field between the electrons and ions. The oxygen gas is introduced into the FCVA system from the oxygen gas inlet such that the metal-oxide species is formed before entering the deposition chamber. A layer of thin film material will be obtained when the metal-oxide species are deposited on the substrate in the deposition chamber [3-80],[3-81].

3.11.3 Radio-frequency (RF) magnetron sputtering

In this section, the principle of radio-frequency (RF) magnetron sputtering is presented. The author used the RF magnetron sputtering to deposit indium tin oxide (ITO) films. The results will be presented in chapter 7 as an additional work. Sputtering is a mature thin film deposition technology [3-82] and it is categorized as physical vapor deposition (PVD) methods. There are many types of sputtering, such as ion beam sputtering, magnetron sputtering, and reactive sputtering [3-83]. The basic principle remains the same regardless the type of sputtering. It is based on the sputter-erosion of the target material (cathode) by incident ions such as argon ions (Ar^+) [3-82].

Consider a sputtering deposition system with a pair of cathode-anode and argon (Ar) gases are introduced into the system. The electrons may collide with the argon atoms when the voltage is applied. If the electrons have high kinetic energy, more Ar^+ ions and electrons will be generated after the collisions. Some electrons may excite the orbital electrons of argon atoms to the excited state. Photons are emitted when the orbital electrons return from excited state to ground state and this results in glow discharge. The plasma is created and maintained at the glow discharge. During sputtering, the Ar^+ ions are accelerated to the target when there is a high and non-uniform electric field between the cathode and the glow region [3-82],[3-84]. As shown in Figure 3-22, the sputtering process occurs when an incident Ar^+ ion firstly collides with the surface atoms of target material. This is followed by the second and successive collisions among the target atoms near the surface. In the collision, some atoms of target material are knocked off from the target material. They are called sputtered atoms. The sputtered atoms will then be deposited onto the substrate and form the thin films.

Figure 3-22: Schematic diagram shows the sputtering process [3-85]

Since the sputtering process is based on the momentum transfer mechanism, it is understandable that materials with high melting point which are difficult to be prepared by the thermal evaporation can be easily accomplished by the sputtering process [3-86]. The sputtering process is generally used if any of the following characteristics are

important: film uniformity over large area, good adhesion, smoothness, good thickness control, and refractory materials [3-82],[3-83]. DC diode sputtering is only applicable to conductive material target because of charge accumulation at the target surface of non-conductive sputtering target [3-87]. To overcome this problem, RF sputtering is used. The operating frequency of the RF sputtering is often set at 13.56MHz because this frequency is allocated for industrial-scientific-medical purpose by the Federal Communications Commission [3-87]. At the frequency of 13.56MHz, the ions are relatively immobile but the electrons are not. The electrons are moving back and forth at the electrodes according to the applied frequency. This has eliminated the problem of charge accumulation at the non-conductive target surface. Magnetic field is very often used in the sputtering process and this process is called magnetron sputtering. The main purpose of employing the magnetic field in the sputtering system is to make better use of the electrons and to create longer mean free path. This is because the presence of a magnetic field over the cathode can trap the electrons around the magnetic lines. This will reduce the loss of electrons in the discharge region. When the electrons in the discharge region are twined around the magnetic lines, the path length of electrons and hence the ionization effect is increased [3-85],[3-86],[3-88]. The RF magnetron sputtering was therefore used to deposit the ITO films in this work.

3.12 Characterization equipment

The author just reviewed the theory of thin film preparation methods employed in this work. Besides that, several characterization tools were used to evaluate the property of the thin film samples. The characterization tools provide very important and substantial information about the property of materials. Based on the information, the author could optimize the process parameters and obtain the desired material properties in this work. These characterization tools complement each other because every characterization tool

has its own niche. In this section, the author elucidates the equipment used, the working principle of the equipment, and the precaution taken when using the equipment throughout this work.

3.12.1 Spectrofluorometer system (SPEX Fluorolog-3)

The photoluminescent (PL) excitation and emission of the thin film samples were measured by a spectrofluorometer at room temperature. The spectrofluorometer was used to characterize the intensity and the wavelength of excitation and emission spectra of the samples. The equipment used in this work was SPEX Fluorolog-3 spectrofluorometer. The main components of SPEX Fluorolog-3 spectrofluorometer were 450W Xenon lamp, excitation monochromator, sample compartment module, emission monochromator, photomultiplier tubes (PMT) detector, and controller. The schematic diagram of spectrofluorometer is illustrated in Figure 3-23.

Figure 3-23: Schematic diagram of spectrofluorometer [3-89]

Xenon lamp was the radiation source that provided broadband emission from 250nm to 2000nm. A diffraction grating in the excitation monochromator was used to disperse the

polychromatic beam into a monochromatic beam. This allowed the user to select the wavelength of interest from Xenon lamp and to guide the monochromatic beam to the sample compartment. The resulting emission signal from sample was then isolated by the emission monochromator and was directed to the PMT detector. To acquire an excitation wavelength, the emission monochromator was fixed at the emission wavelength of the sample and the excitation monochromator was then scanned within the excitation spectra range of interest. After the desired excitation wavelength was obtained, the emission spectra were acquired by scanning the emission spectra range of interest with the use of the desired excitation wavelength [3-90]. Before conducting the measurement, the excitation and emission monochromator of the spectrofluorometer system was respectively calibrated by executing xenon lamp scan (excitation wavelength at 467nm) and water Raman scan (emission wavelength at 398nm). The check was to calibrate the spectrofluorometer system. During measurement, an appropriate optical filter was placed before the PMT detector in order to block unwanted radiation but permit radiation of the desired wavelength to pass. The Xenon lamp was turned on for about 10 minutes so that the intensity of radiation remained stable before measurement. Also, the slit size was kept the same when making measurements. The results of the PL measurement have been normalized to the same thickness.

3.12.2 Photoluminescence system

The UV random laser pumped red emission was realized from the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure. The results of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure will be reported in chapter 6. The equipment used in the measurement was a photoluminescence system. The emission of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure was measured at room temperature. The main components of the photoluminescence system were optical pump source (tripled-frequency Nd:YAG laser at pulsed operation 120ps, 10Hz), separator (1064nm), filter lens (532nm),

attenuator, objective lens, emission monochromator, photomultiplier tubes (PMT) detector, lock-in amplifier, and controller. The schematic diagram of photoluminescence system is illustrated in Figure 3-24.

Figure 3-24: Schematic diagram of photoluminescence system

In the photoluminescence system, a tripled-frequency pulsed operated (10Hz, 6ns) Nd:YAG laser acted as the optical pump source. The output from the Nd:YAG laser went through a separator and a filter lens to eliminate pumping wavelength at 1064nm and 532nm, respectively. With the use of an attenuator, the pump power of Nd:YAG laser (wavelength 355nm) incident on the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure could be varied. The laser was then focused on the sample via an objective lens. After the excitation with the laser, the emission from the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure at wavelength 370nm-410nm (photons emitted from ZnO films) and 600nm-600nm (photons emitted from $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ films) was detected by the PMT detector. The signal was sent to a lock-in amplifier where the lock-in frequency was determined by a built-in frequency detector that was placed near the Nd:YAG laser. For calibration purpose, the laser with wavelength 355nm was incident on the monochromator. This was done in the presence of an attenuator to avoid overloading on the PMT detector.

3.12.3 X-ray diffractometer (Siemens D5005)

The crystalline structures of samples were identified by a *X-ray diffractometer (XRD)*. This was because each crystalline material has a unique diffraction pattern which is considered to be the “fingerprint” of a particular material. In addition to the structures, the diffraction pattern also provided information about the degree of crystallinity and the grain size of a sample. The equipment used in this work was *X-ray diffractometer (Siemens D5005)*. The main components of the XRD were *X-ray tube (CuK_α target)*, sample holder, and scintillation counter (detector). The schematic diagram of *X-ray diffractometer* is illustrated in Figure 3-25.

Figure 3-25: Schematic diagram of X-ray diffractometer [3-91]

The *X-ray tube* was a glass vacuum tube that generated *X-rays*. The sample holder was used to place the sample whereas the scintillation counter was used to detect the scattered *X-rays* from the sample. When a beam of *X-ray* impinged on a crystalline material, the atomic planes scatter the *X-ray* at various angles. Each separate scattered *X-ray* would then interact with each other. There was no diffraction pattern if the scattered *X-rays* were not in phase. However, the scattered *X-rays* reinforced each other if the scattering from successive planes were in phase. The scintillation counter captured

the reinforced X -rays that were scattered from the sample when the Bragg condition was satisfied. The Bragg law (equation 3-30) defines the conditions to obtain X -ray diffraction from a crystalline material when:

$$2d \sin \Theta = n\lambda \quad (3-30)$$

where d is the distance between a set of parallel lattice planes, Θ is the angle between the incident X -ray and an atomic lattice plane, n is the order of diffraction, and λ is the wavelength of incident X -rays [3-90]. Before conducting the XRD measurement, a known sample (e.g. Silicon wafer sample) was used to ensure that the instrument gives the correct diffraction angle. The voltage and tube current settings during measurement were kept the same.

3.12.4 Fourier Transform Infrared Spectrometer (Perkin Elmer Spectrum 2000)

The chemical functional groups and chemical bonds of the samples were identified by using Fourier Transform Infrared (FTIR) absorption measurement. In the solid materials, the constituent atoms are bonded. The bond of the atoms in the material has specific vibration frequency. The material absorbs radiation at frequency corresponds to the vibration frequency of constituent atoms. Hence, the bond of the atoms in the material could be determined based on the vibration frequency acquired in the absorption spectra. The equipment used in this work was Fourier Transform Infrared Spectrometer (Perkin Elmer Spectrum 2000). The FTIR spectrometer consisted of few main components, namely the infrared (IR) source, the interferometer unit (fixed mirror, beam splitter, moveable mirror), sample, detector, and computer. The schematic diagram of FTIR Spectrometer is illustrated in Figure 3-26.

Figure 3-26: Schematic diagram of Fourier Transform Infrared Spectrometer [3-92]

The IR source generated mid-IR radiation ($4000\text{-}200\text{cm}^{-1}$). When the mid-IR radiation impinged on a beam splitter, half was transmitted and half was reflected. The reflected IR beam passed to a fixed mirror whereas the transmitted IR beam passed to a moveable mirror. The two beams reflected off of the respective mirrors and reunited at the beam splitter before the beams were directed towards the sample and detector. Hence, the radiation passed through the sample and detector consisted of two interfering beams that were reflected from the fixed mirror and the moveable mirror. The interfering beams were then either absorbed or transmitted by the sample corresponding to the vibration frequency of constituent atoms of the sample. The resultant signal at the detector was called an interferogram (a plot of intensity versus moving mirror position). To make identification of the molecular vibration, an absorption spectra (a plot of intensity versus wavenumber) was required. The transformation was accomplished by the mathematical process of Fourier transformation which was performed by the computer. The operational mode of the FTIR was based on the ratio between the sample spectrum to the background spectrum (the reference spectrum) [3-90]. Precaution taken was that the background spectrum was firstly registered before measuring the sample. Prior to the measurement, the IR source was turned on for about 10 minutes so that the intensity of

radiation remained stable. Moreover, the purging time of the sample compartment with dry air was remained the same. The purpose of purging was to reduce atmospheric absorption by water and carbon dioxide in the sample compartment. Compared with conventional dispersion infrared spectrometer, the FTIR has higher signal-to-noise ratio because the interferometer has larger optical throughput than grating spectrometer. Moreover, faster measurement speed is achieved because all frequencies are being measured simultaneously.

3.12.5 Surface profile measuring system (Sloan Dektak 3)

The thickness of samples was measured by a surface profiler. The equipment used in this work was a surface profile measuring system (Sloan Dektak 3). The main components of the surface profiler were stylus, linear variable differential transformer (LVDT), amplifier, phase detection modulator, and oscillator. The block diagram of surface profile measuring system is illustrated in Figure 3-27.

Figure 3-27: Block diagram of surface profile measuring system [3-93]

The thickness was measured electromechanically by scanning the sample with a diamond-tipped stylus. The stylus was mechanically coupled to the core of an LVDT. When the position of the LVDT changed, the electrical signals corresponded to the

stylus movement were generated. The variation of the surface topography caused the stylus to be translated vertically and this reflected the thickness of the samples. Before conducting the thickness measurement, a thickness calibration scan on the surface profile measuring system was performed by using a calibration standard with reference thickness of about 9450Å [3-93].

3.12.6 Four-point probe measurement (Cascade Microtech. Inc. CPS-06 Contact Probe Station)

The resistivity of indium tin oxide (ITO) films was measured by a standard four-point-probe technique. The equipment used in this work was a four-point probe station (Cascade Microtech. Inc. CPS-06 Contact Probe Station). The measurement unit consisted of a four-point probe station, a power supply unit, and a digital multimeter. The schematic diagram of four-point probe measurement unit is illustrated in Figure 3-28.

Figure 3-28: Schematic diagram of four-point probe measurement unit [3-94]

The four-point probe station consisted of 4 equally spaced in-line probes. The radius of tungsten carbide probe was 50 μ m whereas the probe spacing was 1mm. The power supply unit provided current (I) through the 2 outer probes during measurement. The digital multimeter measured the voltage drop (V) across the 2 inner probes. The resistivity (ρ) is given as:

$$\rho = \frac{V}{I} t(CF) \quad (3-31)$$

where t is the sample thickness and CF is the correction factor. The CF depends on the sample shape and the geometry of probe tips and the CF used in the measurement is 4.4516 [3-95]. The main purpose of using 4 probes instead of 2 probes was to eliminate the contact resistance. Prior to the resistivity measurement, a reference n -type Silicon wafer with known resistivity was used to calibrate the probe station.

3.12.7 Scanning Probe Microscope (Digital Instruments Dimension™ 3000)

The surface morphology of ITO films and Y₂O₃:Eu³⁺ phosphor films were studied by an atomic force microscope (AFM). The AFM can be of two modes in general, namely tapping mode and contact mode. Compared to contact mode AFM, the tapping mode AFM can produce topographic imaging with higher resolution without inducing damage to the sample surface being scanned due to destructive frictional forces. Hence, the tapping mode AFM was used in this work. The equipment used was a Scanning Probe Microscope (Digital Instruments Dimension™ 3000). The main components of AFM were laser (diode laser less than 1.0mW), scanner tube, cantilever, photodiode array, and instrument electronics (feedback loop and display). The schematic diagram of tapping mode AFM is illustrated in Figure 3-29.

