Synthesis of perovskite electrooptic thin films by polymer modified sol-gel processing

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**SYNTHESIS OF PEROVSKITE ELECTROOPTIC THIN
FILMS BY POLYMER MODIFIED SOL-GEL
PROCESSING**

**DU ZEHUI
SCHOOL OF MATERIALS SCIENCE and ENGINEERING
2009**

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FILMS BY POLYMER MODIFIED SOL-GEL PROCESSING**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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TABLE OF CONTENTS

Acknowledgement	I
TABLE OF CONTENTS	II
Summary	IV
1. Introduction.....	1
1.1 Background	1
1.2 Objectives and scope.....	4
1.3 Organization of the thesis	4
1.4 References.....	6
2 Literature Review	9
2.1 Dielectricity, ferroelectricity and perovskite	9
2.2 Electro-optic effect	13
2.3 Perovskite based electro-optic ceramics	16
2.3.1 PLZT	16
2.3.2 PMN-PT	20
2.3.3 KTN	24
2.3.4 Other EO materials	26
2.4 Applications	27
2.5 Processing of EO thin films	32
2.5.1 Sol-gel processing.....	33
2.5.2 Chemical modification.....	36
2.5.3 Synthesis of PMN-PT films.....	40
2.5.4 Effect of polymers on perovskite formation	43
2.6 References.....	45
3 PLZT thin films prepared by PVP modified sol-gel processing.....	56
3.1 Introduction.....	56
3.2 Experimental Procedure.....	57
3.2.1 Preparation of sols.....	57
3.2.2 Characterization.....	58
3.3 Results and discussion	60
3.3.1 Rheological behavior of PLZT sols	60
3.3.2 Critical thickness of the PLZT films.....	64
3.3.3 Thermal analysis of of the PLZT gels.....	66
3.3.4 Crystallization behavior of the PLZT films	69
3.3.5 Morphology of the PLZT films affected by PVP	71
3.3.6 Formation mechanism of the rosette-like structure	74
3.3.7 Properties of the PLZT films with rosette-like structures.....	82
3.4 Concluding remarks	85
3.5 References.....	86

4	Removal of rosette-like structures in PVP modified PLZT films	89
4.1	Introduction.....	89
4.2	Experimental procedure.....	90
4.3	Results and discussion	95
4.3.1	Removal of rosette-like structures by adding excess Pb.....	95
4.3.2	Removal of rosette-like structures by adding PLT layer	100
4.3.3	Properties of the PLZT films without rosette-like structures.....	103
4.4	Concluding remarks	110
4.5	References.....	111
5	PMN-PT films prepared by PVP modified sol-gel processing	113
5.1	Introduction.....	113
5.2	Experimental procedure.....	114
5.2.1	Preparation	114
5.2.2	Characterization	115
5.3	Results and discussion	116
5.3.1	Thermal analysis of the PMN-PT gels.....	116
5.3.2	Effect of PVP content on the crystallization of PMN-PT films.....	119
5.3.3	Effect of PVP molecular weight on the crystallization.....	123
5.3.4	XPS analysis of the well-crystallized PMN-PT films.....	126
5.3.5	Reaction kinetics of perovskite crystallization	128
5.4	Concluding remarks	136
5.5	References.....	138
6	Perovskite crystallization mechanisms in the PMN-PT films and their properties	141
6.1	Introduction.....	141
6.2	Experimental procedure.....	142
6.3	Results and discussion	143
6.3.1	Perovskite crystallization mechanism in PMN-PT films.....	143
6.3.2	Preparation of PMN-PT films around MPB composition.....	155
6.4	Concluding remarks	167
6.5	References.....	169
7	Conclusions	174
7.1	Conclusions.....	174
7.2	Novelties	176
8	Future work	178
	Appendix (publication list).....	180

Summary

In the present work, $\text{Pb}_{0.91}\text{La}_{0.09}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.9775}\text{O}_3$ (PLZT(9/65/35)) and $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PMN-PT, $x=0.23-0.43$) perovskite electrooptic (EO) thin films have been synthesized by PVP modified sol-gel processing with lead acetate and lead nitrate as lead precursor, respectively. The effects of PVP content and molecular weight on the gel particles towards crystallization and microstructure evolution of the films have been systematically investigated. The mechanisms controlling the perovskite crystallization and microstructure development were discussed. The electrical, optical and electrooptic properties of the as-prepared films have also been studied.

Our results have shown that adding PVP can significantly increase the critical thickness of a single PLZT layer and promote the crystallization of perovskite phase. However, rosette-like structures are always observed in our PVP-modified PLZT films. Although the occurrence of the rosette-like structures has been a typical morphological problem in Pb-containing ferroelectric films, its formation mechanism has not been well understood from sol-gel chemistry yet. Our results indicate that the formation of the rosette-like structures is closely related to a premature nucleation of PbO grains induced by the presence of PVP. The coarse PbO grains, compared to the fine PLZT gel particles, can lead to inhomogeneous distribution of Pb in the resultant films. Pb-rich domains accelerate the growth of perovskite crystals and as a result, a porous rosette-like structure is formed.

Despite the perovskite-promotion effect of PVPs, the presence of rosette-like structure significantly deteriorates the electrical and optical properties of the PLZT films due to its porous nature. Nevertheless, the effective methods for removing rosette-like structures have been found and the resultant films exhibit very promising electrical, optical and EO properties.

With PVP and lead nitrate as precursors, the forming of pyrochlore-free and non-rosette PMN-PT films was also studied. Perovskite phase can directly crystallize from amorphous PMN-PT thin films at the temperature $\leq 430^\circ\text{C}$ and bypass the metastable pyrochlore phase. Kinetic studies have shown that the perovskite crystallization is a diffusion controlled reaction with activation energy of 167.7kJ/mol,

which indicates that the process could follow a columbite-like route. This is further supported by the findings on the formation of special core-shell like gel particles with PVP-Pb²⁺ as shell layer and Mg-O-Nb-(O-Ti) clusters as core in the PVP modified sol-gel solutions. As the cores with Mg-O-Nb-(O-Ti) tend to form columbite-like phases (i.e. MgNb₂O₆) during annealing, external Pb ions could diffuse into the cores, resulting in the direct crystallization of perovskite phase. Our method by developing such unique core-shell like gel-particles could enlighten the synthesis of the other materials in which, pyrochlore phase is difficult to be removed, e.g. PZN (Pb(Zn_{1/3}Nb_{2/3})O₃), Pb(Sc_{1/2}Nb_{1/2})O₃ and PNN (Pb(Nb_{1/3}Nb_{2/3})O₃).

The developed 0.67PMN-0.33PT films exhibit very interesting dielectric behavior, characterized by a diffusive ϵ - T response and independence of $T_{\max}$ on the measured frequency range. The refractive index n_o and n_e of the films are 2.515 and 2.494 respectively, and the quadratic EO coefficient is $1.02 \times 10^{-17} \text{ (m/v)}^2$.

1 Introduction

1.1 Background

Electrooptic (EO) devices, such as optical modulators and optical switches, can transform electrical signals into optical signals by changing the refractive index of an EO material through application of electric field. Such devices have become critical components in modern telecommunication systems. Compared with bulk-based EO devices, thin-film based devices have attracted huge attention as they offer several potential advantages. For example, the reduced physical dimensions of thin films allow large electric fields to be generated with low driving voltages, hence enhance device efficiency. EO thin films have been widely applied in various modulators, such as Mach-Zehnder interferometer(MZI) waveguide modulator,^{1,2} “Y” branch total internal reflection (TIR) modulator,³ and Fabry-Perot interference (FPI) modulator.^{4,5} Based on sol-gel derived PLZT films with thickness $\sim 3\mu\text{m}$, MZI modulators have been developed with a low half-wave voltage of 8.5V and a rise time as fast as 15ns.² The MZI modulator based on epitaxial BaTiO₃ thin films exhibited a low driving voltage of 6-8V at the laser wavelength of 632.3nm.⁶ A “Y” branch TIR modulator using 2.6 μm -thick epitaxial PLZT films as channel, has been reported to possess very fast switching response ($\sim 8\text{ns}$) and a low driving voltage of around 40V.³ FPI modulator has also been developed with the PZT films 5-10 μm thick.⁴ Furthermore, the EO thin films have also been found applications in spatial light modulator (SLM) for displays, similar to those by liquid-crystal materials.⁷

Sol-gel processing has been extensively investigated to develop the perovskite

EO thin films thanks to its flexibility in composition controlling and cost-effectiveness. However, the deposited films crack easily during heat treatment. The critical thickness (the maximum thickness achieved without cracking by one coating) reported is usually less than 100nm,⁸ which makes it difficult to prepare the films with the thickness above 1μm. Two reasons have been reckoned to be responsible for crack formation. They are: (a) the large shrinkage and constrained densification of the gel films, and (b) the mismatch of the coefficient of thermal expansion (CTE) between substrates and films.^{8,9,10} It is nevertheless noted that if the stress due to densification and CTE mismatch is relaxed in a buffer medium such as organic polymer, crack-free films with a high critical thickness can be obtained. A few polymers, such as polyvinylpyrrolidone (PVP), polyvinylacetamide (PVA), poly(ethylene glycol) (PEG), and polyethylenimine (PEI) have been reported to be effective buffer media to avoid film cracking.^{11,12,13} PEI and PEG are also found to be able to improve the epitaxial quality of the resultant oxide films and accelerate the formation of perovskite phase, respectively. Some other polymers like polyvinyl alcohol (PVA) and poly(vinyl acetate) (PVAc), can modulate the ion distribution in sol-gel solutions and therefore facilitate the development of single-phase oxides such as calcium aluminate (CaAl_2O_4) and yttrium aluminate ($\text{Y}_3\text{Al}_5\text{O}_{12}$).^{14,15} Polymer modified sol-gel processing, as a result, has attracted a lot of attention in recent years.

PVP, as an important chemical modifier, has been widely applied in synthesis of BaTiO_3 , $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ and PZT ceramic films to achieve the critical thickness of 0.4-1.2μm.^{16,17,18} It was also found to be able to improve the (100) orientation of PZT films,¹⁹ and be effective in preparing various ferroelectric nanofibers and nanometric particles.^{20,21,22} However, investigation on PVP modified sol-gel processing for the EO thin films such as PLZT and PMN-PT thin films is very limited due to their strict

requirement on transparency, high densification and good crystallization. Systematic studies on the effect of PVP addition and molecular weight on the critical thickness, crystallization and microstructure development of these films are still lacking.

Furthermore, during our studies on the PVP-modified sol-gel derived PLZT films, some large and round grain clusters, so-called rosette-like structures were found. Although the occurrence of the rosette-like morphology has been a typical morphological problem in Pb-containing ferroelectric films, its formation mechanism has not been well understood. Suggested reasons from literature include the diffusion of Pb to the bottom electrodes, Pb volatilization during annealing, and flash decomposition of the sol-gel precursors, etc.^{23,24,25, 26} However, the answers from sol-gel solution chemistry, instead of the film-substrate interaction and annealing profile, have never been discovered yet.

It is also noted that PVP could assist the formation of EO thin films with complex composition, such as PMN-PT, as PVP can be coordinated with metal ions by its carbonyl group (C=O) or C-N group in every repeat unit,^{27,28} and meanwhile form hydrogen bonds to -OH, the common end groups of gel particles.²⁹ Special core-shell like gel particles could be formed in the sol-gel solution, which has been identified beneficial to perovskite crystallization in this work. Furthermore, the occurrence of large amount of heat as a result of combustion of PVPs increases the in-situ temperature of the gel particles. Hence, the low-temperature metastable intermediate phases like pyrochlore can be circumvented and direct crystallization of perovskite phase from amorphous matrix can be realized. The well-crystallized PMN-PT films can be developed with good EO properties.

1.2 Objectives and scope

In the present work, we aim to develop PLZT and PMN-PT thin films by PVP modified sol-gel processing with lead acetate and lead nitrate as lead precursor, respectively.

The significant improvement of PVP on the critical thickness of PLZT thin films will be studied. The effect of PVP content and molecular weight on the gel particles, the crystallization and microstructure evolution of the films will be systematically investigated. Mechanisms controlling the microstructural development will be discussed. Crack-free films $>1\mu\text{m}$ thick will be prepared from the sol-gel solutions with the identified optimal PVP addition. The electrical, optical and EO properties of the films will be characterized.

Based on the findings on PLZT films, PVP will be applied to the synthesis of PMN-PT thin films. The effect of PVP on crystallization behavior and morphology of the films will be investigated, and the crystallization kinetics of perovskite phase in the thin-film systems with and without PVP will be studied. The promotion mechanisms of PVPs on perovskite crystallization will be discussed according to the FT-IR, TEM and XPS characterization results. Finally, the electrical, optical and EO properties of the derived films will be measured.

1.3 Organization of the thesis

The thesis contains 8 chapters, including this introduction as chapter 1.

Chapter 2 gives a brief literature review on the basic physics behind the ferroelectricity and electrooptics. The most common electrooptic ceramics and their applications are introduced. Next, the synthesis techniques with a focus on sol-gel processing are presented. Finally the challenges on the preparation of the materials are

emphasized and the polymers applied to improve perovskite formation are also discussed.

Chapter 3 presents the effects of PVP on critical thickness, gel particles, crystallization and microstructural evolution of PLZT thin films. The mechanisms controlling the microstructure evolution are illustrated and discussed thoroughly.

Chapter 4 presents approaches to solve the problems on the morphology of the PVP modified PLZT thin films. Finally dense and crack-free films above 1 μ m thick are obtained and the electrical, optical and EO properties of the derived films are presented.

In Chapter 5, the PMN-PT thin films with 43 mol% PT are developed by PVP modified sol-gel processing with lead nitrate as lead precursor. The crystallization and morphologies of the PMN-PT films, as a function of PVP molecular weight and content, are studied. The crystallization kinetics of perovskite phase in the films with and without PVP is investigated and the effect of PVP on the perovskite crystallization is preliminarily discussed.

In chapter 6, the preparation of (1-x)PMN-xPT films with PT composition around the morphotropic phase boundary (MPB, i.e. $x=0.23-0.43$) by sol-gel processing with optimized PVP additions is described. FT-IR, TEM and XPS have been employed to investigate the sol-gel precursors and the spatial element distribution of gel particles with and without PVP modification. The mechanisms for improving the perovskite crystallization by adding PVP are discussed. Finally, the PMN-PT films with 33% PT and $\sim 1\mu$ m thick were prepared. Their electrical and optical properties are reported.

Chapter 7 presents the conclusions and Chapter 8 gives the recommendation for future development of the present topic.

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2 Literature Review

Perovskite based EO thin films possess unique dielectric, ferroelectric, optical and EO properties, and hence are widely studied for the application of optical modulators, optical shutters, and other integrated optics since 1970s. This chapter will briefly introduce the relationships of dielectric, ferroelectric, EO properties and perovskite structures. The most common EO ceramics and thin films, their applications and synthesis techniques will be introduced. The challenges on the preparation of the materials will be discussed.

2.1 Dielectricity, ferroelectricity and perovskite^{1,2,3}

Dielectric materials are materials which can be electrically polarized when an electric field is applied. The polarization may come from:

- 1) Electronic polarization which occurs due to distortion of electron density
- 2) Ionic polarization due to elastic deformation of ionic bond lengths or angles.
- 3) Orientational polarization due to changes in orientation of permanent dipoles moments.

The three types of polarization are schematically shown in Figure 2-1. There is a sub-group of dielectric materials, i.e. *ferroelectric materials*, which show *spontaneous polarization* (P_s) without application of electric field. The spontaneous polarization can be reversed to zero under an external electric field. When the electric field is removed, the net polarization does not return to zero, like that of the normal dielectric materials. One important characteristic of ferroelectric materials is the existence of ferroelectric domains and hysteresis loop. In general, the ferroelectric

Figure 2-1 Schematic description of (A) electronic, (B) ionic, and (C) orientational polarization⁴

domains are certain regions with uniform alignment of electric dipoles. The size and structure of the domains depend on many factors, such as crystal symmetry, defect structure, grain size, and the history of sample preparation. For thin films, stable domain structures are also dependent on the lattice parameters and thermal expansion coefficients of the films and the substrates.

Polarization-electric field (P-E) hysteresis loop is created due to the changes of the ferroelectric domains with the applied electric field. Figure 2-2 shows a typical P-E hysteresis loop. As the field strength increases from zero, the polarization increases until all the domains are aligned in one direction (1 to 3). In this state, the crystal is composed of single-oriented domains with the *saturated polarization* denoted by P_{sat} . When the field strength is reduced, the polarization will generally decrease, but it does not return to zero. At zero field (4) a net polarization will remain and is called *remnant polarization* P_r . The remnant polarization will not be removed until the electric field in the opposite direction reaches a certain value (5). The electric field required to reduce

the polarization to zero is called the *coercive field*, E_c . The cycle is completed by increasing the negative field to saturation (6) and then reversing the field direction once again. As shown in the Figure 2-2, the polarization will not return to its virgin state (1) of randomly oriented domains.

Figure 2-2 A typical P-E hysteresis loop of ferroelectric materials⁴

The *spontaneous polarization* will then be estimated by extrapolation of the saturated polarization back to zero field. The area that is enclosed within the ferroelectric hysteresis loop is a measure of the energy required to reverse the polarization twice.

The familiar ferroelectric materials include BaTiO_3 (BT), SrTiO_3 , PbTiO_3 (PT), $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT), $(\text{Pb}, \text{La})(\text{Ti}, \text{Zr})\text{O}_3$ (PLZT), $\text{Pb}(\text{Mg}, \text{Nb})\text{O}_3$ (PMN) and $\text{K}(\text{Ta}, \text{Nb})\text{O}_3$ (KTN). They can readily form solid solution with each other since they share a common cubic crystal structure, i.e. *perovskite* in the form of ABO_3 , as shown in Figure 2-3. The A and B site are occupied by +1 (or +2) and +5 (or +4) ions, respectively, while O site is the O^{2-} ions. The B site is actually at the center of the oxygen octahedron. Under temperature change, external electric field or doping different ions in the solid solution, the lattice can be distorted to tetragonal or

Figure 2-3 Schematic description of ABO_3 perovskite structure

rhombohedral symmetry, inducing the B-site ions to shift along c axis or the body diagonal, respectively. As a result, the electric dipoles are created and the ferroelectric characteristics are observed. Therefore the perovskite structured materials present ferroelectric properties when its phase is non-centrosymmetric, e.g. tetragonal, rhombohedral, or orthorhombic, etc. These structures can be formed below a critical temperature (T_c) called *Curie point*, at which the materials undergo a transition from ferroelectric to non-ferroelectric (paraelectric) phase. For example, $PbTiO_3$ has a T_c at 490°C , meaning that at this temperature, it transforms from a ferroelectric phase with tetragonal symmetry to a paraelectric phase with cubic symmetry upon heating.⁵

Based on the dielectrical and phase transition behavior, ferroelectrics can be divided into three categories: (1) normal ferroelectrics, (2) ferroelectrics with a diffusion phase transition, and (3) *relaxor ferroelectrics*. Figure 2-4 shows the main difference between normal and relaxor ferroelectrics. The normal ferroelectrics show an abrupt decrease in the dielectric constant at the Curie temperature (T_c), while the relaxor ferroelectrics exhibit a broad and frequency-dependent change as a function of

temperature. The broadening of the dielectric peaks can be induced by multiple-cation distribution over the 'B' sites of the perovskite structure.

Figure 2-4 The dependence of dielectric constant on temperature in (a) normal, (b) relaxor ferroelectric materials

2.2 Electro-optic effect⁶

In an anisotropic dielectric crystal, the refractive index is different in different crystal directions. The optical anisotropy is characterized by an index ellipsoid, or optical indicatrix shown in Figure 2-5. The relationship can be defined as:

$$\frac{x^2}{n_x^2} + \frac{y^2}{n_y^2} + \frac{z^2}{n_z^2} = 1 \quad \text{Equation 2-1}$$

where n_x , n_y , n_z are the principle refractive indices. The index ellipsoid can be used to find the two indices of refraction associated with two independent plane waves that can propagate along an arbitrary OP direction in a crystal. The idea is: find the intersection ellipse through the origin that is normal to the direction of the propagation

OP. The two axes (OE and OR) of the intersection ellipse are equal in length to n_{op1} and n_{op2} , where n_{op1} and n_{op2} are the two indices of refraction.

Figure 2-5 The optical indicatrix ⁶

For an anisotropic dielectric crystal, the existence of two rays with different indices of refraction is called *optical birefringence*, usually defined as

$$\Delta n = n_e - n_o \quad \text{Equation 2-2}$$

where n_o is ordinary index, the refractive index perpendicular to the optic axis; while n_e is called extraordinary refractive indices, i.e. the refractive index along the optic axis.

Ferroelectric crystals can produce ion displacement and hence become optical anisotropic as a result of an applied electric field. Such electric-field induced birefringence shift is called *electro-optic effect*. The dependence of the refractive index on the applied electric field can be described as small changes in size, orientation and shape of the optical indicatrix, ΔB_{ij} and can be expressed as:

$$\Delta B_{ij} = \Delta\left(\frac{1}{n_{ij}^2}\right) = r_{ijk} E_K + R_{ijkl} E_k E_l \quad \text{Equation 2-3}$$

or in terms of the polarization, P,

$$\Delta B_{ij} = f_{ijk} P_K + g_{ijkl} P_k P_l \quad \text{Equation 2-4}$$

Where the constants r_{ijk} and f_{ijk} are the *Pockels EO coefficients* and they are third-rank tensor, while R_{ijkl} and g_{ijkl} are *Kerr EO coefficients* and they are fourth-rank tensor. Based on Equation 2-1 and 2-3, the electric induced birefringence shift can be deduced. More detailed deductions can be found in [Ref.1](#) and [Ref.6](#).

For tetragonal crystal class (symmetry group 4mm), when an electric field is directed along x3 axis (indicated in Figure 2-5), the induced linear EO effect can be:

$$\Delta n = \Delta(n_e - n_o) = -\frac{1}{2}n_e^3(r_{33} - \frac{n_o^3}{n_e^3}r_{13})E \quad \text{Equation 2-5}$$

Simplifying,

$$\Delta n = -\frac{1}{2}n^3r_cE \quad \text{Equation 2-6}$$

where, $r_c = (r_{33} - \frac{n_o^3}{n_e^3}r_{13})$. Typical values for r_c lie in the range of 1-100pm/V in the crystals of LiNbO₃, LiTaO₃ and KH₂PO₄, etc.

For cubic crystal class (symmetry group m3m), which is optically isotropic, when an electric field applied along x3 axis, quadratic EO effect will be produced. The induced birefringence is given by:

$$\Delta n = -\frac{1}{2}n^3(R_{11} - R_{12})E^2 \quad \text{Equation 2-7}$$

Simplifying,

$$\Delta n = -\frac{1}{2}n^3RE^2 \quad \text{Equation 2-8}$$

Where $R=R_{11}-R_{12}$. Quadratic EO effect has been found in materials such as KTN, PLZT and PMN-PT, with the typical EO coefficients of around 10⁻¹⁸-10⁻¹⁶(m/V)². Although the relationships between birefringence shift and applied electric field are

deduced from single crystals, polycrystalline ceramic with similar crystal symmetry can also be applied.

2.3 Perovskite based EO ceramics

EO ceramics, such as PLZT, PMN-PT and KTN are a family of ceramic oxides transparent in the wavelength range from 500 to 7000nm. They exhibit many advantages such as extremely high EO coefficient, low half-wave voltage, good ceramic ruggedness and low cost, which are promising properties for almost all the visible and mid-IR optical application. Furthermore, since the ion and electron movement responsible for the EO effect are much faster than that of molecular movement in liquid-crystal materials, nano-second modulation could be realized. A variety of optical devices have been developed using the EO ceramics, such as optical modulator⁷, optical switch⁸, tunable optical filter⁹, and military-applied electric-tunable goggles¹⁰.

2.3.1 PLZT^{11,12,13}

Lanthanum-substituted lead zirconate titanate (PLZT) ceramic is well-known as a transparent ferroelectric material exhibiting strong electrooptical effects. By adjusting the ratio of La/Zr/Ti, PLZT exhibits a variety of phases such as ferroelectric (FE), antiferroelectric (AFE), paraelectric (PE), as illustrated in Figure 2-6. The compositions of PLZT are defined by $x/y/(1-y)$ according to the formula of $(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$. Depending on the ratio of $x/y/(1-y)$, PLZT ceramic exhibits three types of hysteresis loop and electro-optic characteristic, i.e. “memory”, “linear” and “quadratic”, as illustrated in Figure 2-7(a),(b),(c). The compositions for the “memory” ferroelectric and electro-optic effect occupy the “A” zone in the phase diagram (Figure 2-6). One typical composition is 8/65/35, exhibiting a hysteretic

Figure 2-6 Room-temperature phase diagram of $(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$: (A) memory; (B) linear; (C)quadratic ¹¹

Figure 2-7 Hysteresis and electrooptic characteristics of the three main types of PLZT: (a) memory; (b) linear; (c) quadratic ¹²

change in the birefringence with the external electric field, as shown in Figure 2-7(a)(ii).