Figure 3-29: Schematic diagram of tapping mode atomic force microscope [3-96]

In the tapping mode AFM used in this work, the silicon cantilever vibrated vertically in free air at its resonant frequency when a Z-piezo stacked in the scanner tube modulated the cantilever. The vertical height between the cantilever tip and the sample surface was disturbed once the oscillating cantilever was very near to the sample surface. The oscillating cantilever generated return signal by reflecting the incident laser onto photodiode array. This return signal was used as the feedback signal to adjust the tip-sample separation in order to maintain constant amplitude on the sample. Thus, the surface topography of the sample was obtained when the feedback circuit sent vertical control signals to the scanner that was moving up and down to follow the surface topography [3-97]. Prior to the measurement, the focusing of laser beam on the cantilever was performed. The optimal oscillation frequency was also selected. Moreover, the cantilever should be free of contaminant too. This was done through visual inspection on the tip of cantilever by using a built-in optical microscope.

3.12.8 Ultraviolet-visible (UV-Vis) spectrophotometer (Hewlett Packard 8453)

The transmittance of ITO films on the glass substrate was measured by UV-Vis spectrophotometer. The transmittance is the power ratio of the light passes through a sample (i.e. ITO coated on glass) with respect to air. The equipment used in this work was a Ultraviolet-visible (UV-Vis) spectrophotometer (Hewlett Packard 8453). The main components of the UV-Vis spectrophotometer were radiation source (tungsten lamp and deuterium lamp), source lens, shuttle, sample, slit, grating, and detector (photodiode array). The optical system of UV-Vis spectrophotometer is illustrated in Figure 3-30.

Figure 3-30: Optical system of UV-Vis spectrophotometer [3-98]

The deuterium lamp provided ultraviolet light whereas the tungsten lamp provided light from visible to near infrared wavelength range (370nm-1100nm). The source lens firstly received the light from both the deuterium lamp and tungsten lamp and then collimated it. The function of the shuttle was to open and allow collimated light to pass through the sample for measurements. After the light passing through the sample, the amount of transmitted light to the detector was controlled by the slit. The grating dispersed and directed the transmitted light onto a photodiode array detection system. This photodiode array detection system allowed simultaneous measurement of the wavelength range

from 190nm to 1100nm. Prior to the measurement, a reference or blank measurement relative to the air was firstly obtained. Moreover, the radiation source was turned on for about 10 minutes so that the intensity of radiation remained stable.

3.13 Chapter summary

In this chapter, the author has reviewed the theory of luminescence. A good understanding of the luminescence process will be helpful when the author discuss the results in later chapters. The author has also explained the theory of thin film preparations. The knowledge of thin film preparations is essential because it helps to solve the problems during fabrication processes. Finally, the author has also discussed the principle of characterization equipment and precautions during measurements. This is to ensure that the results obtained are reliable. The author begins to discuss the development works of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films from chapter 4 onwards.

Chapter 4 Development of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films by sol-gel

4.1 Introduction

The author has already outlined the justification of using the sol-gel process to prepare $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films in this work in section 2.7. The theory of sol-gel process has been described in section 3.11.1. This chapter is devoted to the development of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. A comprehensive study encompasses the effects of Eu^{3+} dopant concentration, annealing temperature, annealing environment in rapid thermal processor (RTP), annealing time, and post-annealing treatment to the sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films is reported in this chapter as to pave the way to realize high emission efficiency $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films in subsequent works. Two different sol-gel precursors were used to develop the Y_2O_3 host material, namely yttrium (III) isopropoxide and yttrium 2-methoxyethoxide. A more stable sol-gel precursor, namely the yttrium 2-methoxyethoxide, has been identified through this work.

4.2 Preparation of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films with yttrium (III) isopropoxide

The author begins here with the development of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. At the early stage of this work, yttrium (III) isopropoxide was used as the sol-gel precursor. Hence, the development by using the yttrium (III) isopropoxide precursor is presented here. At later stage, another sol-gel precursor (yttrium 2-methoxyethoxide) was used. The work will be described in section 4.3.

4.2.1 Sample preparation procedure with yttrium (III) isopropoxide

Figure 4-1: Preparation of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films by the sol-gel process with yttrium (III) isopropoxide precursor

The preparation of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films with the yttrium (III) isopropoxide precursor is presented in Figure 4-1. Other than yttrium (III) isopropoxide [$\text{Y}(\text{OC}_3\text{H}_7)_3$, Alfa Aesar, 92-95%], the precursors used were europium (III) nitrate [$\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Aldrich, 99.9%] and anhydrous 2-propanol [$\text{C}_3\text{H}_7\text{OH}$, Aldrich, 99.5%]. The processing equipment used were custom-made plastics glove box, spin coater (Laurell Manual Dispense Spin Processor model WS-400-6NPP-LITE), and rapid thermal processor (RTP, Jipelet Jetfirst). Since the yttrium (III) isopropoxide was sensitive to moisture, the chemicals mixing and spin coating processes were performed in the custom-made plastics glove box flushed with dry nitrogen gas to maintain 15% relative humidity (RH) in the glove box. Initially, the yttrium (III) isopropoxide was mixed with the anhydrous 2-propanol in the molar ratio of 1:75 to obtain the Y_2O_3 sol. Because the yttrium (III) isopropoxide was sensitive to moisture, no additional water was added into the mixture to hydrolyze the yttrium (III) isopropoxide precursor. After aging for two hours,

europium (III) nitrate was then added into the Y_2O_3 sol to introduce Eu^{3+} dopants into the Y_2O_3 sol matrix. The Eu^{3+} -doped Y_2O_3 sol was denoted as $\text{Y}_2\text{O}_3:x\%\text{Eu}^{3+}$ in which the $x\%\text{Eu}^{3+}$ indicated the mole% of Eu^{3+} dopants substituting the Y^{3+} ions. Note that the film samples derived from the $\text{Y}_2\text{O}_3:x\%\text{Eu}^{3+}$ sol was also denoted by the same notation. The x values ranged from 2mole% to 16mole% at an increment of 2mole% by varying the concentration of Eu^{3+} dopants. The purpose of varying the concentration of Eu^{3+} dopants was to determine the optimum Eu^{3+} dopant concentration. The sol was again aged for another two hours before spin coating. To obtain the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films, the sol was dispensed on (100) Silicon substrate and spun at 3500 rpm for 30 seconds by using the spin coater. The as-deposited $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films were then densified by using the RTP. The annealed phosphor film samples have the thickness of about 100nm measured by the surface profiler. The major merit of annealing in RTP was fast annealing duration. The annealing profile of RTP is shown in Figure 4-2.

Figure 4-2: Rapid thermal annealing profile

The annealing temperature was varied from 450°C to 950°C at an increment of 100°C for the annealing process in RTP. The main objective of annealing process was to solidify the as-deposited $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. Three different annealing environments, namely nitrogen, oxygen, and vacuum, were used in order study the effects of annealing environment to the sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. The oxygen and nitrogen gases for annealing were supplied from the gas cylinders (Air Product, purity 99.99999%). To achieve the desired annealing environment, the annealing chamber of RTP was purged with nitrogen gases (Air product, purity 99.99999%) and followed by vacuum evacuation for two cycles before the desired annealing gas was pumped in. The annealing time in RTP was also varied from 15 seconds to 55 seconds at an increment of 10 seconds. This was to optimize the required annealing time to obtain high efficiency $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films.

4.2.2 Results and discussion

4.2.2.1 PL excitation and PL emission spectrum

Figure 4-3: PL excitation spectrum of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films from 200nm to 300nm ($\lambda_{\text{emi.}}=613\text{nm}$)

Figure 4-4: PL excitation spectrum of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films from 350nm to 500nm ($\lambda_{\text{emi.}}=613\text{nm}$)

The PL excitation and PL emission spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films were studied by using the spectrofluorometer system (SPEX Fluorolog-3). Firstly, it is important to know the absorption wavelength prior to study the PL emission spectrum of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. Figure 4-3 shows the PL excitation spectrum of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ (or $\text{Y}_{1.76}\text{Eu}_{0.24}\text{O}_3$) phosphor films from 200nm to 300nm. Similarly, Figure 4-4 shows the PL excitation spectrum of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films from 350nm to 500nm. Both the PL excitation spectra were obtained by monitoring the emission wavelength at about 613nm ($^5D_0-^7F_2$ emission transition). The wavelength at 613nm is the strongest emission wavelength of cubic $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor materials [4-1]. Many lanthanide rare earth ion doped-materials show an intense and broad absorption band in the ultra-violet (UV) wavelength range. The absorption band is assigned to transitions in which the electron has moved from a neighboring anion orbital to the orbital of lanthanide rare earth ion, or vice versa. Such absorption band is known as charge-transfer band. The intensity of the charge-transfer band arises from the movement of electronic charge across an inter-atomic distance during the absorption process. Because such transitions require

considerable energy, the absorption is usually centered in the UV wavelength range. During the charge-transfer transition, the absorption of a photon occurs in about 10^{-18} seconds [4-2]-[4-5]. In Figure 4-3, the strongest absorption peak is observed at wavelength 246nm. The broad and intense absorption peak at 246nm is due to the charge-transfer from the oxygen 2p state (O2p state) to the 4f level of Eu^{3+} dopants [4-6]-[4-9], which is usually known as charge-transfer state (CTS). The position of CTS is shown in Figure 4-5(b). Conversely, few relatively weak absorption peaks are observed from 350nm to 500nm. This is shown in Figure 4-4. The absorption peaks at about 362nm, 381nm, 394nm, 414nm, and 466nm is respectively assigned to 7F_0 - 5D_4 , 7F_0 - 5G_7 ($J=2-5$), 7F_0 - 5L_6 , 7F_0 - 5D_3 , and 7F_0 - 5D_2 absorption transition [4-10].

Figure 4-5: (a) PL emission spectrum of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor film from 550nm to 730nm ($\lambda_{\text{ext.}}=246\text{nm}$) (b) The energy diagram shows the excitation and emission transition in the electronic states of Eu^{3+} dopants (Solid arrows denote radiative transition whereas dashed arrows denote non-radiative transition after excitation) [4-11]

After absorption of excitation energy, the excited Eu^{3+} dopants may then drop back down to ground levels from excited levels. As described earlier in section 3.9, the energy can be released radiatively or non-radiatively. Figure 4-5(a) shows the typical PL emission spectrum of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films from 550nm to 730nm using the excitation wavelength of 246nm. In Figure 4-5(a), it is observed that the prominent PL peak occurs at 613nm, which corresponds to the $^5D_0-^7F_2$ emission transition. The other peaks at about 580nm, 593nm, 653nm, and 710nm correspond to the $^5D_0-^7F_0$, $^5D_0-^7F_1$, $^5D_0-^7F_3$, and $^5D_0-^7F_4$ emission transition, respectively [4-10]. These are the characteristic emission peaks of Eu^{3+} dopants. These emission peaks are relatively narrow and sharp because of the shielding effect of $4f^6$ electrons by the outer $5s^2$ and $5p^6$ orbital, as explained in section 3.7. The inset of Figure 4-5(a) shows the intense red emission from a $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor film under excitation of UV source in ambient light. Figure 4-5(b) depicts the emission transition from the CTS to the ground levels through both the non-radiative and radiative relaxation after the excitation. Because the energy separation of adjacent levels is small, the excited Eu^{3+} dopants decay non-radiatively from the CTS to the 5D_0 level of Eu^{3+} dopants. The non-radiative relaxation occurs as a result of multi-phonon bridging, as pointed out in section 3.9.2.1. The radiative transition takes place from the 5D_0 to 7F_J ($J=0-6$) levels. This is because the energy separation between the 5D_0 level and the nearest low lying level (7F_6) is as large as $\sim 12,000\text{cm}^{-1}$ [4-12]. The multi-phonon bridging can hardly take place at the large energy separation.

4.2.2.2 The effect of annealing temperature in RTP

The author has just introduced the excitation and emission transition of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films in the preceding section. The author begins here with the optimization results of process parameters. In general, the annealing process is meant to reduce the defects and improve the crystallinity of phosphor materials [4-13],[4-14]. Other than

these functions, the annealing process is particularly important for sol-gel films because the films usually entrap some water, alcohol, and other organic residues [4-14],[4-15]. The phonon energy of Y-O bonds is very low (phonon cut off $\sim 600\text{cm}^{-1}$) and hence do not cause effective multi-phonon bridging. However, the entrapped residual molecules usually have high phonon energy that are favorable for non-radiative relaxation [4-14]. For example, the phonon energy of O-H stretching vibration is as high as 3400cm^{-1} . Five phonons or less can bridge the energy separation ($\sim 12,000\text{cm}^{-1}$) between the 5D_0 and the next low lying level (7F_6) through multi-phonon bridging [4-16]. Hence, the author firstly varied the annealing temperature in order to eliminate the entrapped residual molecules such as O-H impurities in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. To optimize the annealing temperature, the $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films were annealed in RTP from 450°C to 950°C with an increment of 100°C in vacuum environment for 20 seconds. The vacuum environment was firstly chosen rather than other annealing environments because the author would like to eliminate the potential contamination from other annealing gases.

Figure 4-6: PL intensity of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films at 613nm as a function of annealing temperature in RTP

The comparison of PL intensity at wavelength 613nm for various annealing temperatures is shown in Figure 4-6. The PL intensity at 613nm increases with increasing annealing temperature from 450°C to 750°C. The PL intensity, however, decreases significantly in spite of higher annealing temperature when the temperature above 750°C. The PL results will be explained using the *X*-ray diffraction (XRD) patterns and Fourier Transform Infrared (FTIR) spectra respectively shown in Figure 4-7 and Figure 4-8 below.

Figure 4-7: XRD patterns of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of annealing temperature in RTP

Figure 4-7 shows the XRD patterns of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of annealing temperature. It is observed that the samples annealed at 450°C and 550°C are still in amorphous state since there are no diffraction peaks. The samples show a structural variation from amorphous to polycrystalline as the annealing temperature increases. The sample shows diffraction peaks (indicated by (222), (400), and (440) planes) at about 650°C suggesting the crystallization at this temperature. Sample with better crystallinity is observed at annealing temperature of 750°C compared with the sample annealed at 650°C because the diffraction peaks of sample 750°C are sharper

and more intense. The XRD pattern at 750°C corresponds to the cubic Y_2O_3 (JCPDS 01-0831). Additional diffraction peaks are observed when the annealing temperature is higher than 750°C. The additional diffraction peaks are marked with an asterisk in Figure 4-7. The additional diffraction peaks emerge at annealing temperature above 750°C may be indexed to monoclinic Y_2O_3 in which there is mixed phase of monoclinic and cubic structures at certain temperature [4-17]. Furthermore, the $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films annealed above 750°C in vacuum environment has rough surface through naked eye inspection. The author believes that this may be associated with material non-stoichiometry at annealing temperature above 750°C in vacuum environment.

Figure 4-8: FTIR spectra of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of annealing temperature in RTP

Figure 4-8 shows the FTIR spectra of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of annealing temperature. The $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films samples were annealed in RTP for 20 seconds in nitrogen atmosphere. It is observed that the H_2O molecule bending vibration and O-H stretching vibration are respectively present at about 1500cm^{-1} and 3400cm^{-1} [4-18]-[4-20] for the samples annealed at 450°C, 550°C, and

650°C. At 750°C, the absorption peaks due to H₂O molecule bending vibration and O-H stretching vibration are reduced. The FTIR characterization results show that the high annealing temperature at 750°C can effectively reduce the OH impurities in Y₂O₃:12%Eu³⁺ phosphor films. Above annealing temperature of 750°C (850°C and 950°C), there are absorption peaks marked with an asterisk which could be associated with non-stoichiometry of the samples.

4.2.2.3 The effect of annealing environment in RTP

Figure 4-9: PL emission spectra of Y₂O₃:12%Eu³⁺ phosphor films as a function of annealing environment in RTP ($\lambda_{ext.}=246nm$). Inset shows the FTIR spectra of Y₂O₃:12%Eu³⁺ phosphor films annealed at different environments

To further optimize the process conditions, the influence of annealing environment to the Y₂O₃:12%Eu³⁺ phosphor films is reported in this section. Three different annealing environments were used, namely nitrogen, oxygen, and vacuum. Figure 4-9 presents the PL emission spectra of Y₂O₃:12%Eu³⁺ phosphor films annealed in nitrogen, oxygen, and vacuum at 750°C for 20 seconds in RTP. The PL characterization results show that the vacuum environment is more favorable to produce high efficiency phosphor films

compared to oxygen and nitrogen gases at 750°C. As seen in Figure 4-9, there is a good agreement between the PL intensity and the FTIR results shown in the inset of Figure 4-9. The H₂O molecule bending vibration and O-H stretching vibration are reduced after the sample was annealed at 750°C in vacuum environment. However, the H₂O molecule bending vibration and O-H stretching vibration are still present in the samples annealed in nitrogen and oxygen gases. This indicates that the oxygen and nitrogen gases are not as efficient as vacuum to remove the entrapped organic residues. The entrapped organic residues with high phonon energy could have quenched the radiative transition through multi-phonon bridging.

4.2.2.4 The effect of Eu³⁺ dopant concentration

Figure 4-10: PL intensity of Y₂O₃:Eu³⁺ phosphor films as a function of Eu³⁺ dopant concentration at 750°C

Having determined the optimum annealing temperature (750°C) and annealing environment (vacuum), the Eu³⁺ dopant concentration was then optimized. It is important because the PL intensity is obviously a strong dependence of dopant concentration. Too low concentration of Eu³⁺ dopants will, of course, correspond to less

number of emission centers and consequently the phosphor films will have low emission intensity. However, too high concentration of the dopant in phosphor materials can also cause a reduction of emission intensity. In this study, the Eu^{3+} dopant concentration was varied from 2mole% to 16mole% at an increment of 2mole% in order to determine the optimum Eu^{3+} dopant concentration. Figure 4-10 presents the dependence of PL intensity as a function of Eu^{3+} dopant concentration in this study. On increasing the Eu^{3+} dopant concentration, it is observed that the PL intensity increases gradually from 2mole% Eu^{3+} and reaches the maximum at 12mole% Eu^{3+} . Further increase of Eu^{3+} dopant concentration beyond 12mole% results in the decrease of PL intensity. Hence, 12mole% Eu^{3+} is the optimum dopant concentration in this study. Similar optimum dopant concentration in the same phosphor material has been reported by Chang *et al.* [4-21] and Cho *et al.* [4-22]. The decrease of PL intensity for Eu^{3+} dopants concentration greater than 12mole% is caused by the concentration quenching phenomena. The explanation of concentration quenching phenomenon has been described in section 3.9.2.2 in chapter 3. The author briefly repeats here to explain the results in Figure 4-10. As the Eu^{3+} dopant concentration increases, the distance between the Eu^{3+} dopants decreases. This will lead to effective non-radiative energy transfer among the Eu^{3+} dopants, which may cause the migration of the excited energy to the quenching centers such as OH impurities where the energy is dissipated non-radiatively.

To estimate the critical transfer distance (R_c) between the Eu^{3+} dopants at the optimized Eu^{3+} dopant concentration above, consider that there are N number of cation sites (Y^{3+}) in a Y_2O_3 unit cell and each cation site is a sphere with radius r . Taking the volume of the Y_2O_3 unit cell to be V :

$$V \approx \left(\frac{4}{3} \pi r^3 \right) (N) \quad (4-1)$$

The optimum dopant concentration (X_c) is then introduced to equation 4-1 because this represents the number of cation site (Y^{3+}) being substituted by the Eu^{3+} dopants, that is:

$$V \approx \left(\frac{4}{3} \pi r^3 \right) (N) (X_c) \quad (4-2)$$

Re-arrange equation 4-2 gives:

$$r \approx \left(\frac{3V}{4\pi N X_c} \right)^{\frac{1}{3}} \quad (4-3)$$

The critical transfer distance (R_c) between the two Eu^{3+} dopants can be approximated to twice the radius of a sphere [4-23],[4-24], that is:

$$R_c \approx 2r \quad (4-4)$$

On substituting r from equation 4-3 to equation 4-4, R_c can be described as [4-23],[4-24]:

$$R_c \approx 2 \left(\frac{3V}{4\pi N X_c} \right)^{\frac{1}{3}} \quad (4-5)$$

Repeating here, V is the unit cell volume, N is the number of cation site in the unit cell, and X_c is the optimum dopant concentration in mole%. A Y_2O_3 unit cell consists of 80 ions, with 32 Y^{3+} cations and 48 O^{2-} anions [4-25]. In the calculation, the author takes the lattice parameter of cubic Y_2O_3 as 1.0604nm [4-25],[4-26]. A quick estimation by inserting the values $V=1.19nm^3$, $X_c=0.12$, and $N=32$ [4-25],[4-26] into equation 4-5 shows that the critical transfer distance (R_c) is approximately 0.84nm.

4.2.2.5 The effect of annealing time in RTP

In order to determine the relationship between PL intensity and annealing time, the phosphor films with optimum concentration ($Y_2O_3:12\%Eu^{3+}$) were annealed at 750°C in vacuum environment from 15 seconds to 55 seconds at an increment of 10 seconds. The

PL characterization results shown in Figure 4-11 indicates that there is a relatively high increase in the PL intensity from the annealing time of 15 seconds to 25 seconds. Beyond 25 seconds, there is only slight increase of PL intensity with annealing time. The PL emission spectra correspond to the PL characterization results in Figure 4-11 is shown in Figure 4-12.

Figure 4-11: PL intensity of $Y_2O_3:12\%Eu^{3+}$ phosphor films as a function of annealing time in RTP

Figure 4-12: PL emission spectra of $Y_2O_3:12\%Eu^{3+}$ phosphor films as a function of annealing time in RTP ($\lambda_{ext.}=246nm$). Inset shows the FTIR spectra of $Y_2O_3:12\%Eu^{3+}$ phosphor films annealed at different annealing times

The PL characterization results are consistent with the FTIR spectra shown in the inset of Figure 4-12. The H₂O molecule bending vibration at 1500cm⁻¹ is still present after annealing time of 15 seconds whereas the O-H stretching vibration at 3400cm⁻¹ has disappeared. The existence of H₂O molecule bending vibration could be due to the entrapped H₂O impurities in Y₂O₃:Eu³⁺ phosphor films which is difficult to be removed within short annealing time. Beyond annealing time of 25 seconds, the H₂O molecule bending vibration is no longer prominent compared with the sample annealed at 15 seconds. Therefore, H₂O impurities were effectively removed after annealing time of 25 seconds and this has resulted in higher PL intensity. The author did not further increase the annealing time after reaching the RTP annealing time of 55 seconds because the increase of PL intensity from 25 seconds to 55 seconds is insignificant. Furthermore, the RTP is not designed for long annealing process.

The experimental results of the sol-gel derived Y₂O₃:Eu³⁺ phosphor films are summarized as follows. The optimum process parameters for the Y₂O₃:Eu³⁺ phosphor films developed in this work are annealing temperature of 750°C, vacuum annealing environment, Eu³⁺ dopant concentration of 12mole%, and annealing time of 55 seconds. These process parameters were used as the basic process parameters in the subsequent development of Y₂O₃:Eu³⁺-based phosphor films.

4.3 Preparation of Y₂O₃:Eu³⁺ phosphor films with yttrium 2-methoxyethoxide

In the first part of this work, the author has reported the optimum process parameters of Y₂O₃:Eu³⁺ phosphor films prepared with yttrium (III) isopropoxide precursor. At the early stage, the author faced many challenges to prepare the Y₂O₃:Eu³⁺ phosphor films by using the yttrium (III) isopropoxide precursor because of its moisture sensitive nature. Furthermore, the surface of the Y₂O₃:Eu³⁺ phosphor films was not smooth. The

irregular surface roughness may cause problems in the fabrication process if the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films are used to fabricate multi-layer optoelectronic devices, in which planarization of the rough surface is required. To overcome this problem, the author has therefore searched for a new sol-gel precursor. The next sol-gel precursor used was yttrium 2-methoxyethoxide. The yttrium 2-methoxyethoxide precursor is more stable because the inherent chelat cycles retard the reactivity of precursor. The differences between yttrium (III) isopropoxide and yttrium 2-methoxyethoxide are outlined in the section that follows.

4.3.1 Comparison between yttrium (III) isopropoxide and yttrium 2-methoxyethoxide

Figure 4-13: Comparison of the molecular structure between (a) yttrium (III) isopropoxide and (b) yttrium 2-methoxyethoxide (--- line represents the donation of unshared pair of electrons (lone pair) from the O atom to the Y atom) [4-27],[4-28]

It is worthwhile to show why the yttrium 2-methoxyethoxide has less susceptibility towards hydrolysis compared to the yttrium (III) isopropoxide. Figure 4-13(a) and Figure 4-13(b) respectively shows the molecular structure of yttrium (III) isopropoxide and yttrium 2-methoxyethoxide [4-27],[4-28]. Recall from section 3.11.1 that the oxygen atom of water molecule attacks the positively-charged metal atom (M) through nucleophilic attack in the hydrolysis reaction. Since the adjacent oxygen atom has high

electronegativity, the metal-oxygen bond (M-O) polarizes in the direction of $M^{\delta+}-O^{\delta-}-C$. This makes the metal atom more positively-charged and therefore more susceptible to nucleophilic attack. Moreover, the oxygen atom under the influence of the $M^{\delta+}-O^{\delta-}-C$ polarization is also susceptible to electrophilic attack. If there is electrophilic attack on oxygen atom, this will cause the electron density near the metal atom to be withdrawn and hence the metal atom becomes even more positively-charged [4-29],[4-30]. The combination of these effects makes the yttrium (III) isopropoxide precursor sensitive to moisture. Chelating agent is usually used to control the hydrolysis reaction of reactive metal alkoxide precursor. The passivation is accomplished by complexing the metal atom of the metal alkoxide. Chelating agent is a molecule which possesses unshared pair of electrons (lone pair) which is called donor center. Each donor center is capable of occupying a site in the coordination shell of the metal atom [4-31]. Once the particular coordination shell of the metal atom is occupied, the metal atom of metal alkoxide will become less reactive and hence hydrolysis reaction will be slowed down. Therefore, considerable stabilization can be achieved when larger ring structure or chelat cycle occupies more sites around the metal atom [4-31]. As shown in Figure 4-13(b), the donation of the oxygen lone pair electrons into the empty yttrium orbital results in new bonds and thus the chelat cycle. The chelat cycle reduces the reactivity of yttrium ion in yttrium 2-methoxyethoxide. Thus, the author only needs to use the precursor and solvent to prepare the $Y_2O_3:Eu^{3+}$ sol, without the need of additional chelating agents.

4.3.2 Sample preparation procedure with yttrium 2-methoxyethoxide

Figure 4-14: Preparation of $Y_2O_3:Eu^{3+}$ phosphor films by the sol-gel process with yttrium 2-methoxyethoxide precursor

The preparation procedure and characterization of $Y_2O_3:Eu^{3+}$ phosphor films by the yttrium 2-methoxyethoxide was basically similar to the yttrium (III) isopropoxide presented in section 4.2.1. The major difference was that the $Y_2O_3:Eu^{3+}$ phosphor films were subjected to post-annealing treatment after annealing in RTP. This was because the annealing time in RTP was short (less than one minute) and some H_2O impurities might still be entrapped in the $Y_2O_3:Eu^{3+}$ phosphor films. In addition, the author would like to study the post-annealing effects to the sol-gel derived $Y_2O_3:Eu^{3+}$ phosphor films. The preparation of $Y_2O_3:12\%Eu^{3+}$ phosphor films with yttrium 2-methoxyethoxide is shown in Figure 4-14. The precursors used were yttrium 2-methoxyethoxide [$Y(OOC_3H_7)_3$, Alfa Aesar], europium (III) nitrate [$Eu(NO_3)_3 \cdot 6H_2O$, Aldrich, 99.9%], and anhydrous 2-methoxyethanol [C_3H_7OOH , Aldrich, 99.8%]. The processing equipment used were

custom-made plastics glove box, spin coater (Laurell Manual Dispense Spin Processor model WS-400-6NPP-LITE), rapid thermal processor (RTP, Jipelet Jetfirst), and furnace (Thermolyne 47900). The chemical mixing and spin coating processes were performed in the custom-made plastics dry glove box flushed with dry nitrogen gas to maintain 15% relative humidity (RH). Initially, yttrium 2-methoxyethoxide, 2-methoxyethanol, and water were mixed in the molar ratio of 1:90:3, respectively. After aging for 2 hours, 12mole% Eu^{3+} dopants were subsequently added into the sol mixture. This was the optimum Eu^{3+} dopant concentration developed in the previous section. The resulting mixture was aged for about 15 hours in a sealed condition at room temperature prior to spin coating. The $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ gel films were subsequently annealed using the optimum process parameters developed in previous section: annealing temperature of 750°C , vacuum environment, and annealing time of 55 seconds in RTP. To investigate the post-annealing effect to the $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films, the samples after RTP annealing were further post-annealed in a furnace. The post-annealing treatment was performed in air from 1 hour to 20 hours at 750°C . This process was to ensure H_2O impurities could be effectively removed after the long annealing duration.

4.3.3 Results and discussion

4.3.3.1 The effect of annealing temperature in RTP

Figure 4-15: XRD patterns of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films annealed at different annealing temperatures in RTP

Figure 4-15 shows the XRD patterns of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films annealed in RTP from 450°C to 950°C. There were some changes of film crystallinity when the samples were annealed at annealing temperature above 750°C. The changes were marked with an asterisk in Figure 4-15. This is similar to the $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films prepared by yttrium (III) isopropoxide reported in section 4.2.2.2. The change had not been observed when the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor materials in the thin films form [4-32] or powder forms [4-33] prepared by the sol-gel process and annealed in furnace from temperature range of 400°C to 1250°C. The author mentioned that the $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films show poor crystallinity at annealing temperature above 750°C in vacuum environment in section 4.2.2.2. However, this observation persists when the new sample prepared by yttrium 2-methoxyethoxide precursor underwent the same process conditions in RTP, as explained earlier. To prove the changes again, the author therefore annealed some new samples at different temperatures (750°C, 950°C, 1150°C, and 1250°C) in a furnace for 2

hours. The evolution of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films crystal structure was indeed observed as presented in Figure 4-16. The additional diffraction peaks marked with an asterisk emerge at annealing temperature above 750°C can be indexed to monoclinic Y_2O_3 [4-17]. This has been explained in section 4.2.2.2.