The compositions exhibiting linear EO effect (Pockels effect) tend to come from the PbTiO_3 -rich end of the solid solution range (B zone in Figure 2-6). High PbTiO_3 content favors tetragonal distortion from the cubic structure. A consequence of high tetragonality is that the hysteresis loop exhibits high coercivity. One typical hysteresis loop is shown in Figure 2-7(b)(i). PLZT with the composition in this zone exhibits excellent linear EO effect and the typical composition is 7/40/60 or 8/40/60.

Compositions showing quadratic Kerr effect are those close to the rhombohedral–tetragonal boundary (C zone in Figure 2-6). At room temperature, the crystal structure of PLZT is cubic. However, it will be transformed to rhombohedral or tetragonal ferroelectric phase when an electric field is applied. The induced optical anisotropy increases with respect to E^2 , exhibiting quadratic electro-optic effect, as illustrated in Figure 2-7(c)(ii). The hysteresis loop is shown in Figure 2-7(c)(i). It can be seen that it is very slim and has a very low coercive field. The typical compositions with quadratic electro-optic effect are 9/65/35 and 9.5/65/35. They are widely applied in optical shutter, modulator and display applications. The values of linear and quadratic EO coefficients for a series of PLZT ceramics are listed in Table 2-1.

Table 2-1 Electro-optic properties of some PLZT ceramics¹³

Material	r_c (pm/V)	R ($\times 10^{-18} (\text{m/V})^2$)
PLZT(12/40/60)	140	-
PLZT(8/40/60)	100	-
PLZT(8.5/65/35)	-	3860
PLZT(9/65/35)	-	380
PLZT(9.5/65/35)	-	150

Recently there has been an increasing interest in developing PLZT films for the applications on novel electronic and optical devices, especially large area devices and integrated optics. PLZT films have been developed on sapphire, MgO and fused silica substrates by sputtering, pulsed laser deposition, sol-gel processing and aerosol deposition. Generally speaking, the EO coefficients of thin films are smaller than that of bulk ceramics. For example, the EO coefficient for PLZT 9/65/35 thin films has been reported to be $R \approx 1.0 \times 10^{-16} (\text{m/V})^2$ by Adachi *et al.*¹⁴, and $0.6 \times 10^{-16} (\text{m/V})^2$ by S. Krishnakumar *et al.*¹⁵ These values are obviously lower than that of $3.8\text{--}9.1 \times 10^{-16} (\text{m/V})^2$ for bulk 9/65/35 ceramics.^{13,16} More EO coefficients of the films prepared by various thin-film processing techniques are listed in Table 2-2. The decrease of the EO coefficients has been attributed to the internal clamping stress from substrates,¹³ since both compressive and tensile stress can give rise to the reduction of the field-induced birefringence magnitude. The stress in ferroelectric thin films is primarily induced by the differences in the thermal expansion coefficient (TEC) between the films and the substrates.¹³ Increasing the film thickness can probably reduce the clamping effect from substrates and hence enhance the EO response. For instance, $8.9\text{ }\mu\text{m}$ -thick PZT films have been reported to exhibit a linear EO coefficient of 76 pm/V , much higher

Table 2-2 Electrooptical coefficients of PLZT films prepared by different processing

composition	Processing route	substrate	texture	$R \times 10^{-18} (\text{m/V})^2$	Ref
9/65/35	aerosol deposition	glass	random	2.5	17
9/65/35	sol gel	SrTiO ₃ /quartz	random	4.1	18
9/65/35	pulsed laser deposition	ITO coated glass	110 oriented	81	19
9/65/35	RF magnetron sputtering	C-plane sapphire	110 oriented	60	15

than 14-20pm/V for the 1.8-2.0µm-thick films prepared by the same sol-gel procedure.²⁰ In addition, smaller grain size in thin films than bulk ceramics is some other reason responsible for the weak EO effects.

2.3.2 PMN-PT

Relaxor ferroelectrics are a class of lead based perovskite type compounds with the general formula $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3$ where B1 is a lower valency cation (e.g. Mg^{2+} , Zn^{2+} , Ni^{2+} , Fe^{3+}) and B2 is a higher valency cation like Nb^{5+} and Ta^{5+} and W^{5+} . Pure lead magnesium niobate ($\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$) has the Curie point at about -10°C and is distinguished from normal ferroelectrics by the presence of a broad *diffused phase transition* (DPT) on cooling below the Curie point. The existence of DPT can be attributed to the compositional heterogeneity on a microscopic scale. For example, the B site composition of Mg and Nb is not stoichiometric in micro-regions, resulting in different ferroelectric transition temperatures and the broadening of the dielectric peak.

PT are often added to PMN ceramics as it has a Curie temperature (T_c) of 490°C, which can hence shift the T_c of the system towards a higher temperature. Recently, there is an intensive interest in the investigation of (1-x)PMN-xPT single-crystal solid solutions due to their advantageous properties such as extremely high piezoelectric constants ($d_{33} > 2000 \text{ pC/N}$), ultra-large piezoelectric strains ($> 1.7\%$) and very high electromechanical coupling coefficients ($k_{33} > 92\%$) when their compositions are near to the morphotropic phase boundary (MPB, $x_{\text{PT}} = 35\%$).^{21,22} The mechanisms underlying the distinguished performance of PMN-PT and the possibilities for further improvement have been widely studied.^{23,24,25,26} The explanation is that PbTiO_3 is a tetragonal phase with a large strain (6%)²⁷. When the content of PT approaches the rhombohedral-tetragonal phase boundary, both energy and the electric field necessary to induce ferroelectric polarization will decrease significantly, as evidenced by the

measurement of total enthalpy change during relaxation.²³ This, in turn, gives the giant electromechanical response of these relaxors.²³

The strong piezoelectric response in PMN-PT systems with the composition around MPB stimulated extensive studies on the MPB phases. Shrout *et al.*²⁸ initially suggested that the MPB phases included rhombohedral $R3m$ phase with smaller Ti concentration and the tetragonal $P4mm$ phase with higher Ti content and they were separated by a fairly sharp phase boundary at 35%PT. Noheda *et al.*²⁹ reported a large composition range around the MPB in which the rhombohedral and tetragonal phases coexisted. Optical domain studies showed that the $R3m$ and $P4mm$ phases may coexist at room temperature and $R3m$ phase will transform into the $P4mm$ over a wide temperature interval.^{6,30} Ye and Noheda *et al.*^{31,32} recently updated the phase diagram and verified that there was a stability zone of the monoclinic phase (M_c) at $x=31-37\%$ between the rhombohedral(R) and tetragonal (T) phases, as indicated in Figure 2-8.

Figure 2-8 Modified phase diagram of PMN-xPT around MPB. The symbols separating M_c and T phases represent the temperatures at which M_c -T phase transformation begins to take place.³²

Noheda *et al.*³² have then performed further investigation by synchrotron XRD and found that there was a third minority orthorhombic (O) phase coexists with M_c and T phase, where the M_c phase evolved from the O composition limit to the T limit. The coexistence of R, M, O, and T phase leads to complex phase behavior. It has been postulated that the coexistence of the multiple phases and phase instability are critical to the extraordinary crystal properties.³³

As EO coefficients are closely related to the electric field-induced changes in the lattice structures, the large piezoelectric response suggests a large EO response in these crystals near the MPB. Recently Yin *et al.*³⁴ investigated the electro-optic properties of PMIN-33%PT single crystals under proper AC bias and found that PMIN-33%PT has an extremely large linear electro-optic coefficient, $r_{33} = \sim 9800$ pm/V, much higher than 8000pm/V for $K(Ta_xNb_{1-x})O_3$ crystals which was known as the largest EO coefficient previously.^{35,36} The quadratic EO coefficient of PMN-PT ceramics was also found to be 2-5 times higher than that of PLZT ceramics and nearly 100 times higher than that of $LiNbO_3$ at room temperature, reaching $2.8 \times 10^{-15} (m/V)^2$.³⁷

The quadratic EO coefficients of PMN-xPT thin films around the MPB composition have also been investigated. The (110) oriented 0.67PMN-0.33PT films grown on (1012)-cut sapphire were reported to have an EO coefficient of $1.32 \times 10^{-16} (m/V)^2$.³⁸ The films epitaxially grown on (100)-cut $LaAlO_3$ (LAO) substrates exhibited a slightly higher EO coefficient of $\sim 1.6 \times 10^{-16} (m/V)^2$.^{39,40}

PT content, electric field direction and multi-layer structure of the films, are the factors affecting the EO properties of the PMN-PT films. Figure 2-9 shows that the in-plane quadratic EO coefficient of the films increases significantly when the compositions are close to MPB and reaches maximum when the PT content $x=0.33$.³⁹ Figure 2-9 also shows the applied electric-field direction exerting much influence on

Figure 2-9 In-plane quadratic EO coefficient of PMN-PT films vs PbTiO₃ concentration. The electric field was applied along (a) $\langle 110 \rangle$, (b) $\langle 1\bar{1}0 \rangle$, (c) $\langle 001 \rangle$, (d) $\langle 010 \rangle$ ³⁹

the measured EO coefficients. When the electric field was applied along in-plane $\langle 110 \rangle$, at least two times larger in magnitude of EO effect was found compared with those along in-plane $\langle 001 \rangle$.^{39,40} Meanwhile, it is also noted that an EO superlattice structure composing of alternative PMN-PT rhombohedral ($x_{\text{PT}}=0.40$) and tetragonal phases ($x=0.26$) can remarkably enhance the EO coefficients. Figure 2-10 shows the dependence of both in-plane and out-of-plane EO coefficients on the periodicity of the EO superlattice structure. It is indicated that a strong enhancement of the out-of-plane quadratic EO coefficient has been observed at the period of $\sim 10\text{nm}$, compared to that of single-composition films and that with higher periodicity. Such an enhancement can be attributed to a long range coupling of spontaneous polarizations via structural phonons (resonance).⁴¹ However, the in-plane quadratic EO coefficients, only have a slight dependence on the superlattice periodicity, and maintain a large value of $1.5 \times 10^{-16} (\text{m/V})^2$.⁴¹

Figure 2-10 Dependence of both in-plane and out-of-plane EO coefficients on periodicity of the EO superlattice structure⁴¹

2.3.3 KTN

Potassium tantalum niobate ($\text{KTa}_x\text{Nb}_{1-x}\text{O}_3$, KTN) is a solid solution of potassium tantalite (KTaO_3) and potassium niobate (KNbO_3) (phase diagram shown in Figure 2-11).^{42,43} By controlling the ratio of Nb/Ta, its Curie temperatures (T_c) can

Figure 2-11 Phase diagram of KTN in the KTaO_3 - KNbO_3 system⁴²

vary from 710K for pure KNbO_3 ($x=0$) to ~ 0 K for pure KTaO_3 ($x=1.0$) and it is about 283K (close to room temperature) for $x \approx 0.62$. The ferroelectric and EO properties of KTN are therefore strongly composition dependent. The linear electro-optic effect can be found when the Nb/Ta ratio and crystal temperature give the materials a tetragonal phase, and the quadratic electro-optic effect can be found from that of the non-ferroelectric cubic phase. Quadratic EO coefficient has been obtained in the KTN crystals with the composition near to the cubic - tetragonal phase boundary ($x \approx 0.65$) at room temperature, reaching the highest reported value of $4.8 \times 10^{-15}(\text{m/V})^2$.⁴⁴ The crystals also showed a linear EO coefficient of 600pm/V at a biased field of 60V/mm.⁴⁴ High linear EO coefficient of 7850pm/V was reported when $x=0.48$, and 5770pm/V when $x=0.53$. The EO coefficient was also noted to decrease as Nb content decreases.⁴⁵

Despite the strong EO response in single-crystal KTN, the EO properties of KTN thin films haven't been thoroughly investigated due to the difficulties in removing the pyrochlore phase and easy evaporation of K during post-annealing.^{46,47,48} KTN films exhibited a EO response much weaker than that in the bulk crystals and the EO coefficient became saturated under a few KV/cm electric field, which was thought to be related to the ferroelectric saturation behavior.⁴⁹ The linear EO response of KTN films epitaxially grown on spinel (MgAl_2O_4) substrates has been investigated by changing the Ta content over the entire composition zone ($x=0-1.0$). It is found that the EO property decreases with increasing Ta concentration, and showed a maximum EO coefficient of only 40pm/V under DC bias field poling.⁵⁰

2.3.4 Other EO materials

There are increasing interests in other EO materials especially those Pb-free perovskite based crystals, due to the issues of environment contamination. Barium titanate (BaTiO_3 , BT), BaSrTiO_3 (BST), $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ (NKN) and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BTO) are some examples. The tetragonal Tungsten Bronze-type ferroelectric thin films like $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ (SBN) and $\text{SrBi}_2\text{Ta}_2\text{O}_9$ are also been explored. Table 2-3 lists their EO properties and thin-film growth conditions. The high-quality epitaxial films have been deposited by a variety of techniques, including metalorganic chemical vapor deposition (MOCVD), pulse laser deposition (PLD), RF magnetron sputtering and sol-gel, etc. The films possessed the linear EO coefficients as high as hundreds of pm/V. For example, the EO coefficient of 844pm/V can be obtained in the SBN films with $x_{\text{Sr}}=0.75$. However, the measured coefficients are still lower than that of bulk counterparts, similar to that observed in PLZT systems.

Table 2-3 EO properties of thin film materials

Material	Linear r_c (pm/V) @632.8nm	R ($\times 10^{-18}(\text{m/V})^2$) @632.8nm	Growth conditions	references
BaTiO_3	360	-	MgO MOCVD	51
$\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$	230 ($x=0.3$)	130($x=0.5$)	(100) LaAlO_3 PLD	52
LiNbO_3	10.7	-	Al_2O_3 MOD	53
$\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$	28	-	r-cut sapphire RF magnetron sputtering	1
KNbO_3	470	-	MgAl_2O_4 MOCVD	54
$\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$	350 ($x=0.60$) 844 ($x=0.75$)	-	$\text{MgO}(001)$ PLD	55, 56
$\text{SrBi}_2\text{Ta}_2\text{O}_9$	-	38	$\text{MgO}(110)$ RF magnetron sputtering	57

2.4 Applications

Ferroelectric oxide thin films play a very important role in the development of integrated optoelectronics for communication. A typical optoelectronic integrated circuit includes a transmitter (e.g. laser) and receiver, a light intensity modulator and detector, a multiplexer, a demultiplexer and interconnection waveguides on a single substrate. Information is encoded by modulation, switching, and/or multiplexing, and then transferred between the transmitter and the receiver in the chip. Up to now, most of the modulators and switches in integrated circuits are made of EO materials, e.g. LiNbO₃. The introduction of ferroelectric thin films to modulators can significantly improve the response speed of the circuits, reduce the driving voltage, lower the power consumption and cut down the production cost. Besides EO modulators, ferroelectric thin films can also be used in many other beam steering devices, such as Bragg deflector, optical wavelength filter, mode converters, beam splitter and directional coupler and so on.

Optical modulator can electrically modulate the phase and amplitude of incident laser beam, and therefore convert the analog or digital data from electronic to optical signal. The modulation is more advantageous compared to direct modulation as it has no degrading effect on laser linewidth and stability. EO modulator utilizes the EO effect to change the refractive index of the materials, leading to a change in phase and then converts into intensity modulation according to different designs. The relationship between the phase retardation ($\Delta\Phi$) and the change of the refractive index (Δn) can be expressed as:⁵⁸

$$\Delta\Phi = \frac{2\pi}{\lambda} l \Delta n \quad \text{Equation 2-9}$$

From Equation 2-8 and 2-9, it is further deduced:

$$\Delta\Phi = \frac{\pi}{\lambda} n^3 R E^2 l \quad \text{Equation 2-10}$$

where l is the length of the light path, λ is the wavelength of the incidence light, n is the refractive index of the materials. Ferroelectric thin films are often used in the form of channel waveguide modulator, as shown in Figure 2-12, where the channels can be fabricated by wet chemical etching or ion-beam etching of the EO thin films, or just patterning a strip layer like Si_3N_4 on the films.^{59,60} When a laser propagates along the channel, phase retardation is resulted as a function of the effective channel length l and external electric field. The half-wave voltage V_π is given by:^{61,62}

$$V_\pi = \frac{g}{l} \frac{\lambda}{2n^3 r_{ij}} \quad \text{Equation 2-11}$$

Figure 2-12 Schematic diagram of the channel waveguide modulator

where r_{ij} is the linear EO coefficient, g the electrode gap. By optimizing the electrode gap and channel length, and adopting the films with large EO coefficient, extremely low half-wave voltage and fast response of modulation can be realized.

Using the basic idea of channel waveguide modulation, different configurations of modulators have been designed to meet the demands of telecommunication application, especially on polarization independent operation.

One example is Mach-Zehnder interferometer (MZI) waveguide modulator, as shown in Figure 2-13. When an electric field is applied across one of the arms in the MZI modulator, a phase difference is introduced and constructive or destructive interference is created in the output channel. Thus it is possible to modulate the light between on and off states by applying or not applying an electric field. MZI modulator based on sol-gel derived PLZT films with thickness $\sim 3\mu\text{m}$ has been developed with a low half-wave voltage of 8.5V and a rise time as fast as 15ns.⁶³

Figure 2-13 Schematic diagram of Mach-Zehnder interferometer waveguide modulator⁶⁴

Recently a novel MZI switch with a core ridge of KTN ($\sim 7\mu\text{m} \times 7\mu\text{m}$ in size from cross-section) as propagation channel has been fabricated, as shown in Figure 2-14. A bi-electrode controls one arm and tri-electrode control the other. Since the dominant electric fields are the horizontal component E_x with the bi-electrode, and the vertical component E_y with the tri-electrode, the two types of electrodes control the phase shift in TE (Transverse Electric) and TM (Transverse Magnetic) mode respectively. The KTN switch can switch between TE and TM polarized light by applying same signal voltage without using any polarizing optics. Its half-wave voltages for TE and TM mode were as low as $\sim 3\text{V}$ and 3.3V , respectively.⁴³

Figure 2-14 Schematic configuration of KTN MZI switch⁴³

By using channel waveguide structure, another type of optical switch, i.e. 1x2 Y branch total internal reflection (TIR) switch, have been designed recently and shown in Figure 2-15.⁶⁵ It consists of a layer of ITO (Indium Tin oxide) as top electrodes and a 2.6 μm -thick layer of PLZT films epitaxially grown on Nb doped SrTiO_3 (NST, which is conductive) substrate, as the propagation channel. Laser light introduced from an input facet was divided into two channels at a Y-branch without the application of voltage. When a voltage was applied on one of the top electrodes on the Y-branch and the bottom electrode (NST substrate), the refractive index of the channel waveguide under the electrode decreases and the propagating light was reflected at the edge of the electrode. Therefore, the laser light can be switched on or off by applying an electric field on the electrodes. This kind of TIR switch is characterized by very fast switching response ($<8\text{ns}$) and a low extinction ratio.

Figure 2-15 Top view of Y-branch type 1x2 TIR switch in a PLZT channel waveguide⁶⁵

Figure 2-16 Fabry-Perot optical modulators⁶⁶

Ferroelectric oxides can also be used in the fabrication of longitudinal type modulator, such as the Fabry-Perot interference (FPI) modulator shown in Figure 2-16(a). A few layers of dielectric mirrors were coated on the two sides of about $5\mu\text{m}$ thick PZT films prepared by aerosol deposition technique (AD).^{66,67} When laser light entered the Fabry-Perot etalon, multiple reflections happened between the two reflective surface of PZT films (Figure 2-16 (b)). If the phases of T_1 and T_2 were the same, constructive interference was induced and maximum transmittance was obtained. If T_1 and T_2 were out of phase and destructive interference was induced, the transmittance reached minimum. Therefore the output transmittance of the FPI modulator can be controlled by electrically changing the refractive index of the PZT films.

Using similar mechanism, FPI type optical filter has been fabricated by Roth *et al.* recently.⁹ The filter consisted of ferroelectric oxide, i.e. LiNbO_3 self-standing thin films ($5\text{-}10\mu\text{m}$ thick) as the channel for multiple reflection and $30\text{-}40\text{nm}$ thick silver films as the reflection mirrors. It has shown to exhibit a few advantages such as very large free spectral range (FSR, spacing between two resonant-wavelength peaks,

Figure 2-17), narrow width of the resonant-wavelength peak ($\delta\lambda$), and large area saving when it was integrated with other optics in a chip, compared with liquid-crystal and microelectromechanical-system (MEMs) based FPI etalons. The FPI optical filters were also ever sought for application on laser eye protection devices by dynamically controlling of the transmittance of the devices. When high-power laser came to the eyes, the devices became highly reflective over a broad band, while it was clear in a safe environment.⁶⁸

Figure 2-17 Transmission of the FPI optical filter as a function of wavelength

2.5 Processing of EO thin films

To be applied in integrated optics, EO thin films should have large EO response and low insertion loss. Optical loss by scattering and absorption should be less than 1dB/cm for many applications. Controlling surface roughness of the films to <1nm RMS and reducing pores and large voids at grain boundary can significantly reduce the loss.⁶⁹ Besides, the EO film thickness should be above 1μm to improve the laser mode matching between the optical fibers and the waveguides and to produce enough phase retardation.⁶³ 1-10μm thick films are most often used.

For such thick EO films, it is not easy to fabricate by traditional thin film processing technology such as sputtering and sol-gel route due to the slow deposition

rates and cracking caused by high level of stress generated during processing. The methods of machining and polishing bulk ceramics are not practical due to the fragility of ceramics. Some unique processing techniques like screen printing,⁷⁰ electrophoretic deposition,⁷¹ aerosol deposition,⁷² liquid delivery CVD,⁷³ and modified sol-gel processing may provide the solutions. Comparatively, modified sol-gel processing is an attractive method to prepare EO films due to its ability to coat materials on various shapes and to control the film composition accurately without using expensive equipments.

2.5.1 Sol-gel processing

Sol-gel processing usually involves a few steps, i.e. formation of sol-gel solution, dip/spin coating, pyrolysis and post-annealing. To prepare a stable, uniform sol-gel solution, hydrolysis and condensation reactions should be carefully controlled so that gel particles can be stable in the solutions. The gel particle size is usually <100nm.

The preferred raw materials for preparation of sol-gel solution are metal alkoxides with the common formula of $M(OR)_x$, where M is the metal, R is an alkyl group, and x is the valence state of the metal. Metal alkoxides can be hydrolyzed easily with water by nucleophilic substitution for coordinative saturated metal. When the initial attack of water on metal-alkoxide takes place, proton is transferred to form M-OH species, as shown in Figure 2-18.⁷⁴

Figure 2-18 Reaction of hydrolysis⁷⁴

In the following, condensation reaction shown in Figure 2-19 will occur on the M-OH species by reacting with M-OR or M-OH to form M-O-M bonds, with the removal of alcohol or water respectively. The gel formation is influenced by the extent of unsaturation on the central metal and the transfer ability of protons. Chemical modification of the metal alkoxides is useful to slow down the hydrolysis and prevent cross-linking of the condensation products in too early stage. The sol-gel solutions with homogeneous distribution of various components can therefore be obtained.

Figure 2-19 Reactions of condensation^{74,75}

Upon obtaining stable and uniform sol-gel solution, wet gel films can be deposited by spin or dip coating. The films will be pyrolyzed at around 300-500°C to decompose the organic species bonded with metal ions. For multi-layer films, the coating-pyrolysis cycles will be repeated many times until the desirable thickness of the films is obtained. During annealing, pyrochlore phase usually forms and will

transform to perovskite phase at higher temperature. The post-annealing significantly affects the crystalline development and densification of the films. Cracks are also often found in the films after heating.

The occurrence of cracking limits the critical thickness of the films which is normally $<0.1\mu\text{m}$.⁷⁶ Therefore, to prepare EO films above $1\mu\text{m}$ thick, tens of rounds of deposition and heating are needed. It is very time-consuming and hard to control the optical quality of the films.

The cracking problem is undoubtedly caused by the tensile stresses developed in gel films during pyrolysis and annealing. The total residual stress in the final polycrystalline films consists of extrinsic and intrinsic contributions. Extrinsic thermal stresses are induced upon cooling due to the mismatch between the thermal expansion properties of the films and the substrates. Further extrinsic stress originates from the lattice parameter mismatch between the films and the substrates.⁷⁷ The intrinsic stress is derived from gel shrinkage and constrained densification.⁷⁸ The critical thickness T is inversely proportional to the total tensile stress of the films, as shown in Equation 2-12:

$$T = 0.83 \frac{\Gamma E}{\sigma^2 (1 + \nu) \sqrt{1 - \nu}} \quad \text{Equation 2-12}$$

where E is Young's modulus, Γ is the surface energy per unit area of the film, σ is the internal tensile stress of the film. ν is the Poison's Ratio.⁷⁸

It is believed that the extrinsic stresses give rise to microscopic crack along the grain boundaries which can only be observed by scanning electron microscope (SEM) or transmission electron microscope (TEM). The microscopic crack can be avoided by choosing the substrates with the thermal expansion coefficient matched with that of the films.⁷⁹ The intrinsic stresses, on the other hand, induce macroscopic cracks which

can be observed by naked eyes. The macroscopic cracks can sometimes result in film delamination.⁸⁰ Macroscopic cracks are hence the main factor limiting the maximum thickness of the films. Nevertheless, these cracks can be prevented by suppressing the intrinsic tensile stresses, which can be realized by chemical modification of the sol-gel solution. The modifiers can be DCCA (drying control chemical additive), chelating agent, or stress relaxing agent.