Figure 4-16: XRD patterns of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films annealed at 750°C , 950°C , 1150°C , and 1250°C in furnace

Figure 4-17: PL spectra corresponds to the change of crystal structures from 750°C to 1250°C ($\lambda_{\text{ext.}}=254\text{nm}$)

Figure 4-18: Illustration of two Y^{3+} crystallographic sites in cubic Y_2O_3 [4-1]

The evolution of crystal structure from 750°C to 1250°C is accompanied by the change of PL spectra shown in Figure 4-17. In Figure 4-17, it is observed that the PL intensity at 590nm (5D_0 - 7F_1 emission transition) increases as the annealing temperature increases from 750°C to 1250°C. Conversely, the PL intensity at 613nm (5D_0 - 7F_2 emission transition) decreases at the same annealing temperature range. The change of PL spectra corresponds to the evolution of Y_2O_3 crystal structure may be explained as follows. Figure 4-18 shows the yttrium atom occupy two sites with different crystal symmetry in cubic Y_2O_3 , namely C_2 and S_6 symmetry. 75% of the yttrium cations are in C_2 symmetry whereas the other 25% are in S_6 symmetry [4-34]. In the $Y_2O_3:Eu^{3+}$ phosphor films, the Eu^{3+} dopants statistically substitute for C_2 and S_6 symmetry with equal proportion. The PL peak at 613nm originates from the Eu^{3+} dopants in C_2 symmetry whereas the PL peak at 590nm originates from the Eu^{3+} dopants in S_6 symmetry [4-34]. The ratio of S_6 sites to C_2 sites could be changed because of the evolution of Y_2O_3 crystal structure. The change of S_6 to C_2 ratio leads to the change of PL spectra as presented in Figure 4-17. That is, it is observed in Figure 4-17 that the PL intensity at 613nm is diminishing while the PL intensity at 590nm is dominating as the annealing temperature increases.

Figure 4-19: PL intensity ratio at 590nm to 613nm ($R=I(^5D_0-^7F_1)/I(^5D_0-^7F_2)$) corresponds to the change of crystal structures from 750°C to 1250°C

In the previous paragraph, the author mentioned that the PL intensity at 590nm and 613nm changes as a function of annealing temperature. PL intensity ratio for both the emission wavelengths can be used to indicate the change. The PL intensity ratio at 590nm to 613nm ($R=I(^5D_0-^7F_1)/I(^5D_0-^7F_2)$) of $Y_2O_3:12\%Eu^{3+}$ phosphor films as a function of annealing temperature is shown in Figure 4-19. The PL intensity ratio (R) gradually increases from 0.092 (at 750°C) to 0.483 (at 1250°C). It is clear that the orange emission at 590nm is increasingly dominating when the $Y_2O_3:12\%Eu^{3+}$ phosphor films were annealed from 750°C to 1250°C. In view of the three basic colors (red, green, and blue) are essential for the realization of white light for various photonic applications, the $Y_2O_3:12\%Eu^{3+}$ phosphor films annealed at above 750°C with substantial mixture of orange emission are not very useful. Consequently, the optimum annealing temperature is set at 750°C for the sol-gel derived $Y_2O_3:Eu^{3+}$ phosphor films.

4.3.3.2 The effect of post-annealing treatment

Figure 4-20: PL emission spectra of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of post-annealing time ($\lambda_{\text{ext.}}=254\text{nm}$)

In this section, the effect of post-annealing treatment to the $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films prepared by using yttrium 2-methoxyethoxide is reported. Post-annealing treatment is usually performed in order to enhance the emission efficiency of phosphor materials [4-35],[4-36]. To further enhance the PL intensity of the $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films, the samples were subjected to post-annealing treatment after short annealing time in RTP. Figure 4-20 compares the PL emission spectra of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films with and without post-annealing treatment at 750°C . The corresponding PL intensity at 613nm is presented in the inset of Figure 4-20. It is observed that the PL intensity of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films increases as a function of post-annealing time. This is probably related to the organic residues that might still be entrapped in the phosphor films after short annealing time in RTP. The entrapped organic residues that have high phonon energy could efficiently quench the radiative transition through multi-phonon bridging, as has been discussed in section 3.9.2.1.

Figure 4-21: FTIR spectra of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of post-annealing time

Figure 4-21 compares the FTIR spectra of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films with and without post-annealing treatment at 750°C . Inset of Figure 4-21 enlarges the FTIR region from 1200cm^{-1} to 1800cm^{-1} , which is due to H_2O molecule bending vibration with the peak at about 1500cm^{-1} [4-18]-[4-20]. The FTIR spectra indicate that the H_2O impurities are eliminated from the samples after post-annealing treatment. Since the PL intensity of phosphor materials decreases with the increasing H_2O impurities, the phosphor films with less H_2O impurities can therefore have higher PL intensity. This explanation is consistent with the study of PL intensity as a function of post-annealing time as presented in Figure 4-20. In Figure 4-21, there exist three other absorption peaks after post-annealing treatment other than the absorption peaks of Y_2O_3 at about 570cm^{-1} . The absorption peaks at about 450cm^{-1} , 810cm^{-1} , and 1070cm^{-1} are respectively ascribed to Si-O-Si bending, stretching, and asymmetry stretching [4-37]. This is due to the reaction of the silicon substrate with oxygen atoms to form SiO_2 layer [4-38]. The SiO_2 layer eventually grows to a substantial thickness after long duration of post-annealing treatment.

Despite the efficient elimination of entrapped organic residues from the $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films after post-annealing treatment for 1 hour, the PL intensity still increases with longer post-annealing time. The increase of PL intensity with longer post-annealing time can be attributed to the enlargement of grain size. Grain boundary is believed to be a non-radiative transition routes in phosphor films because the defects are present at the grain boundary [4-39]. The density of grain boundaries and hence the density of defects are reduced if the grains of the phosphor films grow larger. The post-annealing treatment is believed to promote relaxation of lattice strain and reduce the lattice imperfection [4-35],[4-36],[4-39].

Figure 4-22: XRD patterns of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of post-annealing time

Figure 4-22 shows the XRD patterns of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of post-annealing time. The annealing temperature was 750°C . Although the author cannot see clearly from Figure 4-22 that the crystallinity of phosphor films improves with longer post-annealing time, it will be obvious when the author refers to Figure 4-23 later. Figure 4-23 shows the full-width half-maximum (FWHM) of (222) diffraction peak of the samples as a function of post-annealing time at 750°C .

Figure 4-23: The full-width half-maximum (FWHM) of (222) peak decreases with the increase of post-annealing time at 750°C

To interpret the results in Figure 4-23, one should understand the relationship between grain size and FWHM of a diffraction peak, which is explained as follows. According to Scherrer equation shown in equation 4-7, the average grain size of a material is inversely related to the FWHM of the most dominant diffraction peak [4-40]:

$$D = \frac{0.9\lambda}{w' \cos(\theta)} \quad (4-6)$$

where D is the grain size, λ is the X -ray wavelength, w' is the FWHM of the diffraction peak, and θ is the angle of diffraction peak. In Figure 4-23, it is observed that the FWHM of (222) peak decreases with post-annealing time, suggesting an increase of grain size or grain growth. In other words, the decrease of FWHM indicates the reduction of defects at the grain boundaries. This can explain why the PL intensity increases as a function of post-annealing time, as was previously presented in Figure 4-20.

Figure 4-24: Average grain size of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films increases with post-annealing time at 750°C . The grain size is obtained by manually measuring the grains of AFM image

To further prove the result that the FWHM decreases as a function of post-annealing time as shown in Figure 4-23, the average grain size of the samples were measured by using a atomic force microscope (AFM). The plot of average grain size as a function of post-annealing time is shown in Figure 4-24. From Figure 4-24, it is indeed observed that the grain size increases with post-annealing time. Hence, the result of average grain size is consistent with the FWHM of (222) peak shown in Figure 4-23. Surface topography of the $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of post-annealing time is presented in Figure 4-25.

Figure 4-25: AFM images of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of post-annealing time at 750°C : (a) No post-annealing (b) post-annealing 1 hour (c) post-annealing 5 hours (d) post-annealing 11 hours (e) post-annealing 20 hours

4.4 Chapter summary

The author shall close this chapter by recalling the main achievements. The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films have been developed by using the yttrium (III) isopropoxide and yttrium 2-methoxyethoxide sol-gel precursors. The sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films undergo changes of crystal structure upon annealing at temperatures above 750°C . With consideration of pure red emission at wavelength 613nm (5D_0 - 7F_2 emission transition), the optimum annealing temperature received is at 750°C . The optimum dopant concentration is 12mole% Eu^{3+} (or $\text{Y}_{1.76}\text{O}_{0.24}\text{O}_3$). Vacuum environment is more efficient than oxygen and nitrogen to eliminate the OH impurities and hence yields phosphor films with higher PL intensity. The PL intensity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films also depends on the annealing time. Post-annealing treatment appears to be an essential processing step to enhance the PL intensity of phosphor films. This is likely due to the elimination of OH impurities and the increase of grain size. The yttrium 2-methoxyethoxide sol-gel precursor is better than the yttrium (III) isopropoxide sol-gel precursor in terms of stability against moisture sensitivity and ease of handling during the sol preparation process.

Chapter 5 $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films with co-dopants

5.1 Introduction

As mentioned in section 1.2, the first objective of this work is to develop high efficiency $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films. The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films which serve as the base material in this work have been successfully developed and described in chapter 4. Based on the optimized $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films in chapter 4, the author attempted to develop $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films with high emission efficiency in this chapter. One of the most frequently used methods to increase the emission efficiency of phosphor materials is to incorporate the co-dopants into the phosphor materials, as mentioned in section 2.4. In general, the co-dopants can either be lanthanide ions or non-lanthanide ions. The roles of lanthanide co-dopants are generally related to the energy transfer process [5-1]. These mechanisms were outlined in section 3.10. In contrary to that, the roles of non-lanthanide co-dopants are not clear. For example, several possible roles of non-lanthanide co-dopants have been proposed, which have been outlined in section 3.6.3. In order to gain better understanding of the role of non-lanthanide co-dopants, the author therefore incorporated two different co-dopants (Mg^{2+} and Al^{3+} ions) into the sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. To the best of the author's knowledge, the role of Mg^{2+} and Al^{3+} co-dopants in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films has not been explored before.

5.2 Sample preparation procedure of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films with co-dopants

Figure 5-1: Preparation of Mg^{2+} and Al^{3+} co-doped $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films by a sol-gel process with yttrium(III) isopropoxide precursor

The sample preparation flow chart of Mg^{2+} and Al^{3+} co-doped $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films is presented in Figure 5-1. In this experiment, the yttrium (III) isopropoxide precursor was used. The preparation procedure of phosphor films with co-dopants was basically similar to the preparation procedure of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films as described in section 4.2.1. The difference was that the co-dopant chemical was simultaneously added to the sol mixture with the dopant chemicals. The co-dopant chemicals used were magnesium (II) nitrate [$\text{Mg}(\text{NO}_3)_2$, Aldrich, >99.999%] and aluminum (III) isopropoxide [$\text{Al}(\text{OC}_3\text{H}_7)_3$, Aldrich, >98%]. During preparation, the Eu^{3+} dopant concentration was kept at 12mole% (or $\text{Y}_{1.76}\text{O}_{0.24}\text{O}_3$). This was the optimum Eu^{3+} dopant concentration reported in chapter 4. The Mg^{2+} and Al^{3+} co-dopant concentration was varied from 2mole% to 15mole% (2mole%, 5mole%, 7mole%, 10mole%, 12mole%, and 15mole%) and from 0.5mole% to 10mole% (0.5mole%, 1mole%, 2mole%, 4mole%, 5mole%, and 10mole%), respectively. The phosphor films were prepared using the optimum process

parameters from the previous studies (see chapter 4), namely annealing temperature of 750°C in rapid thermal processor (RTP), vacuum annealing environment, and annealing time of 55 seconds. The RTP annealing profile was same as the one shown in Figure 4-2. A $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor film sample without co-dopant was prepared as a reference sample. The annealed phosphor film samples have the thickness of about 100nm measured by the surface profiler.

5.3 Results and discussion

In general, co-dopants may interact with dopants. This interaction may cause change in the excitation or emission spectrum of phosphor materials. For this reason, the author firstly examined the effect of Mg^{2+} and Al^{3+} co-dopants to the PL emission spectrum of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. Prior to examining the PL emission spectrum of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films with Mg^{2+} or Al^{3+} co-dopants, it is important to firstly review the PL emission spectrum of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films (the reference sample) here. Figure 5-2 is the combination of Figure 4-3 and Figure 4-5(a), which have been previously shown in chapter 4.

Figure 5-2: PL emission spectrum of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films ($\lambda_{\text{ext.}}=246\text{nm}$). Inset shows the corresponding PL excitation spectrum of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films

Figure 5-2 presents the PL emission spectrum of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films excited at 246nm. The PL emission spectrum is dominated by the emission peak at about 613nm, which arises from $^5D_0-^7F_2$ emission transition. The other emission peaks at 580nm, 593nm, 653nm, and 710nm respectively corresponds to the $^5D_0-^7F_0$, $^5D_0-^7F_1$, $^5D_0-^7F_3$, and $^5D_0-^7F_4$ emission transition. All these transitions are resulted from the Eu^{3+} dopants, as was mentioned in section 4.2.2.1. The inset of Figure 5-2 shows the PL excitation spectrum of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films from 200nm to 300nm by monitoring the emission wavelength at 613nm. It is found that the highest absorption occurs at 246nm. The broad absorption peak at 246nm is due to the charge-transfer from the oxygen 2p state ($\text{O}2p$ state) to the charge-transfer state (CTS) of Eu^{3+} ions, which is known as charge-transfer transition. This has been discussed in section 4.2.2.1 in chapter 4.

Figure 5-3: PL emission spectra as a function of Mg^{2+} co-dopant concentration in $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films ($\lambda_{\text{ext.}}=246\text{nm}$)

Figure 5-4: PL emission spectra as a function of Al^{3+} co-dopant concentration in $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films ($\lambda_{\text{ext.}}=246\text{nm}$)

Figure 5-3 and 5-4 respectively shows the PL emission spectra of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films with Mg^{2+} and Al^{3+} co-dopants. It is clearly observed that there is no peak shift or spectrum change with the introduction of Mg^{2+} and Al^{3+} co-dopants into the $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films. In other words, the electronic transition of Eu^{3+} dopants does not change with the introduction of co-dopants. The sharp emission peak is attributed to the shielding effect by the outer $5s$ and $5p$ orbital in which the crystal field has less influence on the emission spectrum of lanthanide ions. The explanation for the orbital shielding effect was given in section 3.7.

Inset of Figure 5-3 and 5-4 respectively shows the PL intensity at 613nm as a function of Mg^{2+} and Al^{3+} co-dopant concentration. The insets show that the PL intensity depends on the co-dopant concentration. The PL intensity increases gradually with co-dopant concentration and reaches the maximum at $7\text{mole}\%\text{Mg}^{2+}$ and $2\text{mole}\%\text{Al}^{3+}$, respectively. The PL intensity of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}, 7\%\text{Mg}^{2+}$ and $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}, 2\%\text{Al}^{3+}$ is respectively increased by a factor of 1.7 and 1.3 compared to the reference sample (the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$

phosphor films without co-dopant). Beyond the optimum co-dopant concentration, however, the PL intensity decreases. The decrease of PL intensity is probably due to the defects in Y_2O_3 host material, which can lead to luminescent quenching, as described in section 3.9.2.2. The ionic radius of Y^{3+} , Mg^{2+} , and Al^{3+} is about 0.89Å, 0.66Å, and 0.51Å, respectively [5-2]. Since the ionic radius of Al^{3+} is smaller than Y^{3+} ion while Mg^{2+} has both smaller ionic radius and valency mismatch with Y^{3+} ion, both Al^{3+} and Mg^{2+} co-dopants may introduce distortion and hence defects into the Y_2O_3 host material. Therefore, the decrease of PL intensity is likely to occur when the co-dopant concentration is beyond the optimum concentration. The increase and followed by the decrease of PL intensity with co-dopant concentration has also been reported by Sun *et al.* for Li^+ co-dopant in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor materials [5-3].

Figure 5-5: XRD patterns of Mg^{2+} co-doped $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films at various co-dopant concentrations

Figure 5-6: XRD patterns of Al^{3+} co-doped $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films at various co-dopant concentrations

Figure 5-7: Phase diagram of $\text{MgO}-\text{Y}_2\text{O}_3$ [5-4]

Figure 5-8: Phase diagram of Y_2O_3 - Al_2O_3 [5-4]

Figure 5-5 and Figure 5-6 respectively shows the XRD patterns of Mg^{2+} and Al^{3+} co-doped $Y_2O_3:12\%Eu^{3+}$ phosphor films at different co-dopant concentrations. From the XRD patterns, the author does not observe any additional diffraction peaks indicating the existence of other phases due to the presence of the co-dopants. The phase diagram of MgO - Y_2O_3 and Y_2O_3 - Al_2O_3 is shown in Figure 5-7 and Figure 5-8, respectively. Based on the MgO - Y_2O_3 phase diagram shown in Figure 5-7, there could be a mixed phases of Y_2O_3 and $3MgO \cdot Y_2O_3$ at the annealing temperature of $750^{\circ}C$ [5-4]. Similarly, the mixed phases of Y_2O_3 and the $Y_4Al_2O_9$ could co-exist at the annealing temperature of $750^{\circ}C$ according to the Y_2O_3 - Al_2O_3 phase diagram shown in Figure 5-8 [5-4]. New diffraction peaks can be observed if the excessive dopants cluster in the Y_2O_3 host materials or a mixed phase is formed [5-5] due to the reaction between the co-dopants and the Y_2O_3 host materials. In this experiment, the phases of $3MgO \cdot Y_2O_3$ and $Y_4Al_2O_9$ are still not observed in the XRD results possibly due to the better incorporation of co-dopant into the Y_2O_3 matrix in the sol-gel process since the chemical mixing occurs at molecular level. The crystal structure of Y_2O_3 host material is retained in the samples

with co-dopants. Since there is no change in the XRD patterns of the $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films with co-dopants, the author therefore constructs an energy band diagram. The energy band diagram will be shown in Figure 5-11.

Figure 5-9: PL excitation spectra of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of Mg^{2+} co-dopant concentration ($\lambda_{\text{emi.}}=613\text{nm}$)

Figure 5-10: PL excitation spectra of $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films as a function of Al^{3+} co-dopant concentration ($\lambda_{\text{emi.}}=613\text{nm}$)

Earlier in the introduction section of this chapter, the author mentioned that much less is known about the roles of non-lanthanide co-dopants. Based on the above results, the author would like to propose the role of Mg^{2+} and Al^{3+} non-lanthanide co-dopants in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. Previous XRD patterns in Figure 5-5 and Figure 5-6 prove that the Y_2O_3 crystal structure is still retained even with the presence of co-dopants. From the PL excitation spectra shown in Figure 5-9 and Figure 5-10, it is observed that there is broadening of absorption spectra with increasing concentration of co-dopants. The broadening of the absorption spectra implies that there are more states involve in the absorption, which may be due to the overlap between the defect states created by the co-dopants with the CTS of Eu^{3+} dopants. Based on this explanation, the author proposes an energy band diagram as illustrated in Figure 5-11. The bandgap of Y_2O_3 host material is taken to be about 6eV [5-6]. The charge transfer excitation energy is approximately 5.04eV (246nm) as determined from the PL absorption spectrum shown in the inset of Figure 5-2. Under the excitation of a photon with energy of 5.04eV, an electron from the $\text{O}2p$ state is excited to the CTS of Eu^{3+} dopants. The defect states created by the co-dopants may overlap with the CTS of Eu^{3+} dopants and this leads to the broadening of absorption spectra. The broadening of the CTS of Eu^{3+} dopants causes higher absorption and hence the emission. The excitation process is followed by relaxation process. During the relaxation process, the energy of excited Eu^{3+} dopants is released non-radiatively from the CTS to the 5D_0 level. Red emission at wavelength 613nm is produced when the excited Eu^{3+} dopants relax from the 5D_0 level to the 7F_2 level.

Figure 5-11: Proposed mechanism due to co-dopants. Defect states created by the co-dopants cause the broadening of CTS. The light blue box denotes the broadening of CTS caused by the co-dopants

5.4 Chapter summary

The author finishes this chapter with the remark on the effect of Mg^{2+} and Al^{3+} co-dopants to the PL intensity of sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. The PL intensity is enhanced by introducing the Mg^{2+} or Al^{3+} co-dopants into the $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films. The optimum co-dopant concentration is 7mole% Mg^{2+} and 2mole% Al^{3+} in $\text{Y}_2\text{O}_3:12\%\text{Eu}^{3+}$ phosphor films, respectively. The enhancement of PL intensity is explained in terms of the increase of absorption due to the overlap between the defect states created by the co-dopants and the CTS of Eu^{3+} dopants near the $\text{Y}(4d+5s)$ conduction band. The overlap leads to CTS broadening and consequently induces higher absorption and hence the emission. The schematic energy band diagram of Mg^{2+} and Al^{3+} co-doped $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films are constructed based on the experimental results.

Chapter 6 Efficient radiative energy transfer in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure

6.1 Introduction

As stated before in section 1.2, there are two objectives in this work. The first objective is to develop high efficiency $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films by optimizing the process conditions and by using the Mg^{2+} and Al^{3+} co-dopants. The results have been reported in chapter 4 and chapter 5, respectively. This chapter will present the results of the second objective. As highlighted in the literature review in section 2.6, the energy transfer process from the ZnO to the Eu^{3+} ions is usually mediated by the defect states. However, the efficiency of the energy transfer process is still low and the mechanism is not well understood. Furthermore, the defect states in the $\text{ZnO}:\text{Eu}^{3+}$ materials that involved in the energy transfer process are difficult to control and reproduce. The author therefore aimed to develop the ZnO-based material systems which can show efficient radiative energy transfer process from the ZnO films to the Eu^{3+} ions without the involvement of the defect states. In this work, the author used $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ (ZnO films with varied concentration of cadmium (Cd) dopants) and ZnO films to radiatively transfer the energy to the Eu^{3+} ions of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. In the first part of the experiment, the author deposited the $\text{Y}_2\text{O}_3:12\text{mole}\%\text{Eu}^{3+}$ (or $\text{Y}_{1.76}\text{Eu}_{0.24}\text{O}_3$) phosphor films on top of the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films. The resulting structure was denoted as $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure. The objective of this experiment was to tune the peak wavelength of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films from 381nm (x value is 0mole%) to 394nm (x value is 8mole%) so that the emission spectra of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films overlapped with the absorption spectrum of Eu^{3+} ions peaked at 394nm (${}^7F_0-{}^5L_6$ absorption transition). In the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films, the narrowing of bandgap is expected when the ZnO films and the CdO films with different bandgap are combined. The narrowing of bandgap causes the peak wavelength to shift.

The shift of peak wavelength results in larger spectral overlap and leads to more efficient radiative energy transfer process from the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films to the Eu^{3+} ions of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. Hence, the PL intensity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films at about 611nm (5D_0 - 7F_2 emission transition) increases. In the second part of the experiment, the author deposited the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films on top of the ZnO films. The resulting structure was denoted as $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure. The ultra-violet (UV) random lasing spectra in the wavelength range of about 385–397nm is produced from the polycrystalline ZnO films with an optical excitation by using Nd:YAG laser. The UV random lasing spectra of ZnO films was tuned to overlap with the absorption spectra of Eu^{3+} ions peaked at 394nm (7F_0 - 5L_6 absorption transition) by increasing the pump power of Nd:YAG laser. Increasing the pump power of Nd:YAG laser results in a larger spectral overlap between the UV random lasing spectra of ZnO films and the absorption spectra of Eu^{3+} ions. The large spectral overlap leads to very efficient radiative energy transfer from the ZnO films to the Eu^{3+} ions of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. Hence, the visible UV random laser pumped red emission peaked at about 611nm (5D_0 - 7F_2 emission transition) has been observed. In both the experiments, the results have been explained on the basis of the radiative energy transfer from the emission centers (the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films or the ZnO films underneath) to the absorption centers (the Eu^{3+} ions of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films deposited on top of the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films or the ZnO films).

6.2 Preparation of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure

6.2.1 Sample preparation procedure of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure

Figure 6-1: Preparation of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure by the sol-gel process

The preparation steps of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure is presented in Figure 6-1. Note that both the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films and the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films in this experiment were prepared by the sol-gel process. The precursors used to prepare the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films were zinc acetate dihydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$, GCE Laboratory Chemicals, 99%, cadmium acetate dihydrate $[\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$, Sigma-Aldrich, 98%, 2-propanol $[\text{C}_3\text{H}_7\text{OH}]$, Sigma-Aldrich, 99.5%, and diethanolamine (DEA) $[\text{HOCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH}]$, Sigma-Aldrich, 98%. The processing equipment used was custom-made plastics glove box and spin coater (Laurell Manual Dispense Spin Processor model WS-400-6NPP-LITE). The chemicals mixing and spin coating processes were performed in the custom-made plastics glove box flushed with dry nitrogen gas to maintain 15% relative humidity (RH). Initially, the zinc acetate, 2-propanol, and DEA were mixed in the molar ratio of 1:10:0.8 to obtain the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ sol. The DEA was used as a stabilizing agent. Because the zinc acetate and cadmium acetate were sensitive to moisture, no additional water was added into the mixture to hydrolyze the zinc acetate and cadmium acetate precursors. The $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ sol indicates the $x\text{mole}\%$ of Cd dopants substituting the Zn host atoms. Note that here the Cd dopants refer to the substitutional elements that were added into the ZnO films in order to tune the bandgap of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films. The film samples derived from the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ sols were also denoted by the same notation. The x values of the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ sol range from 0mole% to 8mole% by varying the concentration of Cd dopants. The $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ sol was aged for about 24 hours in a sealed condition at room temperature prior to spin coating. To obtain the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films, the sol was dispensed on (100) Silicon substrate and spun at 3500 rpm for 30 seconds by using the spin coater. The $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ gel films were annealed in a furnace at 750°C for 5 minutes. The thickness of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films was about 150nm. To realize the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure, a layer of $\text{Y}_2\text{O}_3:12\text{mole}\%\text{Eu}^{3+}$ (or $\text{Y}_{1.76}\text{Eu}_{0.24}\text{O}_3$) phosphor film was deposited on top of the Zn_{1-x}

$x\text{Cd}_x\text{O}$ films that had been prepared. The preparation steps of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films have been reported in section 4.3.2. Briefly, a layer of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ film with a thickness of about 100nm was spin-coated on top of the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films after aging for 15 hours. The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure were finally obtained after annealing process at 750°C for 5 minutes in a furnace.

6.2.2 Results and discussion

6.2.2.1 The effect of Cd dopants to the PL of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure

Figure 6-2: The overlapping spectra between the PL emission spectra of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films (solid line, $\lambda_{\text{ext.}}=355\text{nm}$) and the absorption spectrum of Eu^{3+} ions (dash dot line)

Figure 6-2 shows the PL emission spectra of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films with x values range from 0mole% to 8mole% and the PL absorption of Eu^{3+} ions. The PL emission spectra of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films were measured by using the Spectrofluorometer system (SPEX Fluorolog-3) with the 355nm excitation wavelength. The ZnO films without Cd dopants show a broad emission peak at about 381nm, which is related to excitonic recombination [6-1]-[6-3]. The peak wavelength of the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films shifts from 381nm to 394nm with

increasing the concentration of Cd dopants from 0mole%Cd to 8mole%Cd. The shift of peak wavelength with increasing the concentration of Cd dopants is consistent with the results of other research groups [6-4]-[6-6]. The shift of peak wavelength have been related to the narrowing of bandgap, which is associated with the expansion of unit cell volume [6-1] because the smaller Zn^{2+} ions (ionic radius $0.60\text{\AA}$) are substituted by the larger Cd dopants (ionic radius $0.74\text{\AA}$) [6-7]. Furthermore, it is expected that the bandgap of a new compound will take an intermediate value between the bandgap of the constituent materials when the new compound is made of the constituent materials [6-8]. Since the bandgap of ZnO films and CdO films is respectively $\sim 3.4\text{eV}$ [6-9] and $\sim 2.3\text{eV}$ [6-2],[6-3], the bandgap of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films should falls in between the value of 2.3eV and 3.4eV.

Figure 6-3: Interpolation of bandgap of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films prepared in this experiment as a function of Cd dopant concentration. The inset shows the bandgap of ZnO and CdO. The closed squares represent the bandgap of ZnO films obtained in this experiment. The open circle at the other endpoint represents the bandgap of CdO films taken from Ref. 6-2 & Ref. 6-3. The gradient of both dot-dot line is the same

The bandgap of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films is a function of Cd dopant concentrations. Figure 6-3 shows the bandgap of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films prepared in this experiment decreases almost

linearly with increasing x -values from 0mole% (ZnO) to 8mole% ($\text{Zn}_{0.92}\text{Cd}_{0.08}\text{O}$). The inset of Figure 6-3 shows the bandgap of ZnO films and CdO films at two endpoints connected with a dot-dot line. The gradient of the dot-dot line shown in the inset is used as the reference to the author's results.