2.5.2 Chemical modification

DCCA is widely used to prevent cracking in the transparent dried gel monoliths like SiO_2 , $\text{SiO}_2\text{-TiO}_2$, and $\text{LiO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$.⁸¹ It can produce a large scale of sol-gel network with uniform-size pores so that the difference in evaporation rates of solvent in the network is minimized. The sol-gel network shrinks uniformly during drying and therefore the intrinsic tensile stresses can be minimized.

Commonly used DCCA includes formamide (NH_2CHO), N,N-Dimethylformamide ($\text{HCON}(\text{CH}_3)_2$), and oxalic acid ($\text{C}_2\text{O}_4\text{H}_2$). By adopting formamide as DCCA, crack-free PLZT thin films have been successfully prepared.^{82,83,84}

Chelating agent is another effective way to reduce the intrinsic stresses. It was proposed that the chelating agent can regulate the hydrolysis rate of highly reactive alkoxides by forming chelating complex,⁸⁵ and slowing down the gelation reaction. A rigid gel hence formed at a later stage of the thermal decomposition process and hence the intrinsic stresses from gel shrinkage and constrained densification of the coating films were minimized.⁸⁶ It is also explained that the chelating agents such as glycerol and ethylene glycol can be retained in the gel network by chelating into the starting alkoxides and acting as an organic plasticizer.⁷⁸ As a result, high tensile stress will not build up in the gel films and therefore the tendency to crack is substantially reduced.

Ethylene glycol and acetylacetone are the most often used chelating agents in preparing crack-free EO films. By adopting ethylene glycol as chelating agent, Seveno *et al.*⁸⁷ have prepared the films with one-layer thickness of 0.33 μm without cracking and 3.2 μm thick films were deposited by 10 repeated coatings. Hua *et al.*⁸⁸ have obtained the thin films with a single layer 0.13 μm thick and the crack-free 3.82 μm thick film has been fabricated by 30 repeated coating. Without adding ethylene glycol, their sols only allowed four-layer films to be deposited before cracks formed. Poly(ethylene glycol)(PEG) has also been reported to be very effective to reduce the tensile stress and the reduction was more significant with higher PEG molecular weight.⁸⁹ The critical thickness of PEG-modified films can reach 0.175 μm per layer, while the unmodified films can only reach 0.1 μm per layer. By 12 coating, the PEG-modified films can arrive at a thickness of about 2.1 μm.⁹⁰

By using acetylacetone as chelating agent, Soe *et al.*⁸⁶ deposited crack-free PLZT films with the thickness of 0.25 μm in a single coat, and the maximum thickness of the multiple coated films reached 4 μm, four times thicker than that without adding acetylacetone. Recently, Kurchania *et al.*⁹¹ developed a acetylacetone-modified sol gel processing to prepare PLZT films, in which 1,3 propanediol was used as solvent instead of the often used 2-methoxyethanol. Crack-free PLZT films up to 0.5 μm thick per coating have been deposited on platinized silicon and the final thickness up to 10 μm has been realized by 12 coatings. Sriprang *et al.*^{92,93} invented a triol-based sol-gel route for preparing PLZT films, in which “acetylacetonate modified” titanium propoxide i.e. $\text{Ti}(\text{OC}_3\text{H}_7)_2\text{-(CH}_3\text{COCHCOCH}_3)_2$ and zirconium(IV) n-propoxide were used as precursors and 1,1,1-tris(hydroxymethyl)ethane as solvent. The uncracked films had a thickness of 0.4 μm by one coating, but the films were highly porous. On the other hand, Maki *et al.*⁹⁴ discovered a propylene-glycol based sol gel route with

acetylacetone as chelating agent, where the uncracked films are very dense and has a thickness of 0.22 μm by one coating and 0.9 μm by multi-coating. Although acetylacetone has been proven to be effective in increasing the single-coating thickness of the films without cracking, it was also shown to require a higher formation temperature for perovskite phase because of the strong attachment of acetylacetone ligands to Ti and Zr components.⁹⁵

Stress-relaxing agents are a group of chemicals which can reduce intrinsic stress and thus avoid cracking in the thermal decomposition. The chemicals can be organic polymers with amide group such as polyvinylpyrrolidone(PVP) and polyvinylacetamide with the structures shown in Figure 2-20.⁹⁷ This type of polymers can be hybridized with metalloxane polymers in molecular scale through strong hydrogen bonding between the C=O groups of the polymer and the -OH groups of the metalloxane polymers. These C=O groups can be regarded as capping agent for -OH groups of the metalloxane polymers. The hydrogen bonding suppresses the hydrolysis and/or condensation, making the gel network flexible and allowing the structural relaxation in films during heat treatment, as schematically illustrated in Figure 2-21. In addition, the organic polymers like PVP increase the sol viscosity significantly, which helps the formation of the thick gel films over 1 μm . Single-layer, 1.7 μm thick PZT films have been obtained from the $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O} - \text{Zr}(\text{OC}_3\text{H}_7)_4 - \text{Ti}(\text{OC}_3\text{H}_7)_4$ solutions containing PVPs but it was reported that the films were rather porous.⁹⁶

Figure 2-20 The structure of polyvinylpyrrolidone (a) and polyvinylacetamide(b)⁹⁷

Figure 2-21 (a) Condensation and gel pore collapse in gel films under heat treatment, (b) possible capping of the metalloxane polymer OH groups by C=O groups from PVP⁹⁷

Single-layer PZT films as thick as 0.75 μm were also prepared via one-step spin coating from the $\text{Pb}(\text{NO}_3)_2\text{-Zr}(\text{OC}_3\text{H}_7^n)_4\text{-Ti}(\text{OC}_3\text{H}_7^i)_4$ solutions with PVPs. However, the PZT films only exhibited a transmittance of about 65% in the visible wavelength range, indicating that the films were also not fully dense.⁹⁶

Although polymer addition has been proven to be efficient in improving the critical thickness, it exerts some undesirable effects on the microstructural development and properties of the films. Yu *et al.*⁹⁰ found that with an increase in the molecular weight of polymer, the PZT films became less dense and the grains were separated by gaps and voids between them, leading to the decrease of Young's modulus and dielectric constant, as well as the increase of coercive field. Hida *et al.*⁹⁸ reported that the addition of PVP induced large voids between the grains in Fe_2O_3 thin films, and nano-size pores were commonly found in PZN-PZT films and PZT films

derived from PVP-modified solutions.^{99,100} It is noted that the densification of the PZN-PZT films with PVP-modification significantly depended on pyrolysis temperature, but no fully dense films could be obtained by only changing pyrolysis temperature.⁹⁹ Stepwise heat treatment of gel films at 360°C and then at 700°C was found to be more effective in promoting the densification of BaTiO₃ films, as compared with single-step heat treatment,¹⁰¹ but it is reported to be unsuitable for PZT films,¹⁰² as the PZT films cracked badly when preheated at 350°C. The films became rather porous when preheated at lower temperatures of 100°C, 200°C or without preheating. The porous structure was attributed to the phase separation between the organic and inorganic species in gel films during heat treatment.¹⁰² Therefore, densification of the films derived from PVP modified solutions still remains as a challenge.

2.5.3 Synthesis of PMN-PT films

As discussed in Section 2.3.2, PMN based single crystals, especially 0.67PMN-0.33PT, exhibit extraordinary EO properties and show great potentials in the development of integrated optics with low driving voltage and fast response time. However, a major challenge exists in the preparation of this material: it is very difficult to obtain pure perovskite phase without the presence of pyrochlore impurities. Pyrochlore phase has a low dielectric constant (about 200) and is commonly believed to deteriorate the electric properties of the materials.¹⁰³ Pyrochlore phase is thermodynamically more stable and kinetically more favorable to be achieved than the perovskite phase. The existence of pyrochlore phase, like Pb₃Nb₄O₁₃ (P₃N₂, Cubic), Pb₃Nb₂O₈ (P₃N, tetragonal) and Pb₂Nb₂O₇ has been widely reported during the formation of PMN from solid-state reactions between oxides.¹⁰⁴ Pb₃Nb₄O₁₃ was also found in sol-gel derived PMN powders.¹⁰⁵ A new type of pyrochlore phase with Mg

contained formula, i.e. $\text{Pb}_{1.86}\text{Mg}_{0.24}\text{Nb}_{1.76}\text{O}_{6.5}$ was found in sol-gel derived PMN films recently.¹⁰⁶ These pyrochlore phases can transform to perovskite phase by further reacting with Pb^{2+} and Mg^{2+} ions, however, due to the low reactivity of MgO with pyrochlore phase, it is difficult to remove the pyrochlore phase completely.¹⁰⁷

A few methods have been reported to eliminate the pyrochlore phase. Among them, columbite method is an most effective solid-state-reaction route, in which, magnesium oxide and niobium oxide are reacted with each other first to form a columbite phase (MgNb_2O_6), and then further reacted to lead oxide to form perovskite phase of lead magnesium niobate.^{108, 109} The involved reactions are:

The perovskite phase began to appear at $\sim 700^\circ\text{C}$, and fully crystallized at $\sim 900^\circ\text{C}$.¹¹⁰ However, even with the columbite process, a small amount (5%) of pyrochlore phase was still observed. Recently a coating approach for synthesis of pure perovskite phase of PMN-PT has been reported.¹¹¹ A layer of $\text{Mg}(\text{OH})_2$ was coated on Nb_2O_5 particles to separate the inter-reaction between Nb_2O_5 and PbO , and hence prevented the formation of lead-niobate type pyrochlore. Pyrochlore-free PMN powders were obtained after sintering at 900°C . Adding excess MgO and/ or PbO to PMN-based ceramics have also been confirmed to be beneficial in the reduction of the pyrochlore phase.^{112,113} Nevertheless, it should be noticed that too much MgO may induce MgO-rich second phase and reduce the dielectric constant of the PMN ceramics.¹¹³

Sol-gel processing has been reckoned to be a good method to prepare pure PMN-based ceramics. Most of the preparation routes follows the principles of columbite method, i.e. to begin with the synthesis of Mg and Nb double metal

alkoxide, such as $\text{Mg}[\text{Nb}(\text{OEt})_6]_2$ ¹¹⁴, $\text{Mg}[\text{Nb}(\text{OPr}^i)_6]_2$ ¹¹⁵, $\text{Mg}[\text{Nb}(\text{OC}_2\text{H}_4\text{OCH}_3)_6]_2$ ¹¹⁶ or $\text{MgNb}_2(\text{OAc})_2(\text{OR})_{10}$ (R is alkyl group),¹¹⁷ and then mix with $\text{Pb}(\text{OAc})_2$ and/or Ti alkoxides. To obtain stable Mg and Nb double alkoxides, long-time (>2h) reflux is essential to form the strong Mg-O-Nb bonds.¹¹⁸ As metal alkoxides, especially Nb ethoxide and Ti alkoxide, are highly moisture-sensitive, the whole procedure must be carried out in dry glove box. To inhibit the hydrolysis of the alkoxides, complexing agents like acetylacetonate (AcAcH), ethanolamine (TEA) were added in the precursor solutions.¹¹⁹ However, TEA, similar to AcAcH, delayed the onset temperature for the formation of perovskite phase to 750°C and pure perovskite was only obtained at the annealing temperature above 775°C.¹¹⁹

Many studies on the crystallization behavior of perovskite formation in sol-gel derived PMN-PT films has revealed that the annealing temperature for obtaining pure perovskite phase is as high as around 700°C-800°C, although sol-gel route is expected to facilitate molecular-level homogeneity. For example, Gong *et al.*¹²⁰ prepared the PMN-PT films with the insertion of a PbO seeding layer below the films and substrates. Pure-perovskite films were obtained only after heating at 800°C for 5mins. For the films without seeding layer, the crystallization temperature required was as high as 850°C. Hoffmann *et al.*¹²¹ reported that the annealing at 800°C was essential to completely remove the pyrochlore phase in the (1-x)PMN-xPT films (x=0-0.75). Beltrán *et al.*¹²² confirmed that the crystallization of perovskite phase in PMN films took place at ~750°C and pure-perovskite films were obtained at 800°C. Wakiya *et al.*¹²³ reported that the Mg-contained pyrochlore phase, i.e. $\text{Pb}_{1.86}\text{Mg}_{0.24}\text{Nb}_{1.76}\text{O}_{6.5}$ was formed at 700°C and it transformed to perovskite phase at the annealing temperature of 800°C. However, Pb seriously evaporated at the temperature ~800°C and above, the newly-growth perovskite phase can decompose to pyrochlore phase again, as reported

by Shyu *et al.*,¹²⁴ Parola *et al.*,¹²⁵ and Park *et al.*¹²⁶ Therefore the annealing temperature range available for the formation of pure perovskite phase becomes very narrow.

2.5.4 Effect of polymers on perovskite formation

In recent years, polyethylenimine (PEI) and carboxylated polyethylenimine (PEIC) have been proven to be effective in assisting the synthesis of pure oxide films like SrTiO_3 , $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$, and TiO_2 as they can be electrostatically or directly bound to the metal ions such as Ti^{4+} , Sr^{4+} and Ba^{2+} .¹²⁷ Other polymers including polyethylene glycol (PEG, $\text{H}-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{H}$) and polyvinyl alcohol (PVA, $-(\text{CH}_2-\text{CH}(\text{CH}_3))_n-$) have also been used to prepare single-phase oxides, such as calcium aluminate (CaAl_2O_4), yttrium aluminate ($\text{Y}_3\text{Al}_5\text{O}_{12}$), yttrium phosphate (YPO_4),¹²⁸ Ca_2SiO_4 and $\text{Ca}_4\text{Al}_2\text{Fe}_3\text{O}_{10}$.¹²⁹ These polymer species contain either hydroxyl groups, or oxygens which can form complexes with cations and sterically entrap the cations in the entangled polymer network, resulting in better chemical homogeneity and stabilization of the solution.¹³⁰ Fine and single-phase powders can therefore be obtained at a relatively lower external temperature.¹²⁹

PEG is also found to be beneficial to prepare ferroelectric oxides especially those with less stable perovskite structure. Uekawa *et al.*¹³¹ synthesized $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--BaTiO}_3$ (PNN-BT) oxides by sintering PbO , BaTiO_3 and columbite phase (NiNb_2O_6) which was obtained through oxidizing the $\text{PEG}-(\text{Ni}^{2+}\text{Nb}^{5+})$ complex. The addition of PEG greatly accelerated the crystallization of the columbite oxides and hence they can obtain the pure PNN perovskite phase with only a small amount of BT (1~7.5%) as stabilizer. Wan *et al.*¹³² have also synthesized 0.9PMN-0.1PT powders using sol-gel route with the presence of PEG ($M_w=300$). They found that the gelation of colloidal solution was facilitated with a small amount of PEG. Pyrochlore phase

crystallized at a lower temperature of 500-600°C and pure perovskite phase was obtained after calcining at 850°C. Lee *et al.*¹³³ has prepared PZN powders from a solution containing PEG. Perovskite phase was dominant in the resultant powders. The authors mentioned that with the presence of PEG, the interaction between metal ions and anions could be increased, resulting in a homogeneous mixture of the precursors. Very recently, Yu *et al.*^{134, 135} reported that PEG can dramatically promote the formation of perovskite phase while suppress the pyrochlore phase in PZN-PT films. Pure perovskite phase can be obtained by only adding 30% PT as stabilizer and the crystallization temperature is as low as 580°C. They explained that PEG200 has five or six donor oxygens, which can form fairly stable macrocycles with lead ions as shown in Figure 2-22. Therefore, the Pb-based complex is holodirected and the 6s² lone electron pairs lose its directional effect. As a result, the formation of pyrochlore phase with oxygen vacancies is not favored. Meanwhile, the complexing between Pb and PEG also shifted the chemical state of Pb²⁺ towards higher binding energy, facilitating the perovskite formation.

Figure 2-22 Local environment of Pb²⁺ in the PEG-modified precursor. (A) PEG with five oxygen donors; (B) PEG with six oxygen donors. Oxygen donors in the PEG200 arrange themselves in a nearly equatorial plane, leaving two axial sites for anion (CH₃COO⁻) coordination.¹³⁴

In summary, many efforts have been made in polymer-assisted synthesis of various oxides, especially PEG, which shows significant promotion in the formation of perovskite phase. PVP, as another good candidate, has been widely used to modify sol-gel solutions to increase the critical thickness of ferroelectric oxide films. Nevertheless there has been no systematic study on the effect of PVP on the crystallization behavior, morphology and properties of the thin films thus far. The studies on PVP assisted synthesizing the advanced material systems such as PLZT and PMN-PT are also very limited. These will therefore be the focus of this thesis.

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3 PLZT thin films prepared by PVP modified sol-gel processing^{1,2}

3.1 Introduction

There is an increase of interest in fabricating PLZT films above 1 μ m thick for integrated optics. PVP polymer is helpful in the forming of such films as it can significantly increase their critical thickness. However, the preparation of PLZT thin films by adding PVP and its effect on the critical thickness, chemistry of sol-gel solution, crystallization behavior and microstructure development of the films, is still not well reported in the literatures.

In this work, PVPs with various molecular weights including 10k, 40k, 360k, 630k and 1300k (abbreviated as PVP10, PVP40, PVP360, PVP630 and PVP1300) were used to modify the PLZT sol-gel solutions. The PLZT, with a typical composition of $\text{Pb}_{0.91}\text{La}_{0.09}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.9775}\text{O}_3$ has been chosen for the studies due to its promising application on various EO waveguide-based devices. The effect of PVP addition on the critical thickness, crystallization and micro-structural evolution of the PLZT films has been systematically investigated.

Our results showed that with PVP addition, the critical thickness of a single PLZT layer could increase to 600-900nm, much higher than 78nm-thick films prepared without PVP addition. However, some large and round grain clusters, so-called rosette-like structures are observed in the PVP-modified PLZT films. Our results indicate that the formation of the rosette-like structures is closely related with a premature nucleation of PbO grains in the PVP modified sol-gel solutions, which

induced a fluctuant distribution of Pb and hence inhomogeneous nucleation and growth of perovskite phase in the resultant films. Finally, the electrical and optical properties of the films with and without rosette-like structures have been investigated.

3.2 Experimental procedure

3.2.1 Preparation of sols

Vacuum dehydrated lead acetate (>99.5%, Aldrich, Wisconsin, USA), zirconium propoxide (70% solution in 1-propanol, Aldrich), titanium isopropoxide (99.99%, Sigma-Aldrich), lanthanum nitrate (Merck KGaA, Darmstadt, Germany) and PVPs with molecular weights of 1×10^4 , 4×10^4 , 3.6×10^5 , 6.3×10^5 and 1.3×10^6 (Fluka, Buchs, Switzerland) were used as the starting materials. Lead acetate with 10 mol% excess was added to compensate the lead loss due to evaporation during annealing process. Acetylacetone (>99%, Merck KGaA) was used as chelating agent to stabilize the Zr and Ti alkoxides.

At first, zirconium propoxide and titanium isopropoxide were dropped into a solution of acetylacetone and 2-methoxyethanol (2-MOE, 99.3%, Sigma-Aldrich, Steinheim, Germany) and then mixed to form a stable solution. The solution was added to the mixture of lead acetate and 2-MOE with continuous stirring. After that, lanthanum nitrate was added. PVP powders with different molar ratio to PLZT (0.25-1.5) or different molecular weight were finally added to the solution. A sol-gel solution without PVP was also prepared for comparison. Finally, all solutions were refluxed at 60-80°C for 2 hours and then aged for at least 24 hours unless it was specified.

3.2.2 Characterization

The rheological behavior of the sol-gel solutions modified by PVP630 with different molar ratio to PLZT was studied by a rheometer (Viscotester VT550, Haake) after the PLZT solution was allowed to settle for 24 hours. PLZT gel films deposited on silicon wafer from the solutions were studied by FT-IR spectrometer (FT-IR Spectrum GX, PerkinElmer, USA), where silicon wafer was used as the reference. For comparison, pure PVP630 powders were also measured. The solutions were then dried at 100°C for 8 hours to obtain dried gels. Thermal decomposition behavior of the gels with different PVP molecular weight and concentration was studied by differential thermal analysis-thermogravimetric analysis system (DTA-TGA, STA 449C, Netzsch), at a heating rate of 10°C/minute, in air atmosphere. The heating rate of 10°C/minute was chosen because most of the PLZT films prepared in the following were pyrolyzed on hot plate which has an extremely fast heating rate. Fast heating rate was hence favorable for the TG-DTA analysis of the gels. However, if too fast heating rate, e.g. 20°C/minute was used, the DTA peaks can't be differentiated, as shown Figure 3-1. In this work, the heating rate at 10°C/minute was therefore used.

Figure 3-1 TG-DTA curves of the PLZT gels without adding PVP and measured at 20°C/minute

PLZT films were spin-coated on ITO (indium tin oxide)/glass substrates (ca. 15 x 15 x 0.7mm³ in size) from the as-prepared sol-gel solutions, with speeds ranging from 300 rpm to 3000 rpm. The film thickness was evaluated by measuring a level difference between the films surface and substrate using Surface Profiler (Alpha-Step 500, Tencor). The cracking behavior of the films was observed by 1000x optical microscopy and field emission scanning electronic microscope (FESEM, JSM-6340F, JEOL). Most of the films for characterizing crystallization and morphology were prepared by single-coating and followed by pyrolysis at 400°C for 10 minutes on hot plate, except two samples derived from the sols with PVP360 and PVP1300 which were heated to 400°C by 20°C/minute and then dwelled for 10min. After that, the samples were immediately transferred to an electric furnace and heated at temperatures ranging from 450°C to 700°C for 10-30 minutes. The samples for characterizing the electrical and EO properties were prepared by multiple coating-pyrolysis cycles and then annealing at 700°C for 20 minutes.

The crystallization behavior of the PLZT films was studied by a Rigaku ultima type X-Ray Diffractometer (XRD) with an incident angle of 1°. The morphologies of the films were examined by FESEM. The elemental distributions over the film surface were studied by an energy dispersive X-ray analysis (EDX) equipped on SEM (JSM-6360, JEOL). PLZT gel particles derived from the sols with and without PVP360 addition and the square-platelet particles growing on the films heated at 450°C were studied by a high resolution transmission electron microscope and selected area electron diffraction (TEM/SAED, JEOL JEM-2010). The distribution of the gel particle size was measured by a dynamic light scattering system (DLS, Brookhaven Instruments, BI-200SM) and the samples were filtered by filters with a pore size of 0.45 µm before measurement.

The polarization-electric field hysteresis loops of the as-prepared films were measured by a standard Radiant RT6000HVS type ferroelectric tester and the remnant polarization and coercive field were determined. The measurement area is 0.5mm in diameter, with a layer of Pt (~100nm thick) on the film surface as top electrodes and the bottom electrodes were the ITO buffer layers on substrates. An electric field ranging in 0-200kV/cm was applied on the samples to obtain the saturated hysteresis loops. The dielectric properties of the films were tested on the same samples by an HP 4194A Impedance/Gain Phase Analyzer (Hewlett Packard, Santa Rosa). The transmittances of the PLZT samples were measured by an UV-Vis spectrometer (UV-2501PC, Shimazu).

3.3 Results and discussion

3.3.1 Rheological behavior of PLZT sols

The quality of the films deposited by spin coating depends much on the rheological behavior of sol-gel solution. A smooth and uniform film can be obtained only when the solution is Newtonian-type liquid, i.e. the viscosity is shear independent. For the shear thinning or thickening solutions, the films show a shape of bulge or concave in the center of the substrate, respectively.^{3,4} Hence it is essential to study the effect of adding PVP on rheological behavior of the PLZT sols.

Figure 3-2 shows the viscosity curves against shear rate for the PLZT sols with the addition of PVP ranging in 0-1.5 (molar ratio of PVP monomer to PLZT). For the sol without PVP, a shear thinning behavior is observed, with a significant decrease in the viscosity as the shear rate increases. The shear-thinning behavior is usually attributed to the condensation or agglomeration of polymerized metalloxanes in sol-gel solutions.⁵ As the shear rate increases, the agglomerates are broken down, which, in

Figure 3-2 Viscosity versus shear rate for PLZT sol solutions with different PVP concentration (the molar ratio of PVP monomer to PLZT is labeled on each figure above)

turn, frees up the immobilized liquid within the gelled structures and results in the decrease of the viscosity. The shear thinning behavior therefore indicates the existence of agglomeration of polymerized metalloxanes in the PLZT sol without PVP. For the

sols with PVP addition, the viscosity of the sol-gel solutions tends to be less dependent on the increase of shear rate, especially when the PVP content is 0.75 and above. The sols with the PVP addition of 1.0 exhibit nearly Newtonian flow behavior. As has been discussed in Section 2.5.2 of chapter 2, PVP can suppress the hydrolysis and/or condensation reactions by forming strong hydrogen bonding between its C=O groups

Figure 3-3 the interaction between PVP and the M–OH (M: metal ions, e.g. Pb^{2+} , Zr^{4+} , Ti^{4+})⁶

Figure 3-4 FT-IR curves of the PLZT gel films and pure PVP

and –OH, the end groups of the hydrolysis product M–OH (M: metal ions, e.g. Pb^{2+} , Zr^{4+} , Ti^{4+}), as shown in Figure 3-3. This interaction gives rise to a significant red shift of the absorption band for C=O groups, i.e. from 1674cm^{-1} (PVP) to 1647cm^{-1} (in our PLZT gels) in the FT-IR spectra (Figure 3-4). Since the –OH groups have been capped by the C=O groups, further condensation reaction will be suppressed and therefore less H_2O is produced, which in turn inhibits the further hydrolysis reaction. The suppressing behavior will become more significant with the increase of PVP

concentration in the sol-gel solutions. In other words, less polymerization in the precursor solution is formed. Hence the sols tend to be independent of the shear rate.