Other than the PL emission spectra of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films, Figure 6-2 also shows the PL absorption spectra of Eu^{3+} ions. There are two f - f absorption peaks at about 382nm (7F_0 - 5G_J ($J=2-5$) absorption transition) and 394nm (7F_0 - 5L_6 absorption transition) [6-10] in the absorption spectrum of Eu^{3+} ions. There will be a considerable amount of radiative energy transfer if the emission spectrum overlaps greatly with the absorption spectrum [6-11]. In the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure, the peak wavelength of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films shifts from 381nm (x value is 0mole%) to 394nm (x value is 8mole%) with increasing concentration of Cd dopants, which results in larger spectral overlap. With the larger spectral overlap, the radiative energy transfer from the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films to the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films is more efficient. Figure 6-4 shows the red emission intensity at 611nm (vertical left axis) and the estimation of spectral overlap (vertical right axis) as a function of Cd dopant concentrations. The estimation of spectral overlap is obtained by overlaying the emission spectrum of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films with the 7F_0 - 5L_6 absorption transition of Eu^{3+} ions peaks at 394nm. The 7F_0 - 5L_6 absorption transition is chosen because the oscillation strength of this absorption transition is larger than the 7F_0 - 5G_J ($J=2-5$) absorption transition [6-12]. In Figure 6-4, it is clear that the PL intensity of Eu^{3+} ions at 611nm increases with increasing spectral overlap. The results in Figure 6-4 clearly prove that the radiative energy transfer has taken place in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure because the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ films emit photons at 611nm after absorption of photons at 394nm from the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films underneath. Figure 6-5 shows the PL emission spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure in the 550nm to 650nm wavelength

range with the increasing concentration of Cd dopants in the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films. The corresponding red emission intensity at 611nm (the most dominate peak) of the spectra has previously been shown at the vertical left axis in Figure 6-4.

Figure 6-4: The relation between the spectral overlap and the red emission intensity at 611nm of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure as a function of Cd dopant concentration. The ${}^7\text{F}_0-{}^5\text{L}_6$ absorption transition of Eu^{3+} peaks at 394nm is used for the estimation of spectral overlap

Figure 6-5: PL emission spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure at 611nm ($\lambda_{\text{ext.}}=355\text{nm}$)

6.2.2.2 The effect of Eu^{3+} dopant concentration

Figure 6-6: PL emission spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ with different concentration of Eu^{3+} ions deposited on top of the $\text{Zn}_{0.92}\text{Cd}_{0.08}\text{O}$ films ($\lambda_{\text{ext.}}=355\text{nm}$). The inset shows the concentration quenching at 12mole% Eu^{3+} ions

To further verify the radiative energy transfer process in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure, the author fixed the emission wavelength at 394nm by using only the $\text{Zn}_{0.92}\text{Cd}_{0.08}\text{O}$ films and varied the concentration of Eu^{3+} ions in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films from 3mole% to 15mole%. The different concentration of Eu^{3+} ions signifies different numbers of absorption centers (the Eu^{3+} ions) from the same emission centers (the $\text{Zn}_{0.92}\text{Cd}_{0.08}\text{O}$ films). As predicted, the higher the concentration of Eu^{3+} ions, the higher the PL intensity at 611nm will be observed. Figure 6-6 shows the PL emission spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films with different concentration of Eu^{3+} ions deposited on top of the $\text{Zn}_{0.92}\text{Cd}_{0.08}\text{O}$ films. The PL intensity at 611nm progressively increases with increasing concentration of Eu^{3+} ions. The inset of Figure 6-6 shows that the PL intensity at 611nm increases until an optimum level at 12mole% Eu^{3+} ions and then decreases. This is caused by the concentration quenching phenomena, as discussed

earlier in section 3.9.2.2. The optimum concentration is same as the pervious results reported in section 4.2.2.4.

Subsequently, the author prepared the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure. The UV random laser pumped red emission was observed in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure. The UV random laser pumped red emission is resulted through the raditive energy transfer from the UV random lasing of ZnO films to the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films by controlling the pump power of Nd:YAG laser. The very efficient radiative energy transfer process is due to the strong spectral overlap between the emission spectrum of ZnO films and the absorption spectrum of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films.

6.3 Preparation of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure

6.3.1 Sample preparation procedure of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure

The preparation steps of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure is presented in Figure 6-7. The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure was realized by combining two fabrication techniques, namely the sol-gel process for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ films and the filtered cathodic vacuum arc (FCVA) technique for ZnO films. The ZnO films showed UV random lasing and were prepared by another research group by using the FCVA technique [6-13],[6-14]. Prior to the depositions of ZnO films, the quartz substrate was cleaned in an ultrasonic bath for 1 hour in acetone. The quartz substrate was subsequently cleaned in alcohol, deionized (DI) water, and blow-dried with nitrogen gas. To deposit the ZnO films on a quartz substrate, a cylinder zinc target (99.9% purity) was used as a cathode. The arc current was set at 70A. During the depositions of the ZnO films, the oxygen partial pressure was maintained at 2×10^{-4} Torr. The substrate temperature was set at 230°C [6-13],[6-14]. Subsequently, the as-deposited ZnO films were annealed in a furnace at 900°C for 20 minutes. The thickness of ZnO films was about 200nm. To realize the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$

structure, a layer of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor film was deposited on top of the ZnO films. The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor film was prepared by using the sol-gel process that has been described in details in section 4.3.2. Briefly, a layer of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ film with a thickness of about 100nm was spin-coated on top of the ZnO films after aging for 15 hours. The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure were finally obtained after annealing process at 750°C for 5 minutes in a furnace.

Figure 6-7: Preparation steps of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure

6.3.2 Results and discussion

6.3.2.1 Ultra-violet (UV) random lasing of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure

Figure 6-8: The light-light characteristics of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure in UV wavelength range. The inset shows the UV random lasing spectra of the structure at different pump powers ($\lambda_{\text{ext.}}=355\text{nm}$ with Nd:YAG laser)

The lasing characteristics of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure was studied with the 355nm laser excitation by using a frequency-tripled Nd:YAG laser at pulsed operation (120 ps, 10Hz). Figure 6-8 plots the light-light curve of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure from the Nd:YAG laser (355nm) pump power of about 0.05 MW/cm^2 to 1.5 MW/cm^2 . The corresponding UV random lasing spectra of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure are shown in the inset of Figure 6-8. The spectra are obtained at (a) low pump power below the threshold, (b) slightly above the threshold, and (c) high pump power above the threshold. At low pump power below the threshold, the UV random lasing from the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure is not observed. The slope of the light-light curve in Figure 6-8 increases considerably above the threshold which clearly marks the onset of the lasing action in which the output intensity increases rapidly with the excitation intensity. Hence, few sharp UV random lasing peaks from the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure within the

wavelength range of about 385-397nm are observed when the pump power increases above the threshold. The UV lasing emission of the ZnO films in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure is the random lasing with coherent feedback [6-14]-[6-16]. The theory has been reviewed in section 3.4.2.

6.3.2.2 UV random laser pumped red emission of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure

Figure 6-9: The overlapping spectra at three different pump powers at 0.4 MW/cm^2 , 5.5 MW/cm^2 , and 8.0 MW/cm^2 . Dash dot line represents the absorption spectrum of Eu^{3+} ions. Solid lines represent the emission spectra of ZnO films. (The magnification of the ZnO emission spectra is indicated in the bracket) ($\lambda_{\text{ext.}}=355\text{nm}$ with Nd:YAG laser)

Figure 6-9 shows the UV random lasing emission spectra of ZnO films at three different Nd:YAG laser pump powers (0.4 MW/cm^2 , 5.5 MW/cm^2 , and 8.0 MW/cm^2) and the PL absorption spectrum of Eu^{3+} ions. With the increase of Nd:YAG laser pump power, it is observed that the peak wavelength of UV random lasing emission spectra shifts slightly to lower energy. There is also changes between the two emission spectra of ZnO films from the pump power of 0.4 MW/cm^2 to 8.0 MW/cm^2 (20 times increase in pump power). The change is associated with the transition of exciton recombination to

electron hole plasma (EHP) recombination [6-17]. The electron-hole pairs (excitons) are formed at low excitation energy. With the increase of excitation energy, the density of electron-hole pairs is increased too. At high excitation energy, the excitons begin to lose the identity as individual quasi-particle and a new collective phase known as electron–hole plasma (EHP) is formed [6-18]. The presence of a high density of excited carriers will screen the interactions between electrons-ions and electrons-electrons in a material. Here, screening refers to the reduction of the strength of the Coulomb potential in the presence of excited carriers [6-19,6-20]. It is well-known that the bandgap result from the Coulomb potential between the electrons and the ions of a material [6-21,6-22]. The screening reduces the Coulomb potential between the electrons and the ions and thereby causes the bandgap of the material to shrink. The theoretical calculation work reported by Oshlies *et al.* [6-23] proves that the effect of screening caused by the additional electrons is the dominant effect in decreasing the bandgap of material. In another theoretical calculation work, the change of the bandgap (E_g') of GaAs is approximated by using equation 6-1 by considering the effect of screening [6-24]:

$$E_g'(eV) = E_{go} - 1.6 \times 10^{-8} p^{1/3} \quad (6-1)$$

where E_{go} is the bandgap of GaAs (1.424 eV) at 297K and p is the density of dopants (in cm^{-3}).

As shown in Figure 6-9, the UV random lasing intensity and the UV random lasing mode of the ZnO films also increases with the Nd:YAG laser pump power. The UV random lasing intensity of ZnO films increases with the increasing Nd:YAG laser pump power as anticipated. There is an increase in the UV random lasing mode because more random lasing cavities are excited when the Nd:YAG laser pump power increases. The increase in both the UV random lasing intensity and modes contributes to the larger spectral overlap between the UV random lasing emission spectrum of ZnO films and the absorption spectrum of Eu^{3+} ions. The estimation of spectral overlap is obtained by overlaying the UV random lasing emission spectra of ZnO films with the ${}^7F_0-{}^5L_6$ absorption transition of Eu^{3+} ions peaks at 394nm. The method of estimation applied here is same as what has been used for the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure. With the larger spectral overlap, the radiative energy transfer from the ZnO films to the Eu^{3+} ions of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films becomes more efficient. The result is shown in Figure 6-10.

Figure 6-10: The relation between the spectral overlap and the UV random laser pumped red emission intensity at 611nm of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure as a function of Nd:YAG laser pump power. The ${}^7F_0-{}^5L_6$ absorption transition of Eu^{3+} peaks at 394nm is used for the estimation of spectral overlap

Figure 6-10 shows the UV random laser pumped red emission intensity at 611nm (vertical left axis) and the estimation of spectral overlap (vertical right axis) as a function of Nd:YAG laser pump power. It is observed that the UV random laser pumped red emission intensity increases with increasing spectral overlap. At low pump power (point (a) in Figure 6-10), there is little spectral overlap and the UV random lasing emission from the ZnO films absorbed by the Eu^{3+} ions can only result in UV random laser pumped red emission with low intensity. At higher pump power (point (b) and (c) in Figure 6-10), the spectral overlap increases rapidly and the UV random laser pumped red emission intensity at 611nm increases too. Similar to the reason that has been used for the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure, the observation of UV random laser pumped red emission is due to the radiative energy transfer process from the ZnO films to the Eu^{3+} ions of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films as a result of strong spectral overlap.

Figure 6-11: The UV random laser pumped red emission spectra of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure at three different pump powers at (a) 0.4 MW/cm^2 , (b) 5.5 MW/cm^2 , and (c) 8.0 MW/cm^2 ($\lambda_{\text{ext.}}=355 \text{ nm}$ with Nd:YAG laser)

Figure 6-11 shows the UV random laser pumped red emission spectra at three different pump powers at 0.4 MW/cm^2 , 5.5 MW/cm^2 , and 8.0 MW/cm^2 . The corresponding UV random laser pumped red emission intensity at 611nm of the spectra has previously been shown at the vertical left axis in Figure 6-10.

6.4 Schematic diagram of radiative energy transfer in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ and the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure

In the first part of this chapter, the author has reported the increase of PL intensity at 611nm in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure with increasing concentration of Cd dopants. In the second part of this chapter, the UV random laser pumped red emission at 611nm has been observed in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure. The underlying mechanism used to explain the results of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ structure and the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure is quite similar. It is based on the radiative energy transfer process from the emission centers (the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films or the ZnO films underneath) to the absorption centers (the Eu^{3+} ions of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ films deposited on top of the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films or the ZnO films). Hence, an unified schematic diagram of radiative energy transfer process involving the bandgap of ZnO films and energy states of Eu^{3+} ions can be applied to the two structures. The schematic diagram of energy transfer process is constructed and depicted in Figure 6-12.

Figure 6-12: An unified schematic diagram of radiative energy transfer process. E_g is the original bandgap of the ZnO films. E_g' is the new bandgap after doping with 8mole% Cd dopants (for $Y_2O_3:Eu^{3+}/Zn_{1-x}Cd_xO$ structure) or pumped with high power Nd:YAG laser (for $Y_2O_3:Eu^{3+}/ZnO$ structure)

For the $Y_2O_3:Eu^{3+}/Zn_{1-x}Cd_xO$ structure, the bandgap narrowing is due to the incorporation of Cd dopants. The reasons have been discussed in section 6.2.2.21. The reduction of bandgap from E_g to E_g' due to bandgap narrowing is indicated in Figure 6-12. After excitation with the Xenon lamp of the Spectrofluorometer system (SPEX Fluorolog-3) at wavelength 355nm, the $Y_2O_3:Eu^{3+}/Zn_{0.92}Cd_{0.08}O$ structure produces UV emission at about 394nm. The UV emission spectrum of $Zn_{0.92}Cd_{0.08}O$ films overlaps strongly with the absorption spectrum of Eu^{3+} ions peaks at 394nm (7F_0 - 5L_6 absorption transition). Hence, the radiative energy transfer from the $Zn_{0.92}Cd_{0.08}O$ films to the Eu^{3+} ions takes place promoting the Eu^{3+} ions from the ground state (7F_0) to the excited state (5L_6). The Eu^{3+} ions in the 5L_6 excited state undergo non-radiative decay to the 5D_0 state because the energy separation of adjacent levels are small. Radiative transition takes place between the 5D_0 and the 7F_J ($J=0-6$) states because of the larger gap [6-25]. The

radiation is dominated by the red emission peak at 611nm, which arises from the 5D_0 - 7F_2 emission transition.

For the $Y_2O_3:Eu^{3+}/ZnO$ structure, the optical pump source is the tripled-frequency pulsed operated Nd:YAG laser. After the $Y_2O_3:Eu^{3+}/ZnO$ structure was optically pumped at 355nm with Nd:YAG laser at high pump power, the intense UV random lasing emission of ZnO films was produced. The intense UV random lasing emission is due to the electron hole plasma recombination, which causes the reduction of bandgap. This phenomenon is called bandgap renormalization [6-26]. The reduction of bandgap from E_g to E_g' due to bandgap renormalization is indicated in Figure 6-12. The UV random lasing spectrum of ZnO films overlaps strongly with the absorption spectrum of Eu^{3+} ions peaks at 394nm (7F_0 - 5L_6 absorption transition). In this case, very efficient radiative energy transfer from the ZnO films to the Eu^{3+} ions takes place promoting the Eu^{3+} ions from the 7F_0 ground state to the 5L_6 excited state. The relaxation process which finally results in UV random laser pumped red emission at 611nm is similar to the case for the $Y_2O_3:Eu^{3+}/Zn_{1-x}Cd_xO$ structure just explained above.

6.5 Chapter summary

The red spontaneous emission peaks at 611nm (5D_0 - 7F_2 emission transition) has been observed in the $Y_2O_3:Eu^{3+}/Zn_{1-x}Cd_xO$ structure. This is due to the radiative energy transfer process from the $Zn_{1-x}Cd_xO$ to the Eu^{3+} ions of $Y_2O_3:Eu^{3+}$ phosphor films. In the $Y_2O_3:Eu^{3+}/Zn_{1-x}Cd_xO$ structure, the peak wavelength of $Zn_{1-x}Cd_xO$ films was tuned from 381nm (x value is 0mole%) to 394nm (x value is 8mole%) by increasing the concentration of Cd dopants. When the peak wavelength of $Zn_{1-x}Cd_xO$ films shifts towards the absorption wavelength of Eu^{3+} ions peaks at 394nm (7F_0 - 5L_6 absorption transition), this results in larger spectral overlap and hence the PL intensity of Eu^{3+} ions

at 611nm increases. The UV random laser pumped red emission peaks at 611nm has been observed in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure. This is due to the radiative energy transfer process from the ZnO films to the Eu^{3+} ions of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. In the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure, the UV random lasing spectra of ZnO films was tuned to overlap with the absorption spectrum of Eu^{3+} ions by increasing the Nd:YAG laser pump power. The UV random lasing spectrum of ZnO films changes with the increase of Nd:YAG laser pump power. The change results in larger spectral overlap with the absorption spectrum of Eu^{3+} ions and hence the UV random laser pumped red emission at 611nm is produced. An unified schematic energy band diagram has been constructed to explain the radiative energy transfer process in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ and the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure. The findings of this work open the possibility to realize lanthanide ions-based thin film devices.

Chapter 7 Deposition of indium tin oxide (ITO) films

7.1 Introduction

The author has so far focused on the development of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films and ZnO-based material systems ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure). Furthermore, the author has also developed a transparent electrode material in this work, namely indium tin oxide (ITO) thin films. The attractiveness of ITO films is attributed to its low sheet resistance and high optical transmittance from visible to near infra-red wavelength range [7-1]. Since the ITO is a transparent and conductive material (transparent electrode material), the ITO films have important applications in electronic display devices and optoelectronic devices [7-2],[7-3]. Therefore, preparation and characterization results of the ITO films are included in this thesis as an additional work. It is commonly known that the optical and electrical properties of the ITO films depend on the process conditions [7-1],[7-4]-[7-6]. Diffusion of oxygen atoms from air may improve the stoichiometry of ITO films which will increase the transmittance [7-7]-[7-9]. However, the resistivity of ITO films increases after post-annealing treatment in the air. Based on the resistivity characterizations, the well accepted model for the decrease of conductivity is the reduction of oxygen vacancies due to the diffusion of oxygen atoms from the air [7-10]-[7-12]. In this work, the author has shown that the model of oxygen diffusion can also be related to the X-ray diffraction (XRD) patterns and surface morphology. It is observed that the diffusion of oxygen atoms from air results in (400) preferred crystal growth orientation. The atomic force microscope (AFM) images reveal that the ITO films post-annealed in vacuum have larger grain size compared to those post-annealed in air.

7.2 Sample preparation procedure of ITO films

Figure 7-1: Preparation and optimization process flow of ITO films

The optimization process flow of ITO films is presented in Figure 7-1. The ITO films were deposited on glass substrates (Corning Cover glass, 22mm×22mm) by using the radio-frequency (RF) magnetron sputtering deposition. The target was 3" diameter In₂O₃-10wt%SnO₂ sputtering target (Kurt J.Lesker Company, 99.99%). The glass substrates were firstly cleaned in acetone, alcohol (Isopropylalcohol), deionized (DI) water, and blow-dried with nitrogen gas before loaded into the sputtering vacuum chamber. The glass substrates were pre-baked at 300°C for 30 minutes in the sputtering vacuum chamber before deposition of the ITO films. The sputtering vacuum chamber was evacuated to a base pressure of about 3.0×10⁻⁶ Torr before each sputtering deposition process. Prior to the depositions of ITO films on the glass substrates, the sputtering target was pre-sputtered for 5 minutes in order to remove any contaminants that might have been formed on the target. During deposition without oxygen gas, argon

(Ar) deposition pressure was maintained at about 6.0×10^{-3} Torr to attain deposition rate of approximately 43 Å/min. The ITO films typically have a thickness of about 250nm after sputtering time of 1 hour. Other process parameters such as RF power of 40W, target-to-substrate distance of 9 cm, sputtering time of 1 hour, and the cooling time were kept constant. The influence of oxygen gas was investigated by varying the oxygen gas flow rate from 2sccm (sputtering pressure of 6.7×10^{-3} Torr) to 6sccm (sputtering pressure of 7.8×10^{-3} Torr). During deposition with oxygen gas, the Ar deposition pressure was maintained at about 6.0×10^{-3} Torr. The as-deposited ITO films were subsequently subjected to post-annealing treatment in vacuum and air from 350°C to 500°C for 1 hour.

7.3 Results and discussion

7.3.1 The effect of deposition pressure

Figure 7-2: Deposition rate of ITO films as a function of Ar deposition pressure

The deposition rate of ITO films was firstly studied in order to estimate the time required for a deposition process. The substrate temperature was 150°C. Figure 7-2 presents the dependence of ITO films deposition rate on the Ar deposition pressure.

Within the deposition pressure range being studied, it is clear that the highest deposition rate ($\sim 43 \text{ \AA/min}$) is achieved at the deposition pressure of about $6.0 \times 10^{-3} \text{ Torr}$. At the deposition pressure of $4.5 \times 10^{-4} \text{ Torr}$, the content of Ar gas is low. At this condition, a relatively small number of Ar ions are generated and subsequently accelerated to the sputtering target to bombard the target atoms. Therefore, this results in a low deposition rate. However, the deposition rate also shows a decreasing trend for the deposition pressure beyond the optimum deposition pressure ($6.0 \times 10^{-3} \text{ Torr}$). It is because the mean free path of gaseous species decreases when the deposition pressure is increased [7-13] to $1.0 \times 10^{-2} \text{ Torr}$. Mean free path is the average distance that a particle travels before experiencing a collision with other molecules in the gas phase [7-14]. Following the result shown in Figure 7-2, the deposition pressure was maintained at about $6.0 \times 10^{-3} \text{ Torr}$ throughout this experiment in order to achieve the reasonable deposition rate.

7.3.2 The effect of substrate temperature

Figure 7-3: Influence of substrate temperature to the resistivity of ITO films

Next, the author investigated the influence of substrate temperature to the resistivity of ITO films during the deposition process. Figure 7-3 presents the resistivity of ITO films

as a function of substrate temperature. It is clearly seen that the resistivity of ITO films strongly depends on the substrate temperature. On increasing the substrate temperature, the resistivity dramatically decreases. From 150°C to 300°C, the resistivity decreases significantly with the increase of substrate temperature. From 300°C to 400°C, the resistivity of ITO films begins to saturate at about 7.65×10^{-4} ohm-cm. Hence, the substrate temperature at 300°C is considered as the optimum substrate temperature. This trend can be explained by the improvement of ITO films crystallinity with the increase of substrate temperature, as discussed below.

Figure 7-4: XRD patterns of ITO films as a function of substrate temperature

As shown from the XRD patterns in Figure 7-4, the crystallinity of ITO films improves as the substrate temperature increases. At 150°C, the ITO films are still in amorphous state. A transition from amorphous to polycrystalline films is observed at substrate temperature of 250°C. The crystallinity of ITO films improves significantly from 250°C to 400°C. The diffraction peaks can be indexed to the In_2O_3 cubic structure (JCPDS no. 06-0416). At 150°C, the ITO films are still in amorphous state. There is a strong scattering effect on the charge carriers arising from the disorder amorphous network [7-15]. The mobility of charge carrier in amorphous ITO films is therefore reduced. As the

substrate temperature increases to 250°C, small crystals start to grow. The mobility of charge carriers does not improve much because the small grain size at low substrate temperature causes pronounced grain boundary scatterings [7-16],[7-17]. As the substrate temperature increases further to above 300°C, the grain size of the crystals becomes larger and hence the grain boundary scatterings are reduced. This explains the results shown in Figure 7-3.

7.3.3 The effect of oxygen flow

Figure 7-5: Influence of oxygen gas flow rate to the resistivity of ITO films

In this section, the influence of oxygen gas content during deposition process is reported. Oxygen content in ITO films is an important control parameter because there is a critical oxygen content which results in ITO films with lowest resistivity and highest transmittance [7-18]. Figure 7-5 presents the resistivity of ITO films as a function of oxygen gas flow rate deposited at substrate temperature of 300°C. It is shown that the resistivity of ITO films increases with the increase of oxygen gas flow rate. It is well known that the charge carriers of the ITO films are either contributed by Sn^{4+} ions or oxygen vacancies [7-2],[7-4],[7-19],[7-20]. The incorporation of oxygen atoms into the

ITO films causes the decrease of oxygen vacancies and hence this results in the ITO films with higher resistivity [7-21].

Figure 7-6: XRD patterns of as-deposited ITO films as a function of oxygen gas flow rate

XRD patterns in Figure 7-6 compare the ITO films prepared with various oxygen gas flow (0sccm, 2sccm, and 6sccm). The (222) preferred crystal growth orientation is observed when the ITO films were prepared in a condition without oxygen gas flowing into the chamber (0sccm oxygen flow rate). However, the preferred orientation changes from (222) to (400) when the oxygen gas was introduced into the chamber during the depositions of ITO films. This result shows that the incorporation of oxygen atoms into the ITO films has influenced the preferred crystal growth orientation. Change of preferred orientation from (222) to (400) has been observed with the increase of deposition rate [7-22] and substrate temperature [7-23].

7.3.4 The effect of post-annealing treatment

In addition to the effect of substrate temperature and oxygen flow, the properties of ITO films upon post-annealing treatment were also investigated. This is because the post-annealing ambient plays an important part in improving the electrical and optical properties of ITO films. Figure 7-7 shows the AFM images of the as-deposited ITO films at 300°C, ITO films after post-annealing treatment in air (400°C and 500°C) and vacuum (400°C and 500°C). The average grain size of ITO films measured from the AFM images in Figure 7-7 is presented in Table 7-1. Grain growth with increasing post-annealing temperature is observed in both post-annealing ambient. However, the ITO films post-annealed in air have smaller grain size than those in vacuum at the same post-annealing temperature. This is probably because the higher atmospheric pressure in air than those in vacuum suppresses the grain growth of ITO films. Hence, more energy is required for the grain growth of ITO films in air compared to that in vacuum. It has been reported that the polycrystalline silicon films with larger grain size were obtained when the samples were subjected to excimer-laser annealing treatment in vacuum environment compared to those treated in other gases (helium, nitrogen, and argon) and air environment [7-24].

Figure 7-7: AFM images of ITO films: (a) reference sample (as-deposited 300°C)
(b) post-annealing at 400°C in air (c) post-annealing at 500°C in air
(d) post-annealing at 400°C in vacuum (e) post-annealing at 500°C in vacuum

Table 7-1: Comparison of grain size and surface roughness of ITO films post-annealed in vacuum and air. The grain size was obtained by manually measuring the grains of AFM image. The Root-Mean-Square (RMS) surface roughness is an automated statistical measurement by the computer

Preparation conditions	Grain size (nm)	RMS Surface roughness (nm)
As-deposited at 300°C (reference)	48 ± 12	6.2
Post-annealing at 400°C in air	74 ± 14	5.4
Post-annealing at 500°C in air	107 ± 19	4.1
Post-annealing at 400°C in vacuum	81 ± 19	4.8
Post-annealing at 500°C in vacuum	125 ± 23	3.7

Figure 7-8: Influence of post-annealing temperature and ambient to the resistivity of ITO films. 300°C is the as-deposited ITO film which serves as a reference sample

Figure 7-8 compares the resistivity of ITO films post-annealed at different temperatures (from 350°C to 500°C) and ambients (vacuum and air). The as-deposited ITO film at substrate temperature of 300°C taken as a reference sample is also included. It is observed in this experiment that the resistivity of the ITO films decreases when the

films were post-annealed in vacuum from 350°C to 500°C. The improvement of the resistivity is due to the decrease of the grain boundary scatterings, as a result of grain growth after post-annealing treatment, as presented in Table 7-1. It is well known that grain with smaller size may result in greater grain boundary scatterings [7-17]. For the ITO films post-annealed in air as presented in Figure 7-8, however, the resistivity of the ITO films increases with increasing post-annealing temperature from 350°C to 500°C. As shown in Table 7-1 earlier, the ITO films post-annealed in air have also experienced grain growth. Taking into account only the effect of grain boundary scatterings, it is expected that resistivity of the ITO films will decrease. However, during the post-annealing in air, the oxygen atoms from air have inevitably diffused into the ITO films and reduced the oxygen vacancies. Consequently, there is a competition between the reduction of carrier concentration (due to diffusion of oxygen atoms into ITO films) and the increase of carrier mobility (due to increase of grain size). In this case, the reduction of carrier concentration is more dominant than the increase of carrier mobility. It has been reported that the oxygen atoms from air may reduce the degree of oxygen deficiency and hence produce the ITO films with higher resistivity [7-10]-[7-12]. This explains why the ITO films post-annealed in air have higher resistivity than those of as-deposited ITO films in this study.

The author has previously shown in Figure 7-6 that the preferred crystal growth orientation changes from (222) to (400) when the ITO films were prepared in the oxygen-rich condition. Hence, the (400) XRD peak can be related to the degree of oxygen atoms diffusion into the ITO films. The higher (400) XRD peak intensity corresponds to greater diffusion of oxygen atoms from air into the ITO films. As presented in Figure 7-9(a) and Figure 7-9(b), the ITO films post-annealed in vacuum from 350°C to 500°C have relatively low (400) XRD peak intensity compared to that of

the ITO films post-annealed in air. This indicates that there is more oxygen atoms diffuse into the ITO films post-annealed in air. The resistivity of ITO post-annealed in air therefore increases with (400) crystal growth orientation.