However, when the ratio of PVP monomer to PLZT is 1.5, a slightly shear thinning behavior is observed again. This can be attributed to the long-chain PVP itself since pure PVP solutions exhibit shear-thinning behavior. This is because PVP chains can be elongated on application of steady shear and become aligned to flow direction.⁷ When large content of PVP dissolves in the PLZT sol-gel solutions, it could dominate the rheological behavior of the solutions, resulting in the shear thinning behavior.

The viscosities of the sols as a function of PVP concentration are shown in Figure 3-5 with a fixed shear rate of 2000 (1/s). The sol without PVP has a viscosity of about 10.8mPa.s. Adding small amount of PVP, i.e. 0.25, slightly decreases the viscosity due to its inhibition of condensation reaction in the sols. When the addition of PVP is 0.5 and above, the viscosity increases distinctly. For the solution with the ratio of 1.0 and 1.5, the viscosity reached 38.5mPa.s and 88.3mPa.s, respectively. The increase of the viscosity makes it possible to deposit the PLZT films with higher one-coating thickness.

Figure 3-5 Viscosities of PLZT sols vs. PVP concentration at the shear rate of 2000 (1/s)

3.3.2 Critical thickness of the PLZT films

Figure 3-6 shows the effect of PVP concentration on the one-coating thickness of PLZT films. It can be seen that adding PVP can significantly increase the one-coating thickness of the films. The thickness increases more significantly when the PVP addition is 1.0 and 1.5 and especially when the spin speed is below 1000 rpm. This can be ascribed to the remarkable increase of the solution viscosity by PVP addition. The cross(x) in Figure 3-6 denotes the thickness where the films began to crack. The critical thickness of the films should lie between the cross-marked point and the previous point close to it. Based on Figure 3-6, the critical thickness of the films from different sols is summarized in Table 1. It clearly shows that adding PVP can effectively increase the critical thickness of PLZT films. The PLZT films with PVP addition in the concentration of 1.0 and 1.5 have the critical thickness of ~604 and ~926nm respectively, much higher than that of the non-PVP films. It should be pointed out that although higher critical thickness could be achieved by adding more

Figure 3-6 One-coating thickness of PLZT films as a function of the content of PVP630 (molar ratio of PVP monomer to PLZT) and spin speed

Table 3-1 Critical thickness (t_c) of PLZT films affected by PVP content (molar ratio of PVP monomer to PLZT)

PVP content	0	0.25	0.5	0.75	1.0	1.5
$t_c(\text{nm})$	~78	~96	~219	~350	~604	~926

PVP, too high concentration of PVP could lead to non-Newtonian-type sol-gel solution, resulting in non-uniform film surface. It could also induce poor densification of the films.

The effect of PVP molecular weight on the critical thickness of PLZT films was also studied with the molar ratio of PVP monomer to PLZT equal to 1.5 and the results are shown in Figure 3-7. PVP with higher molecular weight also distinctly promotes the critical thickness of films, such as PVP360 and PVP 630, leading to a critical thickness of ~624nm and ~926nm, respectively. These critical-thickness values

Figure 3-7 One-coating thickness of PLZT films as a function of the molecular weight of PVP and spin speed

are comparable to 500-750nm for the PVP modified films reported in literatures on the other material systems.^{8,9} It is interesting that no cracks were found in the films with PVP1300 additions even when the one-coating thickness reached 986nm. However the films were found to be extremely porous.

3.3.3 Thermal analysis of the PLZT gels

Gel pyrolysis is an important stage during crystallization of sol-gel derived ceramic films. Frequently, it has been observed that the onset of crystallization occurs at the temperatures slightly greater than the pyrolysis temperature.¹⁰ Higher the pyrolysis temperature, the ceramic films show higher crystallization temperature.^{11,12}

Similar phenomena were observed in the present PLZT gels. Figure 3-8 and Figure 3-9 show the TG and DTA curves of the PLZT gels with different PVP contents, respectively. The gels without PVP addition experienced a large weight loss (29.8%) at the temperature range of 180-514°C, accompanying three exothermal peaks at 281°C, 313°C, 442°C, respectively (Figure 3-8(A) and Figure 3-9(A)). These exothermal peaks can be accounted for the decomposition of organic species in the gels. Another exothermal peak at 500-600°C and centered at ~544°C can be attributed to the crystallization of the PLZT gels because almost no weight loss is observed at this temperature. The exothermal peak shifted to lower temperature when PVP was added (Figure 3-8 B, C, D and Figure 3-9 B, C, D), reaching 484°C when PVP addition is at the ratio of 0.75. Meanwhile, the pyrolysis temperature is also decreased and the resultant exothermal peak is strong and broad, centered at ~374°C.

When the PVP content is further increased to 1.0 and 1.5, respectively, the exothermal peak corresponding to organic decomposition occurs at ~409°C and ~446°C individually (Figure 3-9 E, F), accompanying ~40% weight loss (Figure 3-8 E,F). However, no peaks corresponding to the occurrence of crystallization is observed.

Figure 3-8 TG curve of PLZT gels with PVP360 addition of 0-1.5 (molar ratio of PVP monomer to PLZT)

Figure 3-9 DTA- curve of PLZT gels with PVP360 addition of 0-1.5 (molar ratio of PVP monomer to PLZT)

It is speculated that the crystallization peak overlapped with the organic-decomposition peaks since the in-situ released heat from the decomposition can instantly increase the environmental temperature and initiate the gel crystallization. It could therefore be concluded that adding PVPs can reduce the onset crystallization

temperature of PLZT films, reaching $\sim 450^{\circ}\text{C}$ with the molar ratio of PVP at 1.5, much lower than that of $\sim 544^{\circ}\text{C}$ for the non-PVP films. This point will be further confirmed by XRD results presented in the following sections.

Figure 3-10 DTA curves of PLZT gels modified by PVP40 and PVP1300 with the heating rate of $10^{\circ}\text{C}/\text{min}$

Our study has also shown that similar pyrolysis behavior was found in the gels modified by different types of PVP, such as PVP10, PVP40, PVP630 and PVP 1300, with the molar ratio of PVP monomer/PLZT = 1.5. Figure 3-10 shows the DTA curves of the gels with PVP40 and PVP1300 addition. Both exothermic peaks corresponding to organic decomposition of the gels locate at $\sim 450^{\circ}\text{C}$ and no crystallization peak is found.

It should be noted that besides the PVP addition, the exothermic peaks in the TG-DTA curves can also be affected by heating rate. With the heating rate increasing, the peaks shift to higher temperature, as have been observed by Chen *et al.*¹³ in thermal analysis of PZT gels. Similar phenomena have been found in the thermal analysis of our PLZT gels. For example, three exothermic peaks at 257, 410 and 487°C

°C were found in DTA curves of the non-PVP PLZT gels with the heating rate of 2.5°C/min (Figure 3-11). These peaks significantly shifted to the higher temperatures of 281, 442 and 544°C respectively when the heating rate was 10°C/min (Figure 3-9(A)). With the heating rate further increasing to 20°C/min, the peak at 281°C moved to ~285°C and the other two peaks were found at ~538-624°C (Figure 3-11).

With different heating rates, the change trends of weight loss in TG curves as a function of heating temperature were similar to each other. However, the temperature corresponding to the complete decomposition of the gels (no weight loss occurred) increased with the increasing of the heating rate, for instance, 450°C for the heating rate of 2.5°C/min, 514°C for 10°C/min and 631°C for 20°C/min.

Figure 3-11 TG-DTA curves of the PLZT gels without adding PVP and measured with different heating rate

3.3.4 Crystallization behavior of the PLZT films

As TG-DTA results have clearly shown that PVPs can reduce the onset crystallization temperature of the PLZT gels, the improvement on the crystallization of the derived films after annealing is expected. This is further evidenced by the XRD results shown in Figure 3-12 (a-b). For the non-PVP films annealed at 600°C, both

Figure 3-12 XRD patterns of the PLZT films with PVP modification by the molar ratio of PVP monomer to PLZT equal to 1.0, heated at (a) 600°C and (b) 700°C for 20 minutes respectively.

pyrochlore and perovskite peaks are observed, but the latter can be seen to be very weak (Figure 3-12(a)). In the films with PVP modification, it is noted that perovskite phase has become the dominant phase after annealing at 600°C and the crystallinity is observed to increase with the increase of PVP molecular weight. It is concluded that PVP can significantly promote the crystallization of perovskite phase in the PLZT films, especially those PVPs with higher molecular weight. For the films modified by PVP630 and PVP1300, a non-ferroelectric phase, i.e. hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, abbreviated as PCO below) is observed. When the annealing temperature increases to 700°C, the PCO phase disappears, however a weak peak corresponding to pyrochlore phase still exists in the PVP modified PLZT films (Figure 3-12(b)). This should be associated with the fluctuant distribution of Pb element in the films, which will be discussed later.

3.3.5 Morphology of the PLZT films affected by PVP

Figure 3-13 shows the FESEM images of the PLZT films with PVP modification by a molar ratio of 1.0 to PLZT and annealed at 700°C for 20mins. The films without PVP addition are also shown here for comparison. Rosette-like structures with the diameter of ~5 to 10 μm are observed in all the PVP-modified PLZT films (Figure 3-13 (b-d)), but not in the films without PVP modification (Figure 3-13 (a)). With the PVP molecular weight increasing, the dimension of rosette-like structures decreases and the number of rosettes in a same area increases. According to our experimental observation, the rosette-like structures appeared in the PVP modified PLZT films irrespective of the substrates used, pyrolysis temperature, dwelling time, heating rate and heating steps. The dimension and number of rosette-like structures changed accordingly with the variation of processing parameters. For example, when the films were heated at 20°C/min to 400°C for pyrolysis in furnace instead of hot

plate (which was used to prepare most of the samples), the rosette-like structures were observed, as shown in Figure 3-14 (a - b). However, the dimension of the rosette-like structures significantly decreased and the number remarkably increased with the Mw of PVP increasing from 360k to 1300k.

Figure 3-13 FESEM images of the PLZT films modified by (a) no PVP, (b) PVP10, (c) PVP360 and (d) PVP1300, heated at 700°C for 20 minutes.

Figure 3-14 FESEM images of the PLZT films modified by (a) PVP360 and (b) PVP1300, preheated at 400°C for 10min and then annealed at 700°C for 30 minutes at a heating rate of 20°C/minutes.

Rosette-like structures were also observed in other Pb-containing ferroelectric films derived from polymer modified sol gel processing, such as PZT films modified by PVPs or PEG (poly(ethylene glycol)) and deposited on Pt/Ti/SiO₂/Si substrates.^{14,15,16} The formation of rosette-like structure is hence reckoned to be closely related to the polymer addition, although the mechanism remains unclear.

The rosette-like structures were further studied by magnifying Figure 3-13(c) to x 20k. A nano-porous morphology is found (Figure 3-15). Both the pore and the grain size are around 50nm. The area in between the rosette-like structures is dense and consists of fine grains with the average size of only a few nanometers.

Figure 3-15 FESEM image (x20k) of the rosette-like structures in PLZT films magnified from Figure 3-13(c)

TEM-SAED images (Figure 3-16(a)) show that the coarse grains in rosette-like structures are perovskite crystals with the zone axis $[2\bar{5}\bar{1}]$, while the fine grains in between the rosette-like domains are mainly pyrochlore phase (Figure 3-16 (b)). The existence of pyrochlore phase is consistent with the XRD results for the PVP360 modified PLZT films presented in Figure 3-12(b). The rosette-like domains are obviously more energetically favorable for the nucleation and growth of perovskite crystals.

Figure 3-16 TEM images and SAED patterns of the grains (a) in rosette-like structures and (b) in between rosette-like structures of PLZT films modified by PVP360, heated at 400°C on hotplate and then at 700°C for 20 minutes. Pe and Py stand for perovskite and pyrochlore phases. The zone axis of the electron diffraction pattern in (a) is $[2\bar{5}1]$.

3.3.6 Formation mechanism of the rosette-like structure

As discussed above, the molecular weight of PVP only affects the dimension and number of the rosette-like grain clusters. All the PVPs used can induce similar rosette-like microstructures. PVP360 was therefore chosen as an example to examine the formation mechanism of rosette-like structures. The PVP360-modified PLZT films used in the present investigation were annealed at temperatures of 450-700°C for 20 minutes. Figure 3-17 shows the XRD patterns of the PLZT films and Figure 3-18 shows the FESEM micrographs. It can be seen that pyrochlore phase initially crystallized at 450°C, together with the presence of perovskite and PCO phase (Figure 3-17(a)). The crystallization of these phases confirms that in the TG-DTA curves of PVP-modified gels (Figure 3-9 F), the exothermal peak at ~446°C is induced by both the gel pyrolysis and crystallization.

Figure 3-17 XRD patterns of PVP360-modified PLZT films annealed at (a) 450°C, (b) 500°C, (c) 600°C and (d) 700°C, respectively

Figure 3-18 FESEM images of PVP360-modified PLZT films annealed for 20 minutes at (a) 450°C, (b-c) 500°C, and (d) 600°C. Image (c) was obtained by enlarging the square zones labeled on (b)

Figure 3-19 TEM image (a) and SAED pattern (b) of the square platelet in the PLZT films heated at 450°C. The inset in (a) is the EDX spectrum of the square platelet crystal. The zone axis of the SAED pattern in (b) is [701]

The PCO crystals detected in Figure 3-17 (a) can be observed as the square platelets in the PLZT films and is marked by the arrows in Figure 3-18(a). This has been confirmed by the TEM-SAED (Figure 3-19(a-b)) and EDX studies (the inset in Figure 3-19(a)). The SAED pattern of the square platelets can be indexed as PCO phase with the zone axis of [701]. The EDX spectrum shows that the composition mainly consists of Pb, O and C elements.

After annealing at 500°C, the perovskite peaks in the XRD pattern (Figure 3-17 (b)) become much stronger, whereas PCO still coexists. By comparing the morphologies of the films annealed at 450°C and 500°C, some round particles are observed in the original sites of the PCO square platelets (Figure 3-18(b-c)). The particles could be the crystals of the newly-grown perovskite phase. Meanwhile, some PCO square-plate crystals can still be observed in the films annealed at 500°C, as indicated by the arrows in Figure 3-18(b). In the films annealed at 600°C, nevertheless,

the perovskite phase becomes a major phase (Figure 3-17 (c)), where the rosette-like structures of $\sim 4\mu\text{m}$ in size turn to be noticeable (Figure 3-18(d)). It can therefore be concluded that the formation of the rosette-like structure is closely related to the crystallization of perovskite phase. In the films annealed at 700°C , the rosette-like structures grow remarkably (as has been shown in Figure 3-13(c)), which is accompanied by significant enhancement on perovskite crystallization (Figure 3-17(d)).

Figure 3-20 Second electron image (a) and EDX spectrum (b) of the films annealed at 600°C . The EDX spectrum was obtained by line scanning along the white-line position in the image (a)

The elemental distribution over the rosette-like structures in the films annealed at 600°C was studied by EDX line scanning and the results are shown in Figure 3-20(b). It is found that the rosette domains are rich in Pb and the Pb content decreases gradually from the rosette area to the non-rosette, while the other elements including Zr, Ti, La and O are homogeneously distributed in the whole film body. Since the rosette-like domains are Pb-rich, the nucleation and growth of perovskite crystals are compositionally favorable. The growth of perovskite grains will be aggressive during further heating at 700°C and thus pores due to organic decomposition and/or Pb evaporation may be trapped in the rosette structure, leading to the porous morphology.

The existence of the Pb-deficient domains should be the main reason that pyrochlore phase cannot be completely removed in the PVP modified PLZT films even after annealing at 700°C (Figure 3-12 (b)).

Since the rosette-like structures are developed from the PCO sites, it is essential to understand where the PCO phase comes from. Figure 3-21 (a) and (b) show the TEM results of the PLZT gel particles with PVP360 modification, together with the gel particles from the sols without PVP360 for comparison (Figure 3-21 (c-d)). It is found that there are some very fine and round particles with a size of ~5 nm and

Figure 3-21 TEM images (a and c) and SAED patterns (b and d) of the gel particles derived from the PLZT sols with PVP360 modification (a and b) and without PVP360 modification (c and d). The inset in image (a) is DLS spectrum of the PLZT sol with PVP360 modification. The electron diffraction pattern in (b) is with the zone axis of [001].

some square-plate particles of about 20-60 nm in size in the PVP360 modified PLZT sol-gel solution (Figure 3-21 (a)). According to the SAED, the square plates are PbO single crystal with the zone axis of [001] (Figure 3-21(b)), while the fine particles are amorphous. The PbO particles were found to gradually disappear under continuing exposure to the electron beam and voids were formed after PbO disappearance, as indicated by the arrows in Figure 3-22. This is consistent with the easy-evaporation characteristic of PbO. The size distribution of the gel particles with PVP modification was also studied by DLS. From the inset of Figure 3-21 (a), it can be seen that the majority of the gel particles have the size of ~5 nm and a small fraction have the size of about 20-60 nm, which is consistent with the TEM observation on the PVP-modified PLZT gel particles.

Figure 3-22 TEM image of the gel particles derived from the PLZT sol with PVP360 modification and after long-time exposure to the electron beam

The PbO crystal could transform to PCO phase when it contacts CO₂ and H₂O which are from air and/or the thermal decomposition of the PLZT gel films.¹⁷ This should be the reason that PCO phase can be observed in the PLZT films heated at

450~600°C (Figure 3-12(a) and Figure 3-17(a-b)). The Pb-rich domains due to the presence of the PCO phase facilitate the nucleation of perovskite phase and aggressive growth of the grains, which therefore produces the rosette-like morphology.

In the PLZT sol-gel solutions without PVP modification, only very fine particles of about 5 nm in size are found and the particles are amorphous according to the SAED pattern (Figure 3-21(c) and (d)). It is therefore conclusive that the formation of platelet PbO phase in the sol-gel solutions is induced by the presence of PVPs. It is well known that PbO crystals can be formed by dehydrating $\text{Pb}(\text{OH})_2$, the hydrolysis product of lead acetate. If this is true, it is more possible that PbO crystals are observed in the non-PVP PLZT sol-gel solutions since PVP has been proved to be able to suppress hydrolysis reaction by forming hydrogen bonds between its $\text{C}=\text{O}$ groups and $-\text{OH}$ groups, the end groups of hydrolysis products.⁶ Thus the PbO crystals are believed to be formed from the other reaction pathway instead of hydrolysis. Several papers have reported that PVP could reduce silver nitrate to metallic silver particles, even in darkness and with H_2O as solvent.^{18,19,20} It is also found that the commercially available PVPs contain hydroxyl end groups ($-\text{OH}$) which can initiate the reduction reactions.^{21,22} Similar reaction mechanism may also take place in the present PVP-modified PLZT sols, inducing the formation of metallic Pb. Since Pb is more active than metallic Ag, it will be oxidized and finally transformed to PbO particles in the PLZT sol solution.

The formation mechanism of rosette-like structures is schematically represented in Figure 3-23. Due to the presence of PVP, PbO grains nucleate and grow up in the PLZT precursor solutions (Figure 3-23(a)). By spin coating of the solutions, PbO is deposited on substrates, together with the fine and amorphous gel particles (Figure 3-23(b)). The PbO grains will be transformed into PCO compound by

reacting to CO_2 and H_2O during heating at 450°C (Figure 3-23(b)). Due to their comparatively large size, the presence of PCO crystals results in Pb-rich domains. Perovskite phase favorably nucleates in these domains and then grows into the matrix of the pyrochlore intermediate phase, until they reach lead-deficient sites (Figure 3-23(c)). Finally the nano-porous rosette-like structures are formed in the films (Figure 3-23(d)).

Figure 3-23 Schematic description on the formation mechanism of rosette-like structures, Pe and Py stand for perovskite and pyrochlore phase

It should be noticed that the development of rosette-like structures is much dependent on the growth of PbO particles. If the particle size is a few nanometers, just close to that of the PLZT gel particles, large area of Pb-rich domains may not be formed in the resultant gel-film body. As a result, rosette-like structures will not be developed. For example, no rosette-like structures were observed in the films derived from fresh PLZT sol-gel solutions, as shown in Figure 3-24. This can be attributed to

the PbO crystals which may just nucleate and have not grown up since there is no aging for the sol-gel solutions. However, the coarse and the fine grains which have been observed in the rosette domains and non-rosette domains respectively (Figure 3-15), are still present in the PLZT thin films (the inset of Figure 3-24).

Figure 3-24 FESEM images of PLZT films coated from fresh PVP360 modified sol-gel solution and annealed 700°C for 20 minutes.

3.3.7 Properties of the PLZT films with rosette-like structures

The effect of rosette-like structures on the ferroelectric and dielectric properties of the PLZT thin films has been investigated. The films were deposited from the PVP360-modified sol-gel solutions and annealed at 700°C. Figure 3-25 (a) shows the hysteresis loops of the films with rosette-like structure, under an electric field of 200kV/cm. The films possess a very slim P-E curve, with a remnant polarization of 0.61 nC/cm² and coercive field of 19.1 kV/cm. The remnant polarization of the films is about 1000 times lower than 1.91 µC/cm² for the non-rosette films (i.e. non-PVP films, Figure 3-25 (b)) although the coercive field is close to that of the non-rosette films (26.8 kV/cm). Furthermore, the relative dielectric constant (ϵ_r) of the films is only 101.5 at 1kHz, much lower than the 362.9 for the non-rosette films, and 350-700 for

films prepared by the other sol-gel techniques.^{23,24,25} The significant deterioration of the electrical properties can be attributed to the presence of the rosette-like structures, which limits the applications of our PLZT films on advanced EO devices.

Figure 3-25 Hysteresis loops of the PLZT films (a) with and (b) without PVP360 modification

Figure 3-26 Transmittance spectra of the PVP360—modified PLZT films and the ITO/Glass substrates

The optical transmittance of the PLZT films with rosette-like structure was also studied. From Figure 3-26, it is shown that the transmittance is very close to that of the ITO/glass substrate in the wavelength of 450-900 nm, oscillating at ~80%. It seems

that the nano-porous rosette-like structure doesn't impair the transmittance of the PLZT films.

Based on the interference oscillations in the transmittance curve of PLZT films, the refractive index (n) of the films can be calculated by “envelope method” developed by Manifacier *et al.* and Swanepoel *et al.*^{26,27} The involved equations are:

$$N_1 = 2n_s \frac{T_{Max} - T_{min}}{T_{Max} T_{min}} + \frac{n_s^2 + 1}{2} \quad \text{Equation 3-1}$$

$$n = [N_1 + (N_1^2 - n_s^2)^{1/2}]^{1/2} \quad \text{Equation 3-2}$$

where, $F = 4n_s^2(T_{max} + T_{min})/(T_{max}T_{min})$, T_{max} is an experimental interference extreme and T_{min} derived from the corresponding envelope (dotted line in Figure 3-26). The refractive index of the substrate ITO/glass is obtained from its own transmittance (T_s) in Figure 3-26 by the equation:²⁷

$$n_s = \frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1\right)^{1/2} \quad \text{Equation 3-3}$$

Figure 3-27 shows the calculated refractive indices of the PLZT films and the trend line through the data. The refractive index of the films decreases dramatically with the increase of wavelength. When the wavelength is 632nm, the refractive index is only 1.89, much lower than that of 2.16-2.51 for the PLZT (9/65/35) films prepared by sputtering, pulsed laser deposition or the other sol-gel processings.^{28,29,30} The low refractive index can be attributed to the presence of the nanometric pores in the rosette-like structures since the air in the voids have a refractive index of only 1.0.

Figure 3-27 Dispersion of refractive indices of the PVP360—modified PLZT films obtained from the optical transmission data shown in Figure 3-26

3.4 Concluding remarks

1. Adding PVP can significantly increase the critical thickness of a single PLZT layer, reaching 600-900nm, much higher than the 78nm where no PVP is added. PVPs can also reduce the onset crystallization temperature and significantly promote the crystallinity of perovskite phase. However, the films exhibit nanoporous rosette-like morphologies.
2. The rosette-like structures are developed from the sites of the $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ intermediate phase. The premature nucleation of PbO grains in the PVP-modified sol-gel solution is responsible for such kind of intermediate phases and thus results in the formation of Pb-rich domains in the film body. The Pb-rich domains accelerate the growth of the PLZT grains and as a result, the porous rosette-like structures are formed.

3. The PLZT films with rosette-like structures possess a slim hysteresis loop with low remnant polarization of only 0.61 nC/cm^2 . The relative dielectric constant is only 101.5 and refractive index is 1.89 @ $\lambda=633\text{nm}$, much lower than that of non-rosette films and the literature data.
4. In the future, removal of rosette-like structures in the PVP modified films will be the main target. Dense and pure-perovskite films are expected to be achieved. Such films are supposed to have much better electrical, optical and EO properties.

3.5 References

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4 Removal of the rosette-like structures in the PVP modified PLZT films

4.1 Introduction

The results in Chapter 3 have showed that despite PVP addition increases the critical thickness and enhances the perovskite crystallization in the sol-gel derived PLZT films, nano-porous rosette-like structures are often observed, together with the consequent pyrochlore phase, which significantly deteriorates the ferroelectric, dielectric and optical properties of the films. Our results also indicate that the formation of rosette-like structures is closely related with premature nucleation of PbO crystals in the PVP modified sol-gel solutions. The presence of the crystals induces a fluctuant distribution of Pb in the resulting films and hence gives rise to inhomogenous nucleation and growth of perovskite phase during the following pyrolysis and annealing. As a result, the porous rosette-like structures are formed.

It is noted that the optical and electrical properties of the films can be improved if the nano-porous rosette-like structures are eliminated. This could be achieved by suppressing the formation of PbO crystals and hence promoting the homogenous distribution of Pb element. Adding complexing agents such as ethylene diamine tetraacetate (EDTA), citric acid may be a feasible method. However, both complexing agents can't dissolve in the solution systems we have developed in the present work. The other agents like 18-crown-6, fail to form perovskite phase in PLZT films, even with high annealing temperature. Therefore, it is the aim in the present chapter to address the challenges, where the approaches include adding excess of Pb and

inserting a seeding layer like PbTiO_3 (PT) or $(\text{Pb},\text{La})\text{TiO}_3$ (PLT). The methods are found to be very promising as they can promote the homogeneous nucleation and growth of perovskite phase. The nanometric pores resulted from the aggressive growth of local perovskite crystals can hence be removed to give final non-rosette and dense films. The electrical and optical properties of the densified films were also characterized.

4.2 Experimental procedure

The PLZT solutions modified by different PVPs (Mw: 10-1300k, PVP monomer/PLZT=1.0 (molar ratio)) were prepared by using the same method as that in Chapter 3 but no aging was carried out. To study the effect of lead excess on the formation of rosette-like structures, lead acetate with 5-35 mol% excess was added to the PVP360 modified solutions.

PLT (La/Zr/Ti: 14/0/100) thin films were chosen as a seeding layer to improve the homogeneous crystallization of the PLZT films. The PLT precursor solutions (~0.2M) were prepared by using lead acetate, titanium isopropoxide and lanthanum nitrate as starting precursors and 2-MOE as solvent. Lead acetate and titanium isopropoxide were mixed in 2-MOE first and then reflux at 120°C for 2 hours, following the addition of lanthanum nitrate. After that, the solution was stirred over night at room temperature.

From the as-prepared solutions, PLT seeding layers were prepared by spin coating on ITO/glass substrates at 3000 rpm and followed by annealing at 575°C for 20 minutes. The PLZT films were coated on ITO/glass, PLT/ITO/Glass or PLT/glass with speeds ranging from 500 rpm to 3000 rpm. The films were prepared by single-coating and followed by pyrolysis at 400°C for 10 minutes and annealing at temperatures ranging from 600 to 800°C for 20-30 minutes. The samples for

characterizing the electrical and EO properties were prepared by repeating a few cycles of coating and pyrolysis until the thickness of $\sim 1.2\mu\text{m}$ was obtained. They were finally annealed at 700°C for 20 minutes.

The crystallization and morphology of the as-prepared PLZT films were studied by XRD, FESEM and AFM (atomic force microscope, Dimension 3100). The ferroelectric properties of the films were studied by a standard Radiant RT6000HVS type ferroelectric tester and the dielectric properties were tested by an HP 4194A Impedance/Gain Phase Analyzer. The measurement area used was 0.5mm in diameter, coated with a layer of Pt ($\sim 100\text{nm}$ thick, by sputtering). The transmittances of the PLZT samples were measured by an UV-Vis spectrometer (UV-2501PC, Shimadzu).

The refractive index and thickness of the PLZT films are important parameters for determination of the electrooptic coefficients and for applications on waveguide type electrooptic devices. They were measured by Prism coupler (model: Metricon 2010, Metricon) with the set-up shown in Figure 4-1. The laser beam was coupled into the films by a prism 200-P-2. The laser beam is either polarized with electric field in the plane of the films (Transverse Electric (TE) mode) or perpendicular to the film surface (Transverse Magnetic (TM) mode). By using the TE and TM polarizations, the ordinary refractive index n_o and the extraordinary refractive index n_e of the films can be determined. A TE mode spectrum can be obtained by measuring the reflected intensity of the laser beam as a function of the incident angle, as shown in Figure 4-2. When the incident angle of the beam at the prism/film interface (θ_p) satisfies the Equation 4-1:¹

$$2kn_1h\cos\theta_m - 2\Phi_{10} - 2\Phi_{12} = 2m\pi, \quad \text{Equation 4-1}$$

Figure 4-1 Schematic diagram of the set-up of the prism coupler -Meticon 2010

Figure 4-2 Intensity of reflected light vs. incident angle in a TE guided mode

a portion of the laser beam is coupled into the waveguide in the films, causing a dramatic decrease of the laser intensity and then increase again at a certain angle of θ_m . Hence a reflectivity dip is formed, as shown in Figure 4-2.

In Equation 4-1, $\sin \theta_m = n_p \sin \theta_p / n_l$, k is the wave number of the light in vacuum, n_l is the refractive index of the films, h is the film thickness, and $m = 0, 1, 2, \dots$, is the order of the modes. According to the total reflection theory developed by Born and Wolf *et al.*², the terms Φ_{10} , and Φ_{12} can be determined respectively by:

For TE mode,

$$\tan\Phi_{12}=(n_1^2 \sin^2\theta_m - n_2^2)^{1/2} / (n_1 \cos \theta_m) \quad \text{Equation 4-2}$$

$$\tan\Phi_{10}=(n_1^2 \sin^2\theta_m - n_0^2)^{1/2} / (n_1 \cos \theta_m) \quad \text{Equation 4-3}$$

For TM mode,

$$\tan\Phi_{12} = n_1 (n_1^2 \sin^2\theta_m - n_2^2)^{1/2} / (n_2^2 \cos \theta_m) \quad \text{Equation 4-4}$$

$$\tan\Phi_{10} = n_1 (n_1^2 \sin^2\theta_m - n_0^2)^{1/2} / (n_0^2 \cos \theta_m) \quad \text{Equation 4-5}$$

where n_0 and n_2 are the refractive index of substrate and air, respectively. Based on Equation 4-1 to Equation 4-5, and the angular position of the TE or TM modes observed in the mode spectra (e.g. TE0, TE1 and TE2 in Figure 4-2), the refractive index n_o , n_e and film thickness can be determined. Normally the film thickness should be above 300nm to get two or more modes to provide sufficient accuracy for the measurement.

The electrooptic properties of the films were characterized by a set-up built in-house, as shown in Figure 4-3. All the optical components such as laser, polarizers, and compensators are from Thorlabs, INC (New Jersey, USA) except those specified. The samples were mounted on a holder with the electrode gap horizontally oriented. A linear light ($\lambda=633\text{nm}$) from Helium Neon laser module was focused at a point on the electrode gap and its propagation path was adjusted along the direction normal to the sample surface. Two polarizers oriented at -45° and $+45^\circ$ with respect to the orientation of the sample electrodes, were mounted before and after the sample, individually. A Soleil-Babinet Compensator was inserted after the sample holder to compensate the phase shift induced by the samples under zero electric field. The transmitted light was finally detected by Si PIN photodiode (DET110, Thorlabs) and the output electric signal was monitored by an oscilloscope (DS5202CA, Rigol, China).

Figure 4-3 Optical system for measuring the electro-optic coefficient

Figure 4-4 Interdigital electrode pattern deposited on sample surface (unit: mm)

Before measurement, an interdigital electrode (IDE) pattern shown in Figure 4-4, was deposited on the sample surface by photolithography, e-beam-evaporation deposition and lift-off. The electric field applied on the electrodes was supplied by a high-voltage power amplifier (PZD2000, Trek, USA) connected with functional generator (FG210, Yokogawa, Japan). Before an electric field was applied, no laser light was detected as the 1st and 2nd polarizer were crossed to each other and the Soleil-Babinet compensator has compensated the phase shift induced by the samples. The output light intensity after 2nd polarizer was modulated when an electric field was applied. The relationship between the light intensity (I_T) and induced phase retardation ($\Delta\Phi$) can be expressed as:³

$$I_T = \frac{1}{4} I_0 \sin^2\left(\frac{\Delta\Phi\pi}{\lambda}\right)$$

Equation 4-6

where I_0 is the intensity incident to the 1st polarizer. Based on Equation 4-6 and Equation 2-10, the quadratic EO coefficient can be obtained. The linear EO coefficient can be calculated based on the Equation 4-6, 2-6 and 2-9. During the EO measurement, the electric field ranging from 0-20kV/mm was applied to the samples.

4.3 Results and discussion

4.3.1 Removal of rosette-like structures by adding excess Pb⁴

In this section, excess lead of 5-35 mol% was added in the PVP360 modified sol-gel solutions to improve the homogeneity of perovskite crystallization in the resultant films so as to avoid the formation of rosette-like structures. The thin film samples have one coating with the thickness of ~0.4μm. Figure 4-5 (a-d) show their FESEM images and Figure 4-6 (a-d) show the XRD results. With the increase of lead

Figure 4-5 FESEM images of the PLZT films annealed at 700°C for 20 minutes and with different lead excess ((a) 5 mol%, (b) 10 mol%, (c) 20 mol%, (d) 35 mol%). The inset in (d) is obtained by enlarging (d).

Figure 4-6 XRD patterns of the PLZT films with lead excess: (a) 5 mol%, (b) 10 mol%, (c) 20 mol%, (d) 35 mol% and annealed at 700°C for 20 minutes.

excess, the number of rosette-like structures in a same area is found to increase. When the lead excess is 20%, the rosette-like structures impinge upon each other (Figure 4-5 (c)). No rosette-like structure is observed in the films with 35% lead excess. Perusal of the film surface (x20k) reveals a dense and smooth microstructure, as shown in the inset of Figure 4-5 (d). The films are found to consist of coarse grains of 100-500nm in size, much bigger than ~50nm for the films with 10% lead excess (Figure 3-15).

Meanwhile, the crystallinity of perovskite phase in the PLZT films is found to increase with the increase of lead excess, and the pyrochlore phase decreases (Figure 4-6 (a-d)). When the lead-excess amount is increased to 35%, no pyrochlore phase is found in the films (Figure 4-6(d)). It is clear that the elimination of the pyrochlore phase accompanies by the disappearance of rosette-like structures.

As each rosette-like structure can be looked on as a nucleation site,⁵ the increase of lead-excess amount increases the density of nucleation sites for perovskite crystallization and thus improves the nucleation homogeneity across the whole PLZT film body. In the films with much higher lead excess (e.g. 35%), the excess Pb could completely compensate the Pb-deficient domains, leading to a homogeneous environment for the growth of newly nucleated grains. When these grains grow up, they touch with each other. Rosette-like structures hence disappear and pyrochlore phase is completely removed as well.

Since the PLZT films with 35% Pb excess exhibit a good densification behavior (the inset of Figure 4-5(d)), the sintering behavior of the PLZT films as a function of annealing temperature from 600°C to 800°C was studied and the results are shown in Figure 4-7(a-e). The films annealed at low temperature of 600°C are found to consist of very fine particles (~20nm in size) and nano-pores can be observed in between the particles (inset of Figure 4-7(a)). In the films annealed at 650°C, the

particles have grown up to hundreds of nanometers and are packed in a completely different way from that of the films heated at 600°C. Macro-pores, instead of nano pores are found in the films (Figure 4-7(b)). Nearly fully dense PLZT films are obtained when the annealing temperature is 700°C (Figure 4-7(c)). However, the nanoporous films with fine particles are formed again when the temperature is increased to 750°C - 800°C (Figure 4-7(d-e)).

Figure 4-7 FESEM images of the PLZT films with 35mol% lead excess and annealed at ((a)600°C, (b)650°C, (c) 700°C, (d)750°C, (e) 800°C for 20 minutes.

The nearly full densification of the PLZT films annealed at 700°C can be attributed to the occurrence of liquid-phase sintering since 35% excess of Pb was added in our material system. Lead oxide has been proven to be able to form a liquid phase in the bulk ceramic systems when the annealing temperature applied is above its melting point (890°C). The liquid phase fills in the pores in between the particles and wets the grain boundaries. Consequently the particles surrounded by the liquid phase are rapidly rearranged, which results in a better particle packing. At the same time, the grains grow up significantly at the expense of the finer grains which are more soluble in the liquid phase.^{6, 7, 8} Liquid phase sintering may also occur in our PLZT films since the pyrolysis of the organic gel films produces in-situ fine and active PbO particles. As the melting point of the nano PbO particles should be much lower due to the large specific surface area,⁹ liquid phase sintering is probably initiated at the annealing temperature of ~700°C. The PbO liquid fills in the nanometric pores produced by the decomposition of polymers in the gel films and assists in the well packing the particles. As a result, the dense film body can be achieved at 700°C.

For the films annealed at 600°C, PbO liquid phase may not be formed due to the relatively lower temperature. Thus, a nano-porous and uneven film body was obtained. PbO liquid phase may begin to form at 650°C, trigger the rearrangement of the particles and consequently improve the densification of the films. However, the macro-pores could not be removed probably due to insufficient formation of liquid PbO, as compared with that at 700°C. The densification of the films deteriorates when the annealing temperature is increased to 750°C-800°C. This could be ascribed to the rapid evaporation of PbO particles. It is therefore concluded that the annealing temperature of 700°C is optimal for the occurrence of liquid phase sintering and thus densification of the films.

4.3.2 Removal of rosette-like structures by adding PLT layer

Adding a seeding layer like PLT has been reported to be effective in the improvement of homogeneous nucleation of perovskite phase. A PLT (14/0/100) seeding layer (~50nm thick) was therefore applied on the bottom or top of the as-prepared PLZT films, as schematically shown in Figure 4-8. The PLZT films were deposited from the solutions modified by PVP with Mw ranging from 10k to 1300k and followed by pyrolysis at 400°C for 10 minutes and annealing at 700°C for 20 minutes. In both cases, no rosette-like structures was found. The morphology and the crystallization of the as-prepared films with PLT seeding layer on the bottom are shown in Figure 4-9 and Figure 4-10, respectively.

Figure 4-8 Models of applying PLT seeding layer on the bottom or top of the PLZT films

The films modified by PVP10 and PVP40 exhibit very uniform grain size and no pyrochlore phase is detected. The surface morphology and crystallization of the PVP40 modified films are shown in Figure 4-9(a) and Figure 4-10(a). For the films modified by PVP with $M_w \geq 360k$, some coarse grains are embedded in the fine-grain matrix and neglectable pyrochlore phase still remains in the films ((Figure 4-9(b-d) and Figure 4-10(b-d))). Some macro-pores are also found, especially for the films modified by PVP630 and PVP 1300, as highlighted by the circles in Figure 4-9(c-d).

Figure 4-9 FESEM image of PVP modified PLZT films with PLT as seeding layer on bottom (molecular weight of PVP: (a)40k, (b)360K, (c)630k, (d)1300K). The circles indicate macro-pores.

Figure 4-10 XRD patterns of the PLZT films with PLT as seeding layer (Mw of PVP: (a) 40k, (b) 360K, (c) 630k, (d) 1300K)

The surface roughness of the films with different PVP modification has been studied by AFM, and Figure 4-11(a-b) show two AFM images of the PLZT films modified by PVP40 and PVP360 respectively. The films modified with PVP40 are very smooth, with the rms roughness of only 1.8 nm across 2.5x2.5 μ m zone (Figure 4-11(a)). For the films modified by PVP360, the film surface is found to be very rough, reaching 4.2 nm (rms roughness) (Figure 4-11(b)). The roughness values of all the films modified by PVP40-1300 are listed in Table 4-1. The increase of the roughness in the films modified by PVP with molecular weight >360k can be attributed to the presence of the coarse grains and macro pores (Figure 4-9(b-d)).

Figure 4-11 AFM image of PVP modified PLZT films with PLT as seeding layer (Mw of PVP: (a) 40k, (b) 360K). The Y scale is 100nm/div.

Table 4-1 Rms roughness (unit: nm) of the PLZT films modified by different types of PVP

Mw of PVP	40k	360k	630k	1300k
Rms roughness	1.8	4.2	2.5	2.8

4.3.3 Properties of the PLZT films without rosette-like structures

Although both methods, namely adding excess Pb (>20%) and inserting a seeding layer of PLT can help to remove rosette-like structures, the latter method was chosen to study the electrical, optical and EO properties of the PLZT films. With that, the effect of PVP molecular weight on the properties of the derived films was also discussed.

The studied PLZT films have been deposited on the PLT/ITO/Glass substrates from the sol-gel solutions modified by PVPs with the molecular weight ranging in 10k-1300k and then annealing at 700°C for 20 minutes. Figure 4-12 shows the hysteresis loops of the films under an electric field of 150kV/cm, and Figure 4-13 shows the dielectric constant of the films as a function of frequency from 0.5kHz to 1MHz. From the figures, remnant polarization, coercive field, and dielectric constant of the films are presented in Table 4-2. The PVP40 modified films possess a saturated hysteresis loop with a remnant polarization of $6.94\mu\text{C}/\text{cm}^2$ and coercive field of $\sim 40\text{kV}/\text{cm}$. Their relative dielectric constant reaches ~ 926.3 at 1kHz (Table 4-2) and the dielectric loss is ~ 0.1 . The remnant polarization and the dielectric constant of the films are much higher than the $0.61\text{nC}/\text{cm}^2$ and 101.5 for the PLZT films with rosette-like structures (Chapter 3). The dielectric constant is also much higher than the 350-700 obtained for the films prepared by the other sol-gel techniques.^{10,11,12}

Figure 4-12 P-E curves of the PLZT films with PLT as seeding layer and modified by different PVPs (Mw of PVP: (a)40k, (b)360K, (c)630k)

Figure 4-13 Dielectric constant of the PVP modified PLZT films as a function of frequency (Mw of PVP: (a)40k, (b)360K, (c)630k)

Table 4-2 Ferroelectric & dielectric (1kHz) properties of the as-prepared PLZT films

Type of PVP	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)	ϵ_r
PVP40	6.94	42.23	926.3
PVP360	3.84	48.36	585.5
PVP630	31.52	111.27	490.9

Although the films with PVP360 modification possess the coercive field close to that of the PVP40 modified films, the remnant polarization is noted to be lower by a half, only $3.84\mu\text{C}/\text{cm}^2$, and the dielectric constant is measured to be only 585.5 (Table 4-2). The films modified by PVP630 exhibit a lower dielectric constant, only 490.9 and a severe dilated hysteresis loop with an extremely high coercive field (111.27kV/cm). The deteriorated ferroelectric properties can be attributed to the significant increase of the dielectric loss (~ 0.3), with comparison of the ~ 0.1 for the

other two films. The worsened dielectric and ferroelectric properties of the PLZT films with large-molecular-weight PVP modification are attributed to the presence of the macro-pores and small amount of remnant pyrochlore phase in the films, as has been discussed in the last sections.

The transmittance of the as-prepared films was also studied and the results are shown in Figure 4-14. It shows that the films with PVP40 modification exhibit a well-oscillating transmittance, which can be attributed to its low roughness in the film surface and good crystallization behavior. The transmittance of the films reaches ~70% in the visible wavelengths and drops rapidly at ~443nm. The absorption edge is at ~350nm. The absorption edge shifts to higher wavelength for the films derived from PVPs with Mw $\geq$ 360k, and meanwhile, the transmittance of the films decreases with the increase of molecular weight of PVPs, which can be ascribed to the low quality of the as-prepared films.

Figure 4-14 Transmittance curves of the PLZT films modified by different types of PVP

As the PLZT films obtained from PVP40 modified sol-gel solutions are found to exhibit much better electrical properties and optical transmittance, the optical and EO properties of the films were further studied. Films around 1 μ m thick were prepared

on PLT coated Corning 1737 glass and then annealed at 700°C for 20 minutes. Figure 4-15 and Figure 4-16 show their guided mode spectra. It is found that five TE modes and three TM modes are excited at the laser wavelength of 633nm. The sharp reflectivity dips in the two spectra indicate a good confinement of the light in the PLZT guiding layers.

Figure 4-15 TE mode spectrum excited at 633nm for the PLZT films

Figure 4-16 TM mode spectrum excited at 633nm for the PLZT films

Based on Equation 4-1 to Equation 4-5 and the angular position of the TE or TM modes in the mode spectra (Figure 4-15 and Figure 4-16), the refractive index n_o and n_e of the as-prepared PLZT films can be estimated to be 2.550 and 2.469 respectively, and the average film thickness is $1.233\mu\text{m}$. The difference between n_o and n_e , i.e. birefringence can be determined to be 0.081, indicating that the films are optically isotropic before applying electric field. The calculated thickness is in good agreement with the results obtained from FESEM micrographs.

The EO properties of the as-prepared PLZT films were characterized by the setup shown in Figure 4-3. When a square-wave voltage with the frequency of 10Hz was applied to the films through the interdigital electrodes like Figure 4-4, strong optical modulation due to field-induced birefringence can be observed, as illustrated in Figure 4-17. The lower trace in the figure is the voltage signal and the upper trace is the transmitted light signal. When the electric field applied is at 10.5kV/mm , the output light intensity can reach 11.48mV from full “close” state (no output light), which indicates a large phase retardation of 4.6° is generated from the sample.

Figure 4-17 Optical modulation of laser beams observed in the PLZT samples

However, the response time of the materials to the applied electric field could not be measured because the rising or falling time of the power supply is too long, ~ 2ms. It is not fast enough to characterize the EO response of PLZT films which are known to have the response speed in the order of nanoseconds.¹³

By changing the external electric field from zero to 10.5kV/mm, different optical intensities have been measured and the induced birefringence shift $\Delta(\Delta n)$ of the samples has been summarized as a function of the external electric field, as shown in Figure 4-18. It is indicated that the PLZT films exhibit very strong quadratic EO effect. The birefringence shift, as a function of the square of the external electric field, has been plotted in Figure 4-19. According to the slope of the linear fitting line, the quadratic EO coefficient R can be calculated as $0.79 \times 10^{-17} (\text{m/v})^2$, which is higher than the $0.25\text{--}0.5 \times 10^{-17} (\text{m/v})^2$ reported in the literatures for the PLZT films prepared by the other sol gel processing or aerosol deposition methods.^{14,15,16,17} The as-developed

Figure 4-18 Electric-field induced birefringence shift vs. electric field for the PLZT films. The solid line is the polynomial fitting to the raw data (■)

Figure 4-19 Birefringence shift as function of the square electric field for the PLZT films. The solid line is linear fitting to the raw data (■).

PLZT thin films have shown potentials to be applied on various EO devices such as Fabry-Perot interference (FPI) modulators and Mach-Zehnder interferometer waveguide modulators. ^{18, 19}

4.4 Concluding remarks

1. The nano-porous rosette-like structures can be removed by adding 20-35 mol% excess of Pb. The 35 mol% excess of Pb can initiate liquid-phase sintering, leading to dense and crack-free films.
2. Rosette-like structures can also be removed by inserting a seeding layer of PLT on bottom or top of the PLZT films. The as-prepared PLZT films with PVP40 modification are dense and smooth, with the rms roughness of ~1.8nm. The films possess a saturated hysteresis loop with remnant polarization of

6.94 $\mu\text{C}/\text{cm}^2$ and coercive field of $\sim 40\text{kV}/\text{cm}$ and their dielectric constant reaches 926.3.

3. The films also exhibit a high transmittance of $\sim 70\%$, the refractive index n_o and n_e of 2.550 and 2.469 respectively, and quadratic EO coefficient of $0.79 \times 10^{-17} (\text{m}/\text{V})^2$.

4.5 References

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5 PMN-PT films prepared by PVP modified sol-gel processing

5.1 Introduction

In the studies of the PLZT films (chapter 3), we found that PVP can reduce the onset crystallization temperature of perovskite phase to around 450°C in comparison to that of 544°C for the non-PVP films and enhance its crystallinity. It is therefore interesting to extend the studies to other ferroelectric film material systems with promising electrooptic properties but reported to have difficulties in removing the undesirable pyrochlore phase, for example, PMN-PT. PVP is seen to be a good candidate to assist the development of PMN-PT films at low temperature, where currently pyrochlore phase can only be completely removed at annealing temperatures as high as $\geq 700^\circ\text{C}$.^{1,2,3,4} As Pb will seriously evaporate at such temperatures and result in the decomposition of the crystallized perovskite phase,^{5,6,7} low temperature annealing exhibits many advantages and is important for the sol-gel process of PMN-PT thin films.

PVPs is believed to be able to assist the development of PMN-PT films at low temperatures also due to several characteristics, for example, (1) PVPs can coordinate with metal ions by its carbonyl groups (C=O) in every repeat unit,⁸ probably leading to special ion distribution in sol-gel solutions which is beneficial for the perovskite crystallization of the films, (2) large amount of heat released from the combustion of PVPs increases the in-situ temperature of the gel particles. Hence, the low-temperature

metastable intermediate phases like pyrochlore can be circumvented and direct crystallization of perovskite phase from amorphous matrix can be realized.

In this chapter, PMN-PT thin films with 43 mol% PT have been selected to study the effect of PVP content and molecular weight on the crystallization of perovskite phase. All the films were deposited on the substrates with a PLT ($(\text{Pb}_{0.86}\text{La}_{0.14})\text{TiO}_3$) seeding layer to avoid the formation of rosette-like structures which have been found in the PVP-modified PLZT thin films in Chapter 3. Lead nitrate instead of the commonly-used lead acetate, was selected as lead source. As nitrate groups are strong oxidizers, they can act as triggering agents for the rapid decomposition of PVPs and hence instantly produce large quantity of in-situ heat. The crystallization and morphologies of the PMN-PT films as a function of PVP content and molecular weight were studied and the PVP addition was therefore optimized. The phase purity of the well-crystallized PMN-PT films (determined by XRD) was also characterized by high resolution XPS (X-ray photoelectron spectroscopy). Finally the crystallization kinetics of perovskite phase in the films with and without PVPs was thoroughly investigated and the effect of PVPs on the perovskite crystallization mechanisms was preliminarily discussed.

5.2 Experimental procedure

5.2.1 Preparation

For the preparation of thin films $0.57\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.43PbTiO_3 , lead nitrate, magnesium acetate (vacuum dehydrated), niobium ethoxide, and titanium isopropoxide were chosen as starting materials and 2-methoxyethanol (2-MOE) was used as a solvent. The polymer additives used include PVP10, PVP40, PVP360, PVP630 and PVP1300, and the molar ratio of PVP monomer to PMN-PT was varied

in the range of 0-1.5. To compensate the Pb loss due to evaporation during post annealing, 15 mol% of Pb excess with respect to the stoichiometric amount was added. The precursor solutions leading to PbO , $\text{Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ and TiO_2 were prepared respectively, and then mixed together according to the flow chart shown in Figure 5-1. PVP was then added into the mixed solution. The final solutions were then vigorously stirred at room temperature for at least 4 hours.

Figure 5-1 Flow chart for the preparation procedure of the PMN-PT sol-gel solutions

5.2.2 Characterization

Thermal decomposition behaviors of the PMN-PT dry gels with different PVP additions were studied by DTA-TGA at a heating rate of $10^\circ\text{C}/\text{min}$, in air atmosphere. The gels were obtained by drying the PMN-PT solutions at 100°C for 8 hours and then thoroughly grinding into fine particles.

PMN-PT films were spin-coated on the PLT/ITO/glass substrates from the fresh sol-gel solutions. The as-coated films were pyrolyzed at $400\text{--}460^\circ\text{C}$ for 2-10

minutes on a hot plate. After that, the samples were immediately transferred into an electric furnace and heat treated at temperatures ranging from 430°C to 700°C for 2-60 minutes. The heating rate used here was extremely fast, estimated >100 °C/second.

The crystallization of the PMN-PT films was studied by Rigaku ultima type X-Ray Diffractometer (XRD) with an incident angle of 1°. The morphologies of the films were examined using a field emission scanning electronic microscope (FESEM, JSM-6340F, JEOL, Japan). The chemical states of the elements in the PMN-PT films coated from PVP40 modified sol-gel solutions and annealed at 650°C for 30 minutes were also studied by XPS spectrometer (PHI 04-500, Perkin-Elmer) using a Mg K α (1253.6eV) X-Ray source operated at 15 KV, 20 mA emission conditions. The data were analyzed by the software of CasaXPS (Version 2.3.12, Casa Software Ltd).

5.3 Results and discussion

5.3.1 Thermal analysis of the PMN-PT gels

Figure 5-2 shows the TG-DTA curves of PMN-PT dry gels with the PVP360 concentrations of 0-1.5 (molar ratio of PVP monomer to PMN-PT). For the gel without adding PVP, weak, broad exothermic peaks can be identified from 130°C to 400°C. Moreover, two endothermic peaks are found at 434 and 452°C respectively, accompanying with a significant weight loss of ~12.7% according to the corresponding TG curve. As the decomposition of alkoxyl groups like acetate, ethoxy (-OCH₂CH₃) and isopropyl from the Mg, Nb and Ti precursors are exothermic, the two endothermic peaks are reckoned to be induced by the decomposition of Pb(NO₃)₂. Figure 5-3 presents the TG-DTA curve of pure Pb(NO₃)₂ powders. Three endothermic peaks are found at around 455, 500 and 534°C respectively, following a weight loss of ~31.1%. The peaks should be attributed to the formation of some intermediate phases

Figure 5-2 TG-DTA curves of PMN-PT dry gels with different concentrations of PVP360. The data were measured under heating rate of 10°C/min and in air.

Figure 5-3 TG-DTA curve of pure $\text{Pb}(\text{NO}_3)_2$ powder. The data were measured under heating rate of 10°C/min and in air.

like $\text{Pb}_2\text{O}(\text{NO}_3)_2$, $\text{Pb}_3\text{O}_2(\text{NO}_3)_2$, $\text{Pb}_4\text{O}_3(\text{NO}_3)_2$, and/or $\text{Pb}_5\text{O}_4(\text{NO}_3)_2$ and so on.^{9,10} The endothermic peak at $\sim 455^\circ\text{C}$ is also found in the TG-DTA curves of the PMN-PT gels without PVP addition but is split into two peaks (Figure 5-2), which indicates that different intermediate phases could be formed in the gels. The other two endothermic peaks at 500°C and 534°C are not observed, instead, one broad exothermic peak is found in the temperature range of $460\text{--}600^\circ\text{C}$ (Figure 5-2), following with a small weight loss of 2.28%. This is ascribed to the further decomposition of the intermediate phases into PbO and gases like NO_2 and O_2 .

For the PMN-PT gels with PVP addition ratio of 0.25, the two endothermic peaks at 434 and 452°C are found to have disappeared in the DTA curves (Figure 5-2), and a broad exothermic peak at $300\text{--}380^\circ\text{C}$ is observed. The exothermic peak is split into two peaks located at ~ 300 and $\sim 374^\circ\text{C}$ when the ratio of PVP addition is increased to 0.5 and above. Meanwhile a new and strong exothermic peak is found at $430\text{--}460^\circ\text{C}$. According to the TG curves, two significant weight losses have happened during the pyrolysis of PMN-PT gels. For the gels with PVP addition ratio of 1.0, the weight loss of 22.7% occurs at the temperature $< 300^\circ\text{C}$ and 16.5% at $300\text{--}460^\circ\text{C}$. The exothermic peaks and weight loss occurring at $< 300^\circ\text{C}$ can be attributed to the decomposition of alkoxyl groups from the Mg, Nb and Ti precursors,¹¹ while those at ~ 374 and 452°C can be ascribed to the combustion of PVPs accelerated by $\text{Pb}(\text{NO}_3)_2$ (strong oxidizer). The exothermic peak at 452°C is extremely sharp and hence indicates large amount of heat generated, which has been identified to be beneficial to perovskite formation according to the studies on the crystallization of PMN-PT films at the temperatures near the peak, i.e. 430°C and 460°C in the next section.

5.3.2 Effect of PVP content on the crystallization of PMN-PT films

Figure 5-4 presents the XRD patterns of the one-coating 0.57PMN-0.43PT films prepared from the modified sol-gel solutions with different PVP contents and annealed at 430°C for 30 minutes. A peak corresponding to pyrochlore phase is observed in the films without PVP modification (Figure 5-4(a)), while for the films with PVP additions, only perovskite phase can be detected and the crystallinity increases with the increase of PVP content (Figure 5-4(b-f)). The onset temperature of perovskite formation in the PVP-modified films is therefore to be 430°C or less, which is much lower than the reported literature values (i.e. 550°C-700°C).^{12, 13, 14} It is worth pointing out that no peaks corresponding to pyrochlore phase, the intermediate product during perovskite crystallization, is observed in the XRD patterns of the PVP modified films (Figure 5-4 (b-f)).

Figure 5-4 XRD patterns of the 0.57PMN-0.43PT thin films on PLT coated ITO/Glass substrates with the PVP360 addition of (a) 0, (b) 0.25, (c) 0.5, (d) 0.75, (e) 1.0, (f) 1.5 to PMN-PT (molar ratio). The films were heated at 430°C for 30 minutes.

Figure 5-5 XRD patterns of the 0.57PMN-0.43PT thin films on PLT coated ITO/Glass substrates with different PVP360 addition of (a) 0, (b) 0.25, (c) 0.5, (d) 0.75, (e) 1.0, (f) 1.5 to PMN-PT (molar ratio). The films were heated at 460°C for 30 minutes.

Figure 5-6 XRD patterns of the 0.57PMN-0.43PT films on PLT coated ITO/Glass substrates with different PVP360 addition of (a) 0, (b) 0.25, (c) 0.5, (d) 0.75, (e) 1.0, (f) 1.5 to PMN-PT (molar ratio). The films were heated at 650°C for 30 minutes.

The pyrochlore phase is also not detected in the films with 0.25-1.0 PVP addition ratio and annealed at 460-650°C (Figure 5-5 (b-f) and Figure 5-6 (b-e)), except the films with PVP addition ratio of 1.5 and heat-treated at 650°C (Figure 5-6 (f)). For the films without PVP addition, the peak intensities of perovskite and pyrochlore phase concurrently increase after heating at 460°C (Figure 5-5(a)) and the pyrochlore phase is still present even after annealing at 650°C (Figure 5-6(a)). The pyrochlore phase can be assigned to $\text{Pb}_{1.83}\text{Nb}_{1.71}\text{Mg}_{0.29}\text{O}_{6.39}$ according to JCPDS-ICDD card #37-0071 and the XRD pattern obtained by slowly scanning in $2\theta=10-80^\circ$ (not shown here), a B-site rich phase. For such type of pyrochlore, it is difficult for Mg^{2+} to diffuse into the B-site to form perovskite phase¹⁵ and therefore the pyrochlore phase is still observed in the non-PVP films even after high-temperature annealing. The XRD results also clearly show that the optimal content of PVPs is in the range of ratio 0.25-1.0, in which the formation of pyrochlore is suppressed and the crystallization of perovskite phase is significantly enhanced.

The morphologies of the PMN-PT films with different PVP additions and annealed at 650°C are shown in Figure 5-7. Rosette-like structure isn't observed in all the PMN-PT films although it was commonly seen in the PVP modified PLZT thin films. This can be attributed to the fresh sol-gel solutions and the seeding layer PLT applied in the present work. The films without PVP modification are seen to consist of particles ~50 nm in size and some much smaller particles (highlighted by the circles in Figure 5-7(a)). The fine particles possibly belong to pyrochlore phase since they have a relatively lower crystallinity as compared to the perovskite phase (Figure 5-6(a)). The films with PVP additions are seen to have uniform grain-size distribution (Figure 5-7(b-e)). Meanwhile, PVP content has been found to have a significant influence on the densification of the films. The optimal contents are identified to be in the range of

ratio 0.5-1.0 (Figure 5-7(c-e)), while the samples with both lower (Figure 5-7(b)) or higher PVP content (Figure 5-7(f)) exhibit rather porous structures. The porous morphology with higher PVP content (Figure 5-7(f)) can be attributed to the decomposition of excessive polymer in the films, which leaves lots of voids during

Figure 5-7 FESEM images of the 0.57PMN-0.43PT films with PVP360 modification (a: 0, b: 0.25, c: 0.50, d: 0.75, e: 1.0, f: 1.5 (PVP monomer/PMN-PT)) and annealed at 650°C for 30 minutes

crystallization. The porous structure of the films with lower PVP content (Figure 5-7(b)) can be due to low exothermal heat produced from PVP decomposition which is hence not enough to trigger the densification procedure of the grains.

5.3.3 Effect of PVP molecular weight on the crystallization

The effect of molecular weights (Mw: 10k-1300k) of PVPs on the crystallization behavior of the PMN-PT films was also studied with the molar ratio of PVP monomer to PMN-PT fixed to be 1.0. When the films were heated at 460°C for 30 minutes, perovskite phase appeared in all the films (Figure 5-8(a-e)). Pyrochlore phase was detected only in the films modified by PVP with long molecular chains (e.g. PVP630 and PVP1300) (Figure 5-8(d-e)). After annealing at 650°C for 30 minutes, however, only perovskite was formed in all the films and all the films were noted to possess good crystallinity (Figure 5-9(a-e)).

Figure 5-8 XRD patterns of the 0.57PMN-0.43PT films on PLT coated ITO/Glass substrates with different PVP modification ((a) PVP10, (b) PVP40, (c) PVP360, (d) PVP630, (e) PVP1300). The films were heated at 460°C for 30 minutes

Figure 5-9 XRD patterns of the 0.57PMN-0.43PT films on PLT coated ITO/Glass substrates with different PVP modification ((a) PVP10, (b) PVP40, (c) PVP360, (d) PVP630, (e) PVP1300). The films were heated at 650°C for 30 minutes.

The formation of pyrochlore phase in the films modified by PVP630 or PVP1300 and heated at 460°C can be ascribed to the steric separation of the polymer species to the metal cations because of their long -C-C- chains. Nevertheless, it can be removed by annealing at 650°C. To avoid the formation of pyrochlore phase at low temperatures, the optimal molecular weight of PVP should be <630k. Furthermore, the

Figure 5-10 FESEM image of the 0.57PMN-0.43PT films modified by PVP630 and annealed at 650°C for 30 minutes. The molar ratio of PVP monomer to PMN-PT is equal to 1.0

densification of the films can be enhanced by using the PVPs with smaller molecular weight. The films with large-molecular-weight PVP (e.g. PVP630) modification exhibit extremely porous morphology, as shown in Figure 5-10.

It should be noted that besides choosing the optimized PVP addition, the fast heating rate used in pyrolysis and annealing of the films is also very important to suppress the pyrochlore formation and obtain pure-perovskite and dense PMN-PT films. As we known, the formation of pyrochlore phases is very favorable at low annealing temperature. Large amount of pyrochlore will be formed if slow heating rate is used and the dwelling time at low temperature ($<600\text{ }^{\circ}\text{C}$) is too long. In addition, the instant increase of the in-situ temperature around the gel particles as a result of the decomposition of the precursors may not be realized because such procedure occurs gradually with the slow heating rate. Consequently, pyrochlore phase can't be removed even after high-temperature annealing and very ununiform microstructure of the films will be observed. One example is shown in Figure 5-11. The sample was pyrolyzed at 460 for 10mins with a very slow heating rate of $2^{\circ}\text{C}/\text{min}$ and then annealed at 650°C for 30 minutes with the heating rate of $40\text{ }^{\circ}\text{C}/\text{min}$.

Figure 5-11 FESEM image of the 0.57PMN-0.43PT films with PVP360 modification. The films were pyrolyzed at 460 for 10mins with the slow heating rate of $2^{\circ}\text{C}/\text{min}$ and then annealed at 650°C for 30 minutes with the heating rate of $40\text{ }^{\circ}\text{C}/\text{min}$.

5.3.4 XPS analysis of the well-crystallized PMN-PT films

High-resolution XPS is a powerful tool to analyze the chemical states of the elements in the as-developed PMN-PT films and hence helpful to further confirm the phase purity of the films. In this section, pure-perovskite 0.57PMN-0.43PT films (confirmed by XRD) have been studied by XPS. The samples were prepared from PVP40 modified solutions with the molar ratio of 1.0 to PMN-PT and annealed at 650°C for 30 minutes. The results are shown in Figure 5-12 and the binding energy of the Pb4f7/2, Nb3d5/2, Ti2p3/2 and O1s are listed in Table 5-1, together with the literature data,¹⁶ except that for Mg which is omitted due to low intensity in the spectra.

As shown in Figure 5-12, the Pb spectra can be fitted into main (M) and one satellite (S_{Pb}) spin-orbit doublets. The binding energies for the main peaks are 138.3eV (Pb4f7/2) and 143.1eV (Pb4f5/2), and for the satellite-peaks are 136.1eV (Pb4f7/2) and 140.9eV (Pb4f5/2). The former can be ascribed to the lattice Pb state and the latter belong to metallic state.^{17, 18} The atomic percentage of the metallic Pb to lattice Pb state is ~3.9%. The small amount of the metallic Pb could be formed due to the in-situ reducing atmosphere created by the decomposition of PVPs. The Ti2p and Nb3d spectra are found to consist of only one spin-orbit doublet at Ti2p3/2=458.1eV, Ti2p1/2=463.7eV and Nb3d5/2=206.7eV, Nb3d3/2=209.5eV, respectively, which indicates Ti and Nb ions exhibit only one chemical state. The binding energies for the lattice chemical states of Pb4f, Ti2p and Nb3d for our samples are found to be equal to or in between those of the 0.63PMN-0.37PT and 0.53PMN-0.47PT single crystals, as shown in Table 5-1.

Figure 5-12 The high-resolution XPS spectra of the Pb4f, Nb3d, Ti2p and O1s photoelectrons for the 0.57PMN-0.43PT thin films prepared from PVP40 modified sol-gel solutions and annealed at 650°C for 30 minutes.

Table 5-1 The binding energies (eV) of the Pb, Nb, Ti and O elements in the PMN-PT films

Samples	Ref.	Pb4f7/2		Nb3d5/2	Ti2p3/2	O1s		
0.57PMN-0.43PT	this work	M	S _{Pb}	206.7	458.1	M	S _{O1}	S _{O2}
		138.3	136.1			529.7	528.0	532.2
0.63PMN-0.37PT	ref.16	M	S _{Pb}	206.5	457.6	M	S _{O1}	S _{O2}
		138.3	137.1			529.4	528.0	532.5
0.53PMN-0.47PT	ref.16	M	S _{Pb}	206.9	458.2	M	S _{O1}	S _{O2}
		138.3	-			529.5	531.2	532.4

The O1s spectra consist of the main peak and two satellites (S_{O1} and S_{O2}) with the binding energies of 529.7, 528.0, and 532.2eV, respectively. The main peak can be attributed to the lattice oxygen and the S_{O2} results from the surface-absorbed H_2O and CO_2 .¹⁹ The S_{O1} component can be related to structural disorder, as reported in the PMN-PT single crystals with PT content $\leq 37\%$ by Kania *et al.*¹⁶ Structural disorder, the characteristic of relaxor ferroelectrics, suggests random distribution of Nb^{5+} and Mg^{2+} ions in the B sites of perovskite lattice and disordered ion displacement.^{16,20} Hence the presence of the small S_{O1} peak probably indicates our PMN-PT films with 43% PT exhibit relaxor ferroelectric behavior.

From the analysis on the chemical states, it can be concluded that pure-perovskite PMN-PT thin films have been developed by using the optimized PVP-modified sol-gel processing with lead nitrate as lead precursors. According to the XRD patterns in the last two sections, perovskite phase most likely crystallizes directly from the amorphous films as a result of PVP addition, instead of following the well-recognized crystallization route: Amorphous $\rightarrow$ Pyrochlore phase $\rightarrow$ Perovskite phase. To help identify the importance of PVPs in promotion of perovskite crystallization, the reaction kinetics of perovskite crystallization in the two PMN-PT film systems, i.e. with and without PVP modification, was investigated in the next section.

5.3.5 Reaction kinetics of perovskite crystallization²¹

The reaction kinetics of perovskite crystallization has been investigated according to the model developed by Johnson and Mehl²² and by Avrami:^{23,24}

$$\ln[1/(1-y)] = (Kt)^n \quad \text{Equation 5-1}$$

where y is the crystallinity of perovskite phase formed; K is the reaction rate constant which depends on the nucleation, growth rate and temperature; t is the calcination time;

and n is the reaction order which is sensitive to the time dependence of the nucleation and growth rate and geometry of the particles. Equation 5-1 can be rewritten as:

$$\ln \ln(1/(1-y)) = n \ln K + n \ln t \quad \text{Equation 5-2}$$

By plotting $\ln \ln(1/(1-y))$ against $\ln t$ and linear regression, the time exponent n can be obtained from the slope and $\ln K$ from the intercept of the $\ln \ln(1/(1-y))$ axis. It is noted from literatures that $n=0.54-0.62$ indicates a diffusion controlled crystallization mechanism,^{25,26,27} and $n=1.0-1.24$ indicates a phase-boundary controlled crystallization mechanism.^{25,26,27} The mechanisms involving simultaneous nucleation and growth are implied by $n=2.0-3.0$.^{28,29}

Meanwhile, the temperature dependence of reaction rate constant K can be described by the Arrhenius equation:

$$K = \nu \exp[-E/(RT)] \quad \text{Equation 5-3}$$

where ν is the frequency factor, E the apparent activation energy of crystallization, and R the gas constant. Hence the activation energy for perovskite crystallization can be evaluated by plotting the $\ln K$ versus the reciprocal temperature and getting the slope.

To study the reaction kinetics of perovskite crystallization in the PMN-PT films without PVP addition, the films were annealed at different temperatures of 460-700°C for 0-60min. The crystallinity of the perovskite phase in PMN-PT films was determined by first determining the ratio of the integrated intensity of the strongest perovskite peak (110) ($2\theta = 31.620^\circ$) over the integrated intensity of the strongest ITO peak (222) ($2\theta = 30.579^\circ$). The ratio was then compared with the values of PMN-PT

Figure 5-13 Perovskite crystallinity for the PMN-PT films without PVP addition, as a function of annealing time and temperature.

Figure 5-14 The intensity ratio of pyrochlore (222) peak to ITO(222) peak for the PMN-PT films without PVP addition, as a function of annealing time and temperature.

thin films annealed at 700°C for 20 minutes, where 100% crystallinity was assumed since the intensities of the perovskite XRD peaks was no longer increased even with a prolonged annealing time. The existence of pyrochlore peaks wasn't taken into account here. This method is similar to the one used by Gregory *et al.* to analyze the crystallinity of their desired phase.³⁰

Figure 5-13 shows the perovskite crystallinity of the PMN-PT films as a function of annealing temperature and dwelling time. The crystallinity of perovskite phase is observed to increase with the increase of annealing temperature and dwelling time, and almost level off at the dwelling time of 30 minutes or longer. At the same time, the pyrochlore crystallinity increases with the increase of annealing time at the temperature of 460-700°C, as shown in the Figure 5-14. The trend then goes down after it reaches a peak. This is attributed to the competition between the crystallization of pyrochlore phase and its transition to perovskite phase. When the transition to perovskite phase is faster, the detected pyrochlore crystallinity decreases.

Figure 5-15 Reaction kinetics following the Johnson-Mehl-Avrami equation for the 0.57PMN-0.43PT films without PVP modification

The relationship of $\ln \ln [1/(1-y)]$ (y is the perovskite crystallinity, $0 < y < 0.9$) versus $\ln t$ is plotted in Figure 5-15 in which, only the kinetic data for $t=2-30$ minutes are included since the crystallinity of perovskite has been stabilized after dwelling in 30 minutes or longer. The result shows a single linear fitting of the kinetic data and hence the perovskite formation at the present range of annealing temperatures can be treated as a single-stage process. The n values (reaction order) are 0.20 at 460°C, 0.32 at 550°C - 700°C. These n values do not fall into any of the exponent ranges mentioned above (i.e. 0.54-0.62, 1.0-1.24 and 2.0-3.0), indicating some other mechanisms dominating the perovskite crystallization in the non-PVP films. This will be discussed later in detail.

According to the Arrhenius equation (Equation 5-3), the $\ln(K)$ versus the reciprocal temperature is plotted in Figure 5-16. The activation energy of perovskite crystallization in the 0.57PMN-0.43PT films can be determined to be 305.3kJ/mol, close to 290kJ/mol for the PMN based ceramics synthesized by solid-state reaction using pyrochlore-type (e.g. $\text{Pb}_3\text{Nb}_2\text{O}_8$) powders as precursors.²⁹

Figure 5-16 Activation energy of perovskite crystallization in the 0.57PMN-0.43PT films without PVP modification derived by fitting to the Arrhenius equation

The high activation energy in our non-PVP thin films can be attributed to the formation of lead-niobate type pyrochlore phases (i.e. $\text{Pb}_{1.83}\text{Nb}_{1.71}\text{Mg}_{0.29}\text{O}_{6.39}$) during the perovskite crystallization. It is well known that the transition of pyrochlore to perovskite phases is usually controlled by diffusion and reaction between pyrochlore and Mg^{2+} and/or Pb^{2+} contained precursors.^{31, 32, 33} However, the reaction order n of 0.20-0.32 for the non-PVP films is far lower than the value of 0.5 for diffusion controlled reaction.

From the TG-DTA analysis of the non-PVP dry gels in Figure 5-2, the decomposition of lead nitrate began at around 434°C and completed at ~600°C. The new-born PbO from $\text{Pb}(\text{NO}_3)_2$ could play a decisive role in the formation of pyrochlore intermediate phases and hence crystallization of perovskite phase. The decomposition kinetics of $\text{Pb}(\text{NO}_3)_2$ therefore controls the crystallization kinetics of the pyrochlore and perovskite phases, leading to the small n value. The perovskite crystallization in the non-PVP films hence probably follows the route of pyrochlore formation, and then transition to perovskite through the diffusion and reaction of Mg^{2+} and/or Pb^{2+} ions. However, the process is controlled by the decomposition kinetics of $\text{Pb}(\text{NO}_3)_2$.

To study the reaction kinetics of perovskite crystallization in the PMN-PT films with PVP addition, the films were annealed at different temperatures of 460-700°C for 0-60min. Figure 5-17 shows the crystallinity of perovskite phase as a function of annealing temperature and dwelling time. According to Equation 5-2, the relationship of $\ln[1/(1-y)]$ versus $\ln t$ is plotted in Figure 5-18. From the linear regression to the kinetic data obtained at the annealing temperatures of 550-700°C, the perovskite crystallization can be treated as one-stage process with n values between 0.45 at 550°C and 600°C and 0.49 at 650°C and 700°C, resulting in a mean value ≈ 0.5 .

Figure 5-17 Perovskite crystallinity for the PMN-PT films with PVP40 addition by the molar ratio of 1.0 to PMN-PT, as a function of annealing time and temperature

Figure 5-18 Reaction kinetics following the Johnson-Mehl-Avrami equation for the 0.57PMN-0.43PT films with PVP40 modification by the molar ratio of 1.0 to PMN-PT

Figure 5-19 Activation energy of perovskite crystallization in the 0.57PMN-0.43PT films with PVP40 modification derived by fitting to the Arrhenius equation

This suggests a diffusion controlled reaction. From the $\ln(K)$ versus the reciprocal temperature plotted in Figure 5-19, the activation energy of perovskite crystallization in the PMN-PT films with PVP addition can be evaluated to be 167.7 kJ/mol, almost two times lower than that for the non-PVP films. The low activation energy can be the reason for the extremely low onset temperature (i.e. $\leq 430^\circ\text{C}$) for perovskite crystallization in the PMN-PT films with PVPs modification. It is very close to 166 kJ/mol, the activation energy for Pb^{2+} (ions) diffusion through the crystallized perovskite interfaces,³⁴ and also close to the reported 160 kJ/mol for the Columbite processed PMN ceramics.³⁵ The columbite process is a process that columbite (MgNb_2O_6) phases are synthesized first by the reactions between MgO and Nb_2O_5 derived precursors, and then react with the Pb^{2+} ions diffusing from the interface of crystallized perovskite phase, finally leading to the formation of perovskite phase. It is reckoned that the perovskite-crystallization mechanisms for our PVP-modified PMN-

PT thin films are dominated by a columbite-like method. This mechanism will be verified in the next chapter by further investigation on the effect of PVPs on the spatial composition distribution and morphology of the gel particles in sol-gel solutions.

It is interesting to note that from the linear regression to the kinetic data of $\ln[1/(1-y)]$ versus $\ln t$ for the annealing temperature of 460°C (Figure 5-18), the perovskite crystallization reaction can be divided into two stages. The first stage occurs in the first 5 minutes with a reaction order n of 0.82; the second stage happens in the following time with $n=0.23$. The n values are completely different from those for the annealing temperature of 550-700°C and also do not fall into any of the exponent ranges discussed above (i.e. 0.54-0.62, 0-1.24 and 2.0-3.0). It is considered that the reaction may be controlled by heat transfer phenomena, as proposed by Hancock *et al.*²⁸ and Narendar *et al.*³⁶ From the TG-DTA curves in Figure 5-2, it is clear that large amount of heat is produced in-situ in a few minutes at the beginning of the annealing at 460°C. The in-situ reaction heat is very effective to promote the perovskite crystallization, therefore leading to the higher n value (i.e. 0.82). In the second stage, the heat released from the decomposition ceases and the external annealing temperature is low, therefore the reaction rate become very low, with the n value of only 0.23. The reaction order at this stage is close to 0.20 for the non-PVP films at 460°C.

5.4 Concluding remarks

In summary, pyrochlore-free PMN-PT films with the composition of PT % = 43 mol% have been synthesized by sol-gel processing with $\text{Pb}(\text{NO}_3)_2$ as lead precursor and PVP as chemical modifier. The crystallization kinetics of the perovskite phase was investigated by Avrami approach. The results can be concluded as follows:

1. With PVP addition, perovskite phase could directly crystallize from amorphous films at the temperature $\leq 430^{\circ}\text{C}$ via bypassing the metastable phase-pyrochlore and the crystallinity is significantly enhanced. Pure-perovskite PMN-PT films can be obtained by adding PVPs with molecular weight $< 630\text{k}$ and at PVP monomer/PMN-PT molar ratio of 0.25-1.0.
2. XPS analysis indicates that the well-crystallized PMN-PT films obtained have similar lattice chemical states for Pb, Nb, Ti and O ions to that of the counterpart single crystals and that O ions also have a chemical state related to structural disorder in perovskite lattice, indicating the films are relaxor-like ferroelectrics.
3. For the PMN-PT films with PVP additions, perovskite crystallization is controlled by heat transfer phenomena at the annealing temperature of $\leq 460^{\circ}\text{C}$. At higher annealing temperature ($550\text{-}700^{\circ}\text{C}$), it is a diffusion controlled reaction with the activation energy of 167.7kJ/mol , which indicates the perovskite crystallization could follow a columbite-like route.
4. For the PMN-PT films without PVP addition, the crystallization of perovskite is always accompanied with pyrochlore formation even at high annealing temperature of $650\text{-}700^{\circ}\text{C}$. The perovskite crystallization at the annealing temperature of $550\text{-}700^{\circ}\text{C}$ can be treated as one-stage process with the reaction order $n=0.32$ and the activation energy of 305.3kJ/mol , which indicates that the crystallization process could follow the route of pyrochlore formation and then transition to perovskite through the diffusion and reaction of Mg^{2+} and/or Pb^{2+} ions, however be controlled by the decomposition kinetics of $\text{Pb}(\text{NO}_3)_2$.

5.5 References

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6 Perovskite crystallization mechanisms in the PMN-PT films and their properties

6.1 Introduction

From chapter 5, it has been shown that with PVP additions, perovskite phase directly crystallizes from the amorphous PMN-PT films at the temperature as low as 430°C and the crystallinity is significantly enhanced. Pyrochlore phase can be bypassed and pure-perovskite PMN-PT films can be obtained by adding PVP with molecular weight <630k and at the PVP/PMN-PT molar ratio of 0.25-1.0. The kinetic studies have shown that PVPs can change the perovskite crystallization route, resulting in lower activation energy. In this chapter, we aim to study how the PVPs interact with the precursor solutions and affect the element distribution in the gel particles which is the origin of the thin film growth and crystallization.

The PMN-PT films with PT content around the vicinity of morphotropic phase boundary (MPB, i.e. PT%=23-43 mol %) were prepared by sol-gel processing with the optimized PVP additions. FT-IR, TEM and XPS were employed to investigate the sol-gel precursors and the element distribution of gel particles with PVP additions. The mechanisms for the improvement of PVPs on perovskite crystallization were also discussed. As PMN-PT with PT%=33 mol% was noted to exhibit interesting electrical and EO properties,^{1, 2} the films with thickness around 1µm were prepared and characterized.

6.2 Experimental procedure

For preparation of the thin films $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ ($x=0.23-0.43$, interval of 0.05), lead nitrate, magnesium acetate (vacuum dehydrated), niobium ethoxide, and titanium isopropoxide were used. The precursor solutions leading to PbO , $\text{Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ and TiO_2 were prepared respectively and then mixed together as introduced in Chapter 5. The polymer additive used was PVP40 and the molar ratio of PVP monomer to PMN-PT varied in the range of 0-1.5.

PMN-PT films were spin-coated on the substrates of PLT/ Corning 1737glass or PLT/ITO/glass from the as-prepared sol-gel solutions with the optimum PVP molar ratio of 1.0 to PMN-PT. The films were pyrolyzed at 460°C for 10 minutes on a hot plate and then immediately transferred into an electric furnace and heat treated at 460°C or 650°C for 30 minutes. The samples for characterization of electrical and EO properties were prepared by multiple cycles of coating and pyrolysis, and pre-annealed at 650°C for 5 minutes after every 3 coatings. The samples were finally annealed at 650°C for 30 minutes.

PMN-PT gel films (with 43mol% PT) deposited on silicon wafer were studied by FT-IR spectrometer (FT-IR Spectrum GX, PerkinElmer, USA), where a bare silicon wafer was used as the reference. For comparison, pure PVP40 and the PVP40 films derived from the solution of PVP and 2-MOE were also measured. The morphology of PMN-PT (with 43mol% PT) gel particles with and without PVP addition was observed by TEM with acceleration voltage of 200kV. The gel particles were obtained by dropping the sol-gel solutions on copper grids and then drying in vacuum. The gel particles were also studied by XPS spectrometer (PHI 04-500, Perkin-Elmer) using a Mg K α (1253.6eV) X-Ray source operated at 15 KV, 20 mA

emission conditions. The data were then analyzed by the software of CasaXPS (Version 2.3.12, Casa Software Ltd).

The crystallization and morphology of the annealed PMN-PT films were studied by XRD, FESEM. The ferroelectric properties of the films were measured by a standard Radiant RT6000HVS type ferroelectric tester and the dielectric properties were characterized by using HP 4194A Impedance/Gain Phase Analyzer over the frequency range of 100Hz-1MHz and the measurement temperature varied in 20-400°C at a rate of 1°C/min. The test area was 0.5mm in diameter, coated with a layer of Pt (~100nm thick) by sputtering. The optical properties of the films were measured by UV-Vis spectrometer and Prism coupler (Metricon 2010) coupled with prism 200-P-2. The EO properties of the films were characterized by the home-built EO characterization system same as that for measuring the PLZT films (shown in Figure4-3 in chapter 4). Before measurement, the films were coated with interdigital electrodes like Figure4-4 by photolithography, e-beam-evaporation deposition and then lift-off. The electrode metals were a layer of Ti (50nm thick) and then a layer of Au (200nm thick).

6.3 Results and discussion

6.3.1 Perovskite crystallization mechanism in PMN-PT films

6.3.1.1 FT-IR analysis on the PMN-PT gel films

The interaction between PVP and metal alkoxides in PMN-PT sol-gel solutions was studied by FT-IR spectrometer, together with pure PVP and the PVP dissolved in 2-MOE for comparison. Figure 6-1 (a-b) shows the spectra of pure PVP40 and the PVP40 dissolved in 2-MOE. The strong peaks at 1672cm^{-1} and 1290cm^{-1} can be

ascribed to the C=O and C-N bonds in pure PVP individually and the peaks at 1300-1500 cm^{-1} can be ascribed to the C-H and C-C bonds.³ These peaks and the C-N peaks slightly shifted 5-10 cm^{-1} when PVP was dissolved in 2-MOE, the solvent we used to prepare PMN-PT solutions. Comparatively, the C=O peak shifted to much lower wavenumber, from 1672 cm^{-1} to 1632 cm^{-1} , which implied strong hydrogen bonds were formed between C=O groups and OH groups from 2-MOE.⁴

Figure 6-1 FT-IR spectra of (a) pure PVP40 and (b) the PVP40 dissolved in 2-MOE

Figure 6-2(a-f) present the FT-IR spectra of the PMN-PT gel films modified by PVP40 with PVP monomer/PMN-PT =0-1.5. For the non-PVP gel films (Figure 6-2(a)), the strong absorption peaks at 806, 1272 and 1378 cm^{-1} can be ascribed to the NO_3^- group.^{5,6} The peaks located at 400-700 cm^{-1} can be attributed to the formation of heterometallic bonds such as Mg-O-Nb or Mg-O-Nb-O-Ti from magnesium acetate, niobium ethoxide, and/or titanium iso-propoxide.^{7,8} It has been reported that the peaks at 1024 and 1071 cm^{-1} can be assigned to the vibrational absorption of asymmetric (ν_{as}) and symmetric (ν_{s}) C-O-Nb bonds, respectively.⁹ Ho *et al.*¹⁰ found that when the double alkoxide $\text{Mg}(\text{OR})_2\text{-Nb}(\text{OR})_5$, as seen in Figure 6-3, was formed, the 1071 cm^{-1} peak shifted significantly to 1056 cm^{-1} while the peak at around 1024 cm^{-1} remained.

Figure 6-2 FT-IR curves of the 0.57PMN-0.43PT films with different PVP40 addition ((a)0, (b) 0.25, (c) 0.5, (d) 0.75, (e) 1.0 and (f) 1.5 (molar ratio of PVP monomer/ PMN-PT))

Figure 6-3 Schematic representation of Mg, Nb double alkoxide ¹¹

The two peaks are also found in Figure 6-2(a), indicating the double alkoxides between Nb and Mg were formed in the PMN-PT solutions during refluxing of the alkoxide precursors. The peaks at 1130, 1195 and 1764 cm^{-1} can be assigned to the ester groups, the by-products of esterification reactions between the Mg and Nb or Ti alkoxides.⁸ The appearance of the ester peaks further proved the formation of heterometallic bonds between the alkoxides. However, it should be noticed that the

heterometallic compounds formed from esterification reactions may not be completely the same as that shown in Figure 6-3.

When PVP was added, the C=O peaks were found to shift to lower wave-number compared with that from PVP/2-MOE (Figure 6-1(b)). With the PVP content increasing from 0.25 to 1.5, the peak shifted from 1621 to 1607 cm^{-1} . The band shift can be attributed to the formation of PVP- M^{n+} complexes (M^{n+} : metal ion) between the C=O groups and the metal cations from the precursors.^{12,13} The complexes gave rise to the distinct color change of the sol-gel solutions, as shown in Figure 6-4. With the PVP content increasing, the solution turned gradually from colorless to yellow color, indicating more complexes formed. Meanwhile, it is reckoned that the formation of PVP- M^{n+} complexes does not destroy the heterometallic bonds of Mg-O-Nb and/or Mg-O-Nb-O-Ti as most of the corresponding peaks are still observed in Figure 6-2 (b-e). Only at PVP addition ratio of 1.5, the peaks at 400-700 cm^{-1} were weakened. Compared with the cations of Mg^{2+} , Nb^{5+} and/or Ti^{4+} from the alkoxides, it is more possible that the PVP- M^{n+} complexes come from the coordination of C=O groups with Pb^{2+} since Pb^{2+} can be more easily ionized from $\text{Pb}(\text{NO}_3)_2$. Hence, there could be the case where PVP- Pb^{2+} clusters and Mg-O-Nb-(O-Ti) clusters coexisting in the solutions.

Figure 6-4 0.57PMN-0.43PT solutions with PVP40 addition increasing from 0 to 1.5 (PVP monomer/ PMN-PT molar ratio) (from left to right)

6.3.1.2 TEM analysis of the PMN-PT gel particles

Figure 6-5 (a-d) shows the HRTEM images of the PMN-PT gel particles with and without PVP additions. The gel particles in the solutions with PVP modification are very uniform, about 10-20nm in size (Figure 6-5(a)). When the image is enlarged, it is found that the particles have a core-shell like structure¹⁴ although the shell layers do not completely cover on the cores, as highlighted by the arrows in Figure 6-5(b). The core-shell like structures are not observed in the non-PVP solutions (Figure 6-5(c)). Instead, some of the gel particles agglomerate with each other (indicated by the arrows in Figure 6-5(d)), resulting in the particle size ranging in ~20-100nm.

Figure 6-5 HRTEM images of the 0.57PMN-0.43PT gel particles with PVP modification (molar ratio to PMN-PT: 1.0) (a-b) and without PVP modification (c-d)

Figure 6-6 Schematic representation of the core-shell like gel particles in the PVP modified PMN-PT sol-gel solutions. A-A is the cross-section of the gel particle.

One of the core-shell like gel particles highlighted by dotted circle in Figure 6-5(b) is schematically represented in Figure 6-6. It is reckoned that the cores of the gel particles could be Mg-O-Nb-(O-Ti) clusters, while the shell layer could be PVP-Pb²⁺ clusters. PVPs have been widely used as anchor agent to induce coating on nanoparticles and hence form core-shell like structures, such as Ag/polypyrrole,¹⁵ silica/Fe₃O₄,¹⁶ and Ag/SiO₂.¹⁷ In the following section, the core-shell like gel particles will be further analyzed by using XPS.

6.3.1.3 XPS analysis of the PMN-PT gel particles

In this section, XPS is used to detect the surface composition of the core-shell like gel particles. The high-resolution XPS spectra of the Pb4f, Mg2p, Nb3d, Ti2p and O1s photoelectrons from the PMN-PT gel particles without and with PVP addition have been shown in Figure 6-7(a-b). The Gauss-fitting curves are also shown in the spectra. For the gel particles without PVP addition (Figure 6-7(a)), the Pb4f can be resolved into four components. The peaks of Pb4f_{7/2} at 139.35eV and Pb4f_{5/2} at 144.15eV can be assigned to the binding energy of Pb²⁺ in Pb(NO₃)₂, while the small peaks at 137.64eV and 142.44eV can be assigned to the hydrolysis product Pb(OH)₂.¹⁸

Figure 6-7 High-resolution XPS spectra of the Pb4f, Mg2p, Nb3d, Ti2p, and O1s photoelectrons for the 0.57PMN-0.43PT gel particles, (a) without PVP, (b) with PVP addition. (PVP monomer/PMN-PT=1.0)

or Pb^{2+} ions coordinated with the alkoxy groups from the other precursors. When PVP is added, the peaks representing Pb^{2+} from $\text{Pb}(\text{NO}_3)_2$ shift to 138.92eV and 143.72eV, 0.43eV lower than that in the non-PVP gel particles (Figure 6-7(b)). The lower shift of the binding energy further confirms the formation of PVP-Pb^{2+} complex.¹⁹ Another significant downward shift of the binding energy is located at 136.35eV and 141.15eV (Figure 6-7(b)). The doublet peaks could be ascribed to Pb^0 metallic chemical state.^{20,21} Although we detected the Pb^0 metallic chemical state in the PMN-PT gel particles, we didn't observe the large PbO square-plate crystals as that in the PLZT sol-gel solutions (shown in Figure 3-21(a)). This is possibly another reason that we did not observe the formation of rosette-like structures in the PMN-PT films.

From Figure 6-7(a) and (b), it is also found that the peaks of the $\text{Mg}2p$, $\text{Nb}3d$ and $\text{Ti}2p$ from the non-PVP gel particles are much stronger than those from the PVP-modified gels, although the peak intensities for the two $\text{Pb}4f$ spectra are very close. The $\text{Ti } 2p$ and $\text{Nb}3d$ consist of only one spin-orbit doublet peak, indicating the Nb^{5+} and Ti^{4+} ions exhibited only one chemical state with the binding energies of $\text{Nb}3d_{5/2}=207.65\text{eV}$, $\text{Nb}3d_{3/2}=210.49\text{eV}$ and $\text{Ti}2p_{3/2}=459.10\text{eV}$, $\text{Ti}2p_{1/2}=464.31\text{eV}$, respectively. The binding energies of Mg^{2+} ions in both gels and the Nb^{5+} and Ti^{4+} ions in the PVP-modified gels can't be confirmed due to the weak peak intensity.

The $\text{O}1s$ peak of the non-PVP gel particles is very asymmetrical and can be decomposed into three peaks at 530.67, 532.61 and 534.50eV, respectively (Figure 6-7(a)). They are assigned to oxygen chemical states in the $-\text{O}^*-\text{M}(\text{OR})_n$ (M: metal ion, R: alkyl) from Mg, Nb and/or Ti heterometallic alkoxides, $-\text{O}^*-\text{N}$ from nitrate,²² and $\text{C}-\text{O}^*-\text{C}$ from the esterification products,²³ respectively. In the $\text{O}1s$ spectrum of PVP modified gel particles, the intensity of the peak corresponding to $-\text{O}^*-\text{M}(\text{OR})_n$ significantly decreases, while the peak for $-\text{O}^*-\text{N}$ becomes much stronger (Figure

6-7(b)). This change is consistent with the weakening of the Mg2p, Nb3d and Ti2p peaks in the spectra and hence illustrates that the content of Mg²⁺, Nb⁵⁺ and Ti⁴⁺ ions in the surface layer of the PVP-modified gel particles is much lower than that of the non-PVP gels. Meanwhile, there is a new peak corresponding to the C=O groups from PVP, located at 532.03eV in the O1s spectrum in Figure 6-7(b). Compared with pure PVP (531.3eV),²⁴ the O1s peak shifts 0.69eV to higher binding energy, indicating that the electron density around the oxygen decreases due to strong interaction between the PVP molecule and the Pb²⁺ ions.²⁵

According to the peak area of every element and their relative sensitivity factors (RSF) which are obtained from the database of Casa XPS software (Casa Software Ltd), the atomic percentages in the two kinds of films can be calculated on the basis of the relationship as following:²⁶

$$Atomic\% = \frac{\frac{I_A}{S_A}}{\sum_i \frac{I_i}{S_i}} \times 100\%$$

Equation 6-1

where I_A is the peak area of element A, S_A is the sensitivity factor of element A, i means all the elements. Based on the atomic percentages, the atomic ratio of all the elements can be obtained.

Figure 6-8 (a-b) shows the atomic ratio of Pb, Mg, Nb, Ti and O from the as-prepared PMN-PT gel particles with and without PVP addition, together with the theoretical composition ratio. Theoretically, the molar ratio of the elements in PMN-PT films should be Pb/Mg/Nb/Ti/O = 1.15/0.19/0.38/0.43/3. According to Figure 6-8(a), it is undoubted that the atomic ratio of Mg, Nb and Ti in the surface layer of the PVP-modified gel particles is much lower than the theoretical ratio, although the

Pb content is equal to the theory and O is slightly higher. Only 32.5% of Ti, 10.5% of Nb, and 27.3% of Mg can be detected. The XPS results therefore indicate that most of Pb is distributed on the shell layer of the core-shell like gel particles (Figure 6-5(a-b)), while the majority of the Mg, Nb and Ti atoms locate in the core part. For the non-PVP gel particles, the atomic ratio for all the elements is very close to the theory, except O which is 44% higher (Figure 6-8(b)). The higher oxygen content in both types of gel particles can be attributed to the surface-absorbed H₂O and CO₂.²⁷

Figure 6-8 Atomic ratios of the 0.57PMN-0.43PT gel particles (a) with and (b) without PVP addition. The red bars show the theoretical composition.

The formation of the unique core-shell like gel particles in our PMN-PT sol-gel solutions can be attributed to the presence of PVPs. As we have known, PVPs have the functional groups of C=O, which can easily form chemical bonds with hydroxyl groups²⁸ and also absorb metal ions, like Pb^{2+} . According to the preparation procedure of the sol-gel solutions shown in Figure 5-1, Mg^{2+} , Nb^{5+} and Ti^{4+} precursors were refluxed for 4 hours before mixing with the other component precursors. This treatment results in the formation of relatively stable Mg^{2+} , Nb^{5+} and/or Ti^{4+} heterometallic clusters, as has been confirmed by the FT-IR studies (Figure 6-2). When these heterometallic species are mixed with other precursors, i.e. lead nitrate and PVPs, PVPs tend to combine with the free Pb^{2+} ions to form PVP- Pb^{2+} complexes through the carbonyl groups (C=O). With further stirring of the solutions, part of the heterometallic clusters are slowly hydrolyzed with the moistures in air, resulting in the gel particles with hydroxyl as end groups. Some of them could form strong hydrogen bonds to the unoccupied C=O groups from the PVP chains. Therefore the core-shell like gel particles with PVP as interconnection layer between Pb^{2+} and Mg-O-Nb-(O-Ti) clusters are formed. A schematic representation of the interactions between the components in the core-shell like gel particles is shown in Figure 6-9.

Figure 6-9 Schematic representation of the interactions between the components of the core-shell like gel particles

Such core-shell like nanostructures should be beneficial to the crystallization of perovskite phase during heat treatment since the direct reaction between lead and niobium precursors can be significantly reduced due to the presence of PVPs. The formation of lead niobate types of pyrochlore phase could hence be inhibited. From Figure 5-2, large quantity of released heat as a result of decomposition of PVP and nitrate groups can instantly increase the in-situ temperature of the gel particles. As a result, perovskite phase directly crystallizes from amorphous films at the temperature $\leq 430^{\circ}\text{C}$ via bypassing the metastable phase-pyrochlore, and its crystallinity is significantly enhanced.

As the core part of the core-shell like gel particles consists of Mg-O-Nb-(O-Ti) clusters, columbite-like phases (i.e. MgNb_2O_6) could be formed prior to perovskite formation. When the external Pb ions diffuse into the core part, perovskite phase will be formed. The formation rate is therefore dominated by the Pb diffusion rate. The perovskite crystallization in the PVP modified PMN-PT films is hence a diffusion controlled reaction and the columbite-like crystallization route is the reason for the low activation energy for the perovskite formation in the PMN-PT films with PVP modification.

Although the Mg-O-Nb-(O-Ti) clusters have also formed in the non-PVP solutions, free Pb^{2+} ions could attack and spoil the heterometallic species. During heat treatment, Nb^{5+} ions prefer to react with Pb^{2+} instead of Mg^{2+} ,²⁹ thus the formation of columbite-like phase is suppressed. As a result, the lead-niobate type pyrochlore phases were always detected in the PMN-PT films without PVP modification.

Development of core-shell like precursor particles has been attempted in literatures to separate lead from niobium precursors so as to prevent the formation of pyrochlore phase. For example, Gu *et al.*^{30,31} reported a core-shell like nanostructure

with $\text{Mg}(\text{OH})_2$ as shell and Nb_2O_5 powders as the core. Perovskite phase was found to crystallize at 900°C without passing through any pyrochlore phases during solid-state reaction. Meyer *et al.*³² introduced macrocyclic complexing agent, e.g. 18-crown-6, to the PMN-PT precursor solutions to anchor the Pb ions and hence reduce the interaction to Nb alkoxides. Pyrochlore phases were significantly suppressed, however, can't be completely removed. The unique core-shell like gel particles developed in the present work has shown an effective route to develop pure-perovskite PMN-PT.

It is worth mentioning that the sol-gel processing with nitrate as lead precursor and PVP as an anchor agent may be also helpful in preparing the other ferroelectric crystals in which pyrochlore phase is difficult to remove, for example, PZN ($\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$), $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ and PNN ($\text{Pb}(\text{Nb}_{1/3}\text{Nb}_{2/3})\text{O}_3$).

6.3.2 Preparation of PMN-PT films around MPB composition

According to the literature review in chapter 2, $(1-x)\text{PMN}-x\text{PT}$ with compositions in the vicinity of morphotropic phase boundary (MPB, i.e. $x=0.23-0.43$) remains as a research focus due to its disputable phase transition and promising electrical, optical and EO properties. However, it is difficult to obtain high-quality samples since pyrochlore phase usually accompanies with lower PT contents. It is therefore interesting to investigate the effect of PVP addition on phase formation of the PMN-PT films with the compositions around MPB.

6.3.2.1 Crystallization behavior of the films

Based on the optimized PVP addition conditions identified in chapter 5, PVP40 was used to modify the sol-gel solutions with the molar ratio of 1.0 to PMN-PT. The

Figure 6-10 XRD patterns of the (1-x)PMN-xPT films derived from PVP40 modified sol-gel solution with different x values: (a)0.23, (b)0.28, (c)0.33, (d)0.38, (e)0.43. The films were coated on (100) oriented PLT/Glass and heated at 460°C for 30 minutes.

Figure 6-11 Enlarged (100) peaks from the XRD patterns of (1-x)PMN-xPT films with different x values: (a)0.23, (b)0.28, (c)0.33, (d)0.38, (e)0.43 in Figure 6-10.

Table 6-1 lattice parameters of the as-developed (1-x)PMN-xPT films with x=0.23-0.43

PT content	0.23	0.28	0.33	0.38	0.43
Lattice parameter(Å)	4.026	4.023	4.018	4.013	4.002

films were formed by one-coating and annealed at 460°C and 650°C for 30 minutes, respectively.

At the annealing temperature of 460°C, only strong perovskite peaks are detected in all the PMN-PT films (Figure 6-10(a-e)). When the annealing temperature is increased to 650°C, very similar XRD patterns are obtained for all the films except the sample with 23% PT that contains a small pyrochlore peak. This indicates that the PVP additives play a crucial role in the formation of pure perovskite phase. If without PVP additions, it is impossible to obtain pure perovskite phase in the PMN-PT films even with a higher PT content (43%) (Figure 5-4(a), 5-5(a), 5-6(a)).

The enlarged XRD patterns (Figure 6-11) shows that the (100) peaks of the films have significantly shifted to higher 2-theta degrees with the increase of PT content, indicating that the perovskite lattice has shrunk. The calculated lattice parameters are listed in Table 6-1. It can be seen that the values are just located in between the pseudo cubic lattice parameters of 4.045 Å for pure PMN (JCPDS-ICDD card #27-119) and 3.961 Å for PT (JCPDS-ICDD card #40-99). The lattice parameter for the PMN-PT films at the MPB composition, i.e. x=0.33, is 4.018 Å, which is near to the literature data of 4.018-4.020 Å.^{33,34}

6.3.2.2 Electrical properties of 0.67PMN-0.33PT films

As PMN-PT bulk ceramics with the composition at MPB ($x_{PT}=33\%$) are reported to exhibit attractive electrical properties, this section investigates the

properties of the 0.67PMN-0.33PT thin films. The films were prepared by PVP40 modified sol gel method and deposited on PLT/ITO/Glass by repeating 10-20 cycles of coating and heating treatment and finally annealed at 650°C for 30 minutes.

Figure 6-12(a-c) shows the XRD patterns of the PMN-PT films with different thickness, together with the films derived from the non-PVP sol-gel solutions. Strong pyrochlore peaks are present in the XRD pattern of the non-PVP films(Figure 6-12 (a)), while pure perovskite phase with high crystallinity is detected in the PVP-modified

Figure 6-12 XRD patterns of 0.67PMN-0.33PT thin films prepared from the solutions (a) without PVP addition and 20-layer thick, (b) with PVP40 addition and 20-layer thick, (c) with PVP40 addition and 10-layer thick

Figure 6-13 FESEM images of the 0.67PMN-0.33PT films with PVP40 addition and 20-layer thick

films 10-layer thick ($\sim 0.6\mu\text{m}$) (Figure 6-12 (c)). The crystallinity is further enhanced with the film thickness at 20 layers ($\sim 1.2\mu\text{m}$) (Figure 6-12(b)). The small pyrochlore peaks for the films can be attributed to the lead loss due to too many cycles of pyrolysis and annealing. Figure 6-13 shows the morphology of the 20-layer films with PVP addition. The films consist of uniform grains with the size of $\sim 50\text{nm}$, which is very similar to that of the films with 43% PT content (Figure 5-7(e)).

The polarization-electric field (P-E) hysteresis loop of the 20-layer 0.67PMN-0.33PT films was characterized under the electric field of 100kV/cm and the result is shown in Figure 6-14. The P-E loop is slim, with the remnant polarization P_r of $3.8\mu\text{C/cm}$ and coercive field E_c of 12.3kV/cm .

Figure 6-14 P-E hysteresis loops for the 20-layer 0.67PMN-0.33PT films under the electric field of 100kV/cm

Figure 6-15 shows the relative dielectric constant of the PMN-PT films as a function of frequencies from 100Hz to 1MHz . In the measured frequency range, the

Figure 6-15 Dielectric properties of the 0.67PMN-0.33PT films as a function of frequency in 100Hz-1MHz and at T=25°C.

Figure 6-16 Relative dielectric constant vs temperature of 0.67PMN– 0.33PT thin films measured at 1k,10k and 100kHz

dielectric constant slightly decreases with the frequency increasing and the dielectric loss tends to increase. At 1 kHz and room temperature, the dielectric constant reaches ~1964 and the dielectric loss is ~0.10. The dielectric constant obtained here is significantly higher than the 1000-1600 obtained by pulsed laser deposition,^{35,36,37} or the other sol-gel processing techniques.^{38,39}

Temperature dependences of the relative dielectric constant of the PMN-PT films at the frequency of 1k, 10k and 100 kHz are presented in Figure 6-16. The as-prepared sample shows relaxor-like ferroelectric behavior, characterized by a diffusive (broad) $\epsilon-T$ peak. The maximum dielectric constant ($\epsilon_{\max}$) at the three measured frequencies is 2047, 1950 and 1805, respectively, and all occur at ~119°C (i.e. $T_{\max}$). Similar $\epsilon-T$ response with $T_{\max}=110-120^\circ\text{C}$ has also been reported in the sol-gel derived PMN-PT films by Park *et al.*⁴⁰ and Calzada *et al.*⁴¹

The extent of diffusiveness for the $\epsilon-T$ curves can be evaluated by using the modified Curie-Weiss equation as below:⁴²

$$1/\epsilon - 1/\epsilon_{\max} = (T - T_{\max})^r / C$$

where C is the Curie-Weiss like constant and r is the parameter to quantify the diffusivity of materials. $r=1$ indicates the material is normal ferroelectrics, whereas $1 < r < 2$ for relaxor. According to the plots of $\ln(1/\epsilon - 1/\epsilon_{\max})$ versus $\ln(T - T_{\max})$ in Figure 6-17, r values can be determined to be 1.31-1.42 for our 0.67PMN– 0.33PT thin films in the measured frequency range. This result confirms that the as-developed films belong to relaxor ferroelectrics. However, they are not absolute relaxor ferroelectrics since $T_{\max}$ does not change much with the increase of measured frequency (f) and hence deviate from the Vogel-Fulcher relationship of $f = f_0 \exp(-E_a / (T_{\max} - T_f))$, another characteristic feature of relaxor ferroelectrics.⁴³ The overall dielectric behavior of the films is much like a mixture of the typical relaxor and normal ferroelectrics, as

Figure 6-17 Linear fitting to the raw data of $\ln(1/\epsilon-1/\epsilon_{\max})$ versus $\ln(T-T_{\max})$ for the 0.67PMN–0.33PT thin films at 1k, 10k and 100kHz

reported by Wang *et al.*³⁵ on the 0.65PMN-0.35PT thin films.

It is interesting that there is noticeable difference between the dielectric behavior of our samples and the single crystals or bulk ceramics reported in literature. 0.67PMN-0.33PT single crystals are reported to exhibit the properties of normal ferroelectrics with a sharp $\epsilon-T$ peak,^{44,45} while the $\epsilon-T$ peak for bulk ceramics is less sharp with $r=1.08$.⁴⁶ The $T_{\max}$ is 150-170°C for both materials, which is higher than 119°C for our samples.

Moreover, the broadening of the $\epsilon-T$ peaks is also found in the as-prepared PMN-PT thin films with 43%PT although their counterpart single crystals and bulk ceramics are well recognized as normal ferroelectrics with a sharp $\epsilon-T$ peak.^{47,48} Figure 6-18 shows the diffusive $\epsilon-T$ curves of the films with $r \sim 1.36$ (the plots of $\ln(1/\epsilon-1/\epsilon_{\max})$ versus $\ln(T-T_{\max})$ are not shown here), in which, the maximum dielectric constant ($\epsilon_{\max}$) at the frequencies of 1k, 10k and 100kHz all occur at $\sim 210^\circ\text{C}$ ($T_{\max}$). The $T_{\max}$ is slightly lower than $\sim 220^\circ\text{C}$ for the single crystals with the same

composition.^{47,49} The characteristic of broadening ϵ - T peak is hence noted to exist in most of our investigated composition ranges for the PMN-PT thin films (i.e. $x_{PT}=0.33$ -0.43).

The broadening of the ϵ - T peaks and lower T_{max} have also been reported in the 0.7PMN-0.3PT and PbTiO₃ ceramics when their grain size decreases to <100nm.^{50,51} The origin has been attributed to the size dependence of tetragonal distortion behavior of crystal structures. This explanation could be applied to our cases as the as-developed PMN-PT films consist of nanocrystallines ~50nm in size (Figure 5-7(e) and Figure 6-13). Meanwhile, the presence of the oxygen chemical state related to structural disorder in perovskite lattice can be another reason (O1s spectrum in Figure 5-12).

Figure 6-18 Relative dielectric constant vs temperature of 0.57PMN-0.43PT thin films measured at 1k, 10k, and 100kHz

6.3.2.3 Optical and EO properties of the PMN-PT films

The PMN-PT thin films with 33% PT content were also prepared on the (100) oriented PLT/glass substrates for characterization of optical and EO properties. The

films were prepared by repeating 10-20 cycles of coating, pyrolysis and pre-annealing, and finally annealing at 650°C for 30 minutes. The films show slightly (100) orientation and the morphology is similar to Figure 6-13.

The TE guided-mode spectra of the films with 10 and 20 layers are shown in Figure 6-19 and Figure 6-20 respectively. The TM mode spectra aren't shown here as only one mode is obtained for both films. For the 10-layer films, three TE modes are excited at the laser wavelength of 633nm and there are four TE modes for the 20-layer

Figure 6-19 TE mode spectrum excited at 633nm for the 0.67PMN-0.33PT films with 10 coatings

Figure 6-20 TE mode spectrum excited at 633nm for the 0.67PMN-0.33PT films with 20 coatings

films. For the thicker films, the reflectivity dips become weak. This is ascribed to the optical scattering due to the voids in the films and some impurity particles on the film surface.

Based on Equation 4-1 - Equation 4-5 and the angular position of the TE modes in Figure 6-19 and Figure 6-20, the ordinary refractive index n_o and film thickness of the two kinds of films can be calculated. For the 10-layer films, n_o and the film thickness are 2.572 and 0.683 μm , respectively. According to this film thickness, n_e can be estimated as 2.568. For the 20-layer films, the refractive index n_o and n_e can be calculated as 2.515 and 2.494 respectively and the film thickness is 1.207 μm . It can be clearly seen that the refractive index of the films slightly decreases with the film thickness increasing from 0.683 μm to 1.207 μm . The refractive indices are close to 2.5-2.7 for the PMN-PT single crystals and bulk ceramics with PT content above 30%.⁵²

Figure 6-21 Transmittance curves of the 0.67PMN-0.33 PT films with different thickness

The transmittance of the as-prepared films was also studied. Figure 6-21 shows that both films exhibit well-oscillating transmittance. The 10-layer films are highly transparent in visible region with a transmittance of ~80%. The transmittance drops rapidly at $\lambda \approx 380\text{nm}$ and the absorption edge is located at $\sim 329.9\text{nm}$. For the 20-

coating films, the absorption edge shifts to higher wavelength of ~347nm and the transmittance of the films decreases to 70-75%.

The EO properties of the 20-coating films were investigated by applying a square-wave voltage with the frequency of 10Hz to the surface interdigital electrodes shown in Figure 4-4. A strong field-induced optical modulation can be observed. When the external electric field was changed from zero to 16kV/mm, different modulated optical intensities have been observed and the birefringence shift $\Delta(\Delta n)$ has been summarized as a function of the external electric field, as shown in Figure 6-22. The electric-field induced birefringence shift reaches $\Delta(\Delta n)=0.020$ under the electric field of 16kV/mm. The birefringence shift, as a function of the square of the external electric field, is plotted in Figure 6-23. From the slope, the quadratic EO coefficient R can be calculated as $1.02 \times 10^{-17} \text{ (m/V)}^2$. The R value is much higher than $0.74 \times 10^{-18} \text{ (m/V)}^2$ for the 0.67PMN-0.33PT thin films ($0.42 \mu\text{m}$ thick) grown on MgO by pulsed

Figure 6-22 Birefringence shift vs. electric field for the 0.67PMN-0.33PT films with 20 coatings.
The solid line is the polynomial fitting to the raw data (▪)

Figure 6-23 Birefringence shift as a function of the square electric field for the 0.67PMN-0.33PT films with 20 coatings. The solid line is linear fitting to the raw data (▪).

laser deposition⁵³, however, is lower than $7.5\text{--}13.8 \times 10^{-17} (\text{m/V})^2$ for the epitaxial PMN-PT films on (100) LaAlO_3 reported by Lu *et al.*^{54,55} They found that the EO coefficients of PMN-PT films were strongly dependent on the applied electric-field direction. When the electric field was applied along (011) plane instead of (100) of the perovskite lattices, the films exhibited a quadratic EO coefficient 60% higher. The EO coefficients along the pseudocubic (010) or (100) axes are very small, only $< 1 \times 10^{-17} (\text{m/V})^2$. The comparatively low EO coefficient of our PMN-PT films can be attributed to the low orientation degree of the films and hence failure to effectively control the electric-field directions along the desirable crystal axes of perovskite lattices.

6.4 Concluding remarks

In summary, pyrochlore-free PMN-PT films with the composition around MPB (PT% = 23%–43 mol%) have been synthesized by sol-gel processing with $\text{Pb}(\text{NO}_3)_2$ as lead precursor and PVP40 as modifier. The effects of PVPs on the sol-gel solutions

and gel particles have been studied with the aids of FT-IR, TEM and XPS. Perovskite crystallization mechanism has been discussed. The electrical, optical and EO properties of the derived PMN-PT films have been demonstrated. The results can be concluded as following:

1. PVP addition results in the formation of special core-shell like gel particles with PVP-Pb²⁺ clusters as shell layer and Mg-O-Nb-(O-Ti) clusters as core part. Since the cores with Mg-O-Nb-(O-Ti) clusters can form columbite-like phases (i.e. MgNb₂O₆) after organic decomposition and the external Pb ions could diffuse into the cores, perovskite phase is crystallized via a columbite-like route. The formation of core-shell like gel particles and the large quantity of in-situ heat released from the decomposition of PVPs should be the reasons for the promotion of perovskite crystallization and the diffusion controlled crystallization mechanism.
2. The sol-gel processing with nitrate as lead precursor and PVP as an anchor agent may be helpful in preparing the other ferroelectric crystals where pyrochlore phase is difficult to remove, such as PZN (Pb(Zn_{1/3}Nb_{2/3})O₃), Pb(Sc_{1/2}Nb_{1/2})O₃ and PNN (Pb(Nb_{1/3}Nb_{2/3})O₃).
3. The as-developed 0.67PMN-0.33PT films exhibit a slim P-E loop with the remnant polarization of 3.8μC/cm and coercive field of 12.3kV/cm. The dielectric constant reaches ~1964 and the dielectric loss is ~0.10 at 1kHz and room temperature. The dielectric behavior as a function of temperature is much like a mixture of typical relaxor and normal ferroelectrics, characterized by a diffusive ϵ - T response and independence of $T_{\max}$ on the measured frequency range.

4. The 0.67PMN-0.33PT films with the thickness of $\sim 1.2\mu\text{m}$ exhibit the refractive index n_o and n_e of 2.515 and 2.494 respectively and the transmittance reaches 70-75%. The films exhibit strong quadratic EO effect with $R=1.02\times 10^{-17} (\text{m/v})^2$.

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7 Conclusions

7.1 Conclusions

In summary, PLZT (9/65/35) and PMN-PT thin films with the composition near MPB have been studied by PVP modified sol-gel processing. The effects of PVP addition and its molecular weight on the gel particles, crystallization and microstructural evolution of the films have been systematically investigated. Special attention has been focused on the formation of rosette-like structure and promotion of perovskite phases by PVPs in the derived thin films. The electric, optical and EO properties of the films have also been studied. Based on the present work, the following major conclusions are drawn:

- I. PVPs can significantly increase the critical thickness of a single PLZT layer to 600-900nm compared with 78nm in case of without PVP. PVPs also promote the formation of perovskite phase and reduce the onset crystallization temperature. However, the films exhibit porous rosette-like morphologies.
- II. The rosette-like structures are found to develop from the sites of the $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ intermediate phase. The premature nucleation of PbO grains in the PVP modified sol-gel solution is responsible for such kind of intermediate phases and thus results in the formation of Pb-rich domains in the film body. The Pb-rich domains accelerate the growth of the PLZT grains and as a result, porous rosette-like structure is formed. The presence of the rosette-like structures significantly deteriorates the electrical and optical properties of the PLZT films.

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- III. Rosette-like structures can be removed by adding 20-35% excess of Pb or inserting a seeding layer of PLT on bottom or top of the PLZT films. The non-rosette PLZT films with PLT as bottom seeding layer are dense and smooth, with the rms roughness of $\sim 1.8\text{nm}$. The films possess a saturated hysteresis loop with a remnant polarization of $6.94\mu\text{C}/\text{cm}^2$ and coercive field of $40\text{kV}/\text{cm}$ and its dielectric constant reaches 926.3. The films also exhibit a high transmittance of $\sim 70\%$. the refractive index n_o and n_e of 2.550 and 2.469 respectively and quadratic EO coefficient of $0.79 \times 10^{-17} (\text{m}/\text{V})^2$.
- IV. With PVP addition, perovskite phase can directly crystallize from amorphous PMN-PT thin films at the temperature $\leq 430^\circ\text{C}$, and the crystallinity is significantly enhanced. Pure-perovskite PMN-PT films can be obtained by adding the PVPs with molecular weight $< 630\text{k}$ and at PVP monomer/PMN-PT molar ratio of 0.25-1.0.
- V. Kinetic studies show that perovskite crystallization in the PVP modified PMN-PT thin films is controlled by heat transfer phenomena at the annealing temperature of $\leq 460^\circ\text{C}$. At higher annealing temperature ($550\text{-}700^\circ\text{C}$), it is a diffusion controlled reaction with the activation energy of $167.7\text{kJ}/\text{mol}$, which indicates that the perovskite crystallization could follow a columbite-like route. Such speculation is supported by the findings in the formation of special core-shell like gel particles with PVP-Pb²⁺ clusters as shell layer and Mg-O-Nb-(O-Ti) clusters as core in the PVP modified sol-gel solutions. Since the cores with Mg-O-Nb-(O-Ti) clusters can form columbite-like phases (i.e. MgNb_2O_6) after organic decomposition and the external Pb ions could diffuse into the cores, perovskite phase is crystallized via a columbite-like route. The formation of core-shell like gel particles and the large quantity of in-situ heat released from

the decomposition of PVPs should be the reasons for the promotion of perovskite crystallization and the diffusion controlled crystallization mechanism.

- VI. For the PMN-PT films without PVP addition, the crystallization of perovskite phase is always accompanied with the formation of lead-niobate type pyrochlore phases ($\text{Pb}_{1.83}\text{Nb}_{1.71}\text{Mg}_{0.29}\text{O}_{6.39}$) even at high annealing temperature of 650-700°C. The perovskite crystallization at 550-700°C can be treated as a one-stage process with the reaction order $n=0.32$ and the activation energy of 305.3kJ/mol.
- VII. The as-developed 0.67PMN-0.33PT films with PVP additions exhibit a slim P-E hysteresis loop with the remnant polarization of 3.8μC/cm and coercive field of 12.3kV/cm and the relative dielectric constant of ~1964 at 1kHz and room temperature. The temperature dependence of the relative dielectric constant shows the films are much like a mixture of typical relaxor and normal ferroelectrics, characterized by a diffusive $\varepsilon-T$ response and independence of $T_{\max}$ on the measured frequency range.
- VIII. The 0.67PMN-0.33PT films with the thickness of ~1.2μm exhibit the refractive index n_o and n_e of 2.515 and 2.494 respectively, the transmittance of 70-75%, and the quadratic EO coefficient of $R=1.02 \times 10^{-17} (\text{m/v})^2$.

7.2 Novelities

The main novelties of the present work can be summarized as following:

- The application of PVP modified sol-gel process on the synthesis of PLZT thin films with good EO properties has been attempted.

- The formation mechanism of rosette-like structures from sol-gel solution chemistry instead of traditionally from substrate interaction and annealing profile has been proposed.
- The effective methods for removing rosette-like structures have been proposed and verified.
- It is the first time to study the crystallization kinetics in PMN-PT thin films and the effect of PVPs on the kinetics.
- The development of core-shell like gel particles to reduce the direct interaction between Pb^{2+} and Nb^{5+} ions has been attempted. Pure-perovskite PMN-PT thin films have been successfully prepared via bypassing the formation of pyrochlore phase.
- The idea of engineering the morphology and spatial composition distribution of gel-particles by using core-shell like nanostructures could provide a feasible method to develop the other ferroelectric material systems in which, pyrochlore phase is difficult to be removed and perovskite phase has low thermal stability.

8 Future work

In order to have more detailed understanding on the present studies, the following future work is proposed.

Firstly, the premature nucleation of PbO grains in the PVP modified sol-gel solution is noted to be the origin for the development of rosette-like structures, especially when the PbO grains have grown up and are coarse in size. It is worth investigating the possible chemical additives which can hinder the nucleation and/or crystal growth of PbO. This could further facilitate the formation of thick and rosette-free PLZT films.

As perovskite crystallization can be significantly promoted and pyrchlore phase can be circumvented in the PMN-PT thin films prepared by sol-gel processing with PVP and $\text{Pb}(\text{NO}_3)_2$ as precursors, it is meaningful to extend this method to the synthesis of other EO thin film systems, such as PZN, PZMN, PNN (lead nickel niobate), and KTN etc. Meanwhile, other polymers which can help to form the core-shell like gel particles could also be studied.

The grain size has been found to significantly affect the dielectric properties of the films according to literature and the present studies. However, little effort has been reported on its effect on the EO properties and response time of the films. Since the as-prepared PLZT and PMN-PT films consist of the grains with the size in the order of tens of nanometers, it will be interesting to investigate the EO properties of the films as a function of grain size in the nanometric scale.

The EO properties of the as-developed PMN-PT thin films with the compositions varied around MPB are worth