Figure 7-9: (a) XRD patterns of ITO films post-annealed in air from temperature 350 °C to 500°C (b) XRD patterns of ITO films post-annealed in vacuum from temperature 350°C to 500°C. In both figures, 300°C is the as-deposited ITO film which serves as a reference sample

Figure 7-10: Influence of post-annealing temperature and ambient to the transmittance of ITO films. 300°C is the as-deposited ITO film which serves as reference sample

Figure 7-10 compares the measured transmittance of ITO films post-annealed at different pot-annealing temperatures and ambient. The results in Figure 7-10 shows that the transmittance of ITO films post-annealed in vacuum is slightly higher compared to the ITO films post-annealed in air and reference sample (as-deposited ITO film at 300°C). The higher transmittance could be related to the surface roughness of the ITO films. As shown in Table 7-1, the ITO films post-annealed in vacuum have lower surface roughness compared to the ITO films post-annealed in air. Park *et al.* explains that the ITO films with lower surface roughness have higher transmittance because of less scattering [7-25]. With the larger grain size, the ITO films post-annealed in vacuum reduce the light scattering and hence give higher transmittance.

7.4 Chapter summary

The study on ITO films may be summarized as follows. Good quality ITO films were obtained through a systematic study on several process parameters such as substrate temperature, oxygen gas flow rate, post-annealing temperature, and post-annealing ambient. The resistivity of ITO films increases with increasing oxygen content. Grain growth has been observed in the ITO films post-annealed from 350°C to 500°C in either vacuum or air environment. The reduction of oxygen vacancies and pronounced grain boundary scatterings have caused the ITO films post-annealed in air to have higher resistivity. The ITO film with lowest resistivity ($\sim 3.49 \times 10^{-4} \Omega\text{-cm}$) has been prepared through post-annealing at 500°C in vacuum environment. Based on the results, the author has showed that the model of oxygen diffusion can be related to the XRD patterns and AFM images. The diffusion of oxygen atoms from air into the ITO films affects the crystal growth orientation of ITO films. The AFM images show that the ITO films post-annealed in vacuum have larger grain size compared to the ITO films post-annealed in air.

Chapter 8 Conclusion and Recommendations

The author has reported the results of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films, the radiative energy transfer from the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ and the ZnO films to the Eu^{3+} ions in the ZnO-based material systems ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure), and the indium tin oxide (ITO) films from chapter 4 to chapter 7. This chapter is presented in order to recall all the main achievements of this work and to offer recommendations for future work.

8.1 Conclusion

Recall that there are two objectives of this work. The first objective is to develop high efficiency $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films by optimizing the process conditions of sol-gel process and by using the Mg^{2+} and Al^{3+} co-dopants. The second objective is to develop ZnO-based material systems which can show efficient radiative energy transfer process from the ZnO films to the Eu^{3+} ions without the involvement of the defect states. Both objectives have been achieved.

In the first part of this work, the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films were developed by using the sol-gel process. Two sol-gel precursors, namely yttrium 2-methoxyethoxide and yttrium (III) isopropoxide, were used in the fabrication of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. The yttrium 2-methoxyethoxide is better than the yttrium (III) isopropoxide in terms of higher stability against moisture sensitivity and the ease of handling during the preparation. The process parameters such as concentration of Eu^{3+} dopants, annealing temperature, annealing environment, and annealing duration were optimized in order to prepare high efficiency $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. The optimum concentration of Eu^{3+} dopants is found to be 12mole% Eu^{3+} to achieve the highest emission of the film

prepared. Further increase in the concentration of Eu^{3+} dopants beyond 12mole% leads to the decrease of photoluminescent (PL) intensity of the film at about 613nm (5D_0 - 7F_2 emission transition). This phenomenon is called concentration quenching. Based on the optimized Eu^{3+} dopant concentration, the critical transfer distance (R_c) between the Eu^{3+} dopants is estimated to be about 0.84 nm. Moreover, the influences of annealing temperature, annealing environment, and annealing duration in the rapid thermal processors (RTP) to the PL intensity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films were investigated. The results show that the sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films annealed at 750°C yield the highest PL intensity at 613nm. Annealing temperature beyond 750°C makes the orange emission to become more dominant due to the change of crystal structures. It has also been found that, to eliminate H_2O impurities, annealing using the RTP in the vacuum environment is more efficient than that in the oxygen and nitrogen atmosphere. The PL intensity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films was also influenced by the annealing time. After short annealing (15 seconds) in the RTP at 750°C in vacuum environment, there were still some H_2O impurities entrapped in the sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. It has been found that the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films post-annealed in a furnace (1, 5, 11, and 20 hours) have higher PL intensity compared to the films only annealed in RTP. This is due to the further elimination of H_2O impurities from the films and the grain growth.

The sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films were incorporated with the Mg^{2+} and Al^{3+} co-dopants in order to enhance the emission efficiency. It has been found that the Mg^{2+} and Al^{3+} co-dopants can further enhance the PL intensity of sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films at 613nm (5D_0 - 7F_2 emission transition). The optimum co-dopant concentration is 7mole% Mg^{2+} and 2mole% Al^{3+} in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films, respectively. The enhancement of PL intensity at 613nm by the Mg^{2+} and Al^{3+} co-

dopants is explained in terms of the creation of defect states near the $Y(4d+5s)$ conduction band, which overlap with the charge-transfer state (CTS) of Eu^{3+} ions. The overlap leads to CTS broadening and consequently induces higher absorption and hence the increase of the PL intensity. From the experiment results, a schematic energy band diagram of $Y_2O_3:Eu^{3+}$ phosphor films with Mg^{2+} and Al^{3+} co-dopants has been constructed.

In the second part of this work, the author developed the ZnO-based material systems which show efficient radiative energy transfer process from the ZnO films to the Eu^{3+} ions without the involvement of the defect states. The $Zn_{1-x}Cd_xO$ films (ZnO films with varied concentration of cadmium (Cd) dopants) and the ZnO films were used in two separate experiments. The author deposited the sol-gel derived $Y_2O_3:Eu^{3+}$ phosphor films on top of the $Zn_{1-x}Cd_xO$ films and the ZnO films. The resulting structure was denoted as $Y_2O_3:Eu^{3+}/Zn_{1-x}Cd_xO$ structure and $Y_2O_3:Eu^{3+}/ZnO$ structure. For the $Y_2O_3:Eu^{3+}/Zn_{1-x}Cd_xO$ structure, the peak wavelength of $Zn_{1-x}Cd_xO$ films was tuned from 381nm (x value is 0mole%) to 394nm (x value is 8mole%) so that the emission spectrum of $Zn_{1-x}Cd_xO$ films overlapped with the absorption spectrum of Eu^{3+} ions peaked at 394nm (${}^7F_0-{}^5L_6$ absorption transition). The peak wavelength of $Zn_{1-x}Cd_xO$ films shifts with the increasing concentration of Cd dopants because the bandgap of $Zn_{1-x}Cd_xO$ films takes an intermediate value between the bandgap of ZnO and cadmium oxide (CdO). The shift of the peak wavelength of $Zn_{1-x}Cd_xO$ films towards the absorption wavelength of Eu^{3+} ions at 394nm (${}^7F_0-{}^5L_6$ absorption transition) leads to a larger spectral overlap. The larger spectral overlap results in more efficient radiative energy transfer from the $Zn_{1-x}Cd_xO$ films to the Eu^{3+} ions. Hence, the PL intensity of $Y_2O_3:Eu^{3+}$ phosphor films at about 611nm (${}^5D_0-{}^7F_2$ emission transition) increases.

For the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure, the ultra-violet (UV) random lasing spectrum of ZnO films was tuned to overlap with the absorption spectrum of Eu^{3+} ions peaked at 394nm (7F_0 - 5L_6 absorption transition) by increasing the pump power of Nd:YAG laser. The UV random lasing spectrum in the wavelength range of about 385-397nm have been produced from the polycrystalline ZnO films by using the Nd:YAG laser. When the pump power of Nd:YAG laser increases, it has been found that the peak wavelength of UV random lasing shifts slightly to lower energy (shrinkage of bandgap). This is attributed to the electron hole plasma recombination. Furthermore, both the UV random lasing intensity and the UV random lasing modes also increase with the increase of Nd:YAG laser pump power. The increase of UV random lasing intensity and the UV random lasing modes contributes to a larger spectral overlap between the emission spectrum of ZnO films and the absorption spectrum of Eu^{3+} ions. The large spectral overlap leads to very efficient radiative energy transfer from the ZnO films to the Eu^{3+} ions. Hence, the visible UV random laser pumped red emission centered at about 611nm (5D_0 - 7F_2 emission transition) has been observed. An unified schematic energy band diagram has been constructed to explain the radiative energy transfer process in the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Zn}_{1-x}\text{Cd}_x\text{O}$ and the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ structure. The experimental results above show that the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films and the ZnO-based material systems have potential to be used for photonic applications in future.

Other than the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ -based phosphor films and the ZnO-based material systems, the ITO films were developed by the radio-frequency (RF) magnetron sputtering deposition. The effects of several process parameters such as substrate temperature, oxygen gas flow rate, post-annealing temperature, and post-annealing environment to the ITO films were studied. It has been found that the resistivity of ITO films increases with increasing oxygen gas flow. The incorporation of oxygen atoms into the ITO films

leads to the decrease of oxygen vacancies. Grain growth of ITO films has been observed in the ITO films post-annealed from 350°C to 500°C either in vacuum or air environment. The atomic force microscope (AFM) images reveal that the ITO films post-annealed in vacuum have larger grain size compared to those post-annealed in air environment. The ITO films post-annealed in air have higher resistivity compared to the ITO films post-annealed in vacuum because of two reasons, namely the reduction of oxygen vacancies (due to the diffusion of oxygen atoms into ITO films) and the pronounced grain boundary scatterings (due to smaller grain size). The author also showed that the model of oxygen diffusion from air into the ITO films during post-annealing could be related to the X-ray diffraction (XRD) patterns. The diffusion of oxygen atoms from air results in (400) preferred crystal growth orientation. The ITO films developed by the RF magnetron sputtering deposition can be readily used as a transparent electrode material in many photonic devices.

8.2 Recommendations for further research

This section outlines the recommendations for future works that can be possibly undertaken by other researchers in future as a continuation of the author's works.

- 1) Development of high emission efficiency $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films by using other co-dopants: The author has shown that the Mg^{2+} and Al^{3+} co-dopants can further enhance the PL intensity of sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. Future research works could be focused in this direction since there are many other elements that can be possibly used as the co-dopants for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films. For example, the future works could be focused on the other elements with the same group as Mg and Al. Since these elements have similar chemical and physical properties as the co-dopants (Mg^{2+} and Al^{3+}) used in this

work, similar results as shown in this work could be expected. Nevertheless, a more systematic investigation on these elements is required.

- 2) Electrically-pumped photonic devices: The red spontaneous emission peaks at 611nm (5D_0 - 7F_2 emission transition) has been observed in the $Y_2O_3:Eu^{3+}/Zn_{1-x}Cd_xO$ structure with an optical excitation. Furthermore, the author has also demonstrated the UV random laser pumped red emission at 611nm from the $Y_2O_3:Eu^{3+}/ZnO$ structure by using the Nd:YAG laser. The electrically-pumped photonic devices are desirable for practical applications. Therefore, the future challenge is to design and fabricate the electrically-pumped photonic devices. To realize the electrically-pumped devices, the ZnO-based *pn* junctions (contact between a *p*-type and a *n*-type semiconductor) could be used. Hence, the development of *p*-type ZnO and *n*-type ZnO is imperative. The efforts to obtain reliable *p*-type ZnO have so far been mainly unsuccessful. This will be a challenge to fabricate the electrically-pumped devices. If the electrically-pumped devices could be realized, the emission wavelength of the device could be conveniently tuned by using dopants, as demonstrated in this work by using the Cd dopants. Another way to realize the electrically-pumped devices is to embed ZnO nanocrystals into an active layer doped with Eu^{3+} dopants. In such a device, the energy transfer process from the ZnO nanocrystals to Eu^{3+} ions could also involve the non-radiative energy transfer process.
- 3) Modifying the morphology of films: In section 2.4, the author has reviewed the approaches that have been dedicated to increase the emission efficiency of $Y_2O_3:Eu^{3+}$ phosphor films. The approaches include developing the process conditions, varying the composition of materials, and modifying the morphology of films. The author has developed high efficiency $Y_2O_3:Eu^{3+}$ -based phosphor films by optimizing the process conditions of sol-gel process and by using the

co-dopants (Mg^{2+} and Al^{3+}). The third approach (modifying the morphology of films) was not included in this work. Therefore, the author suggests that the future research works could also be focused on modifying the morphology of the films to increase the light extraction efficiency. For example, an effective etching technique with precise directional control should be developed in order to etch deep trench or particular patterns into the phosphor layers. By using the etching technique, the surface morphology of phosphor layers can be tailored conveniently.

Author's Publications

1. **M.K.Chong**, K.Pita, and C.H.Kam, "Photoluminescence of sol-gel-derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ thin-film phosphors with Mg^{2+} and Al^{3+} co-doping," *Applied Physics A: Materials Science & Processing*, vol. 79, pp. 433-437, Aug 2004.
2. **M.K.Chong**, K.Pita, and C.H.Kam, "Photoluminescence of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ thin film phosphors by sol-gel deposition and rapid thermal annealing," *Journal of Physics and Chemistry of Solids*, vol. 66, pp. 213-217, Jan 2005.
3. **M.K.Chong**, K.Pita, and C.H.Kam, "Thermal annealing effect on $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films prepared by yttrium 2-methoxyethoxide sol-gel precursor," *Materials Chemistry and Physics*, vol. 100, pp.329-332, Dec 2006.
4. **M.K.Chong**, A.P.Abiyasa, K.Pita, and S.F.Yu, "Visible red random lasing in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{ZnO}$ polycrystalline thin films by energy transfer from ZnO films to Eu^{3+} ," *Applied Physics Letters*, vol. 93, pp. 151105-151105, Oct 2008.
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6. **M. K. Chong**, Q. V. Vu, and K. Pita, "Red emission through radiative energy transfer from wavelength-tunable $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ layers to $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films," *Electrochemical and Solid State Letters*, vol. 13, pp. J50-J52, Feb 2010.
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8. E.S.P.Leong, S.F.Yu, **M.K.Chong**, O.K.Tan, and K.Pita, "Metal-oxide- SiO_2 composite ZnO lasers," *IEEE Photonics Technology Letters*, vol. 17, pp. 1815-1817, Sep 2005.

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Appendices

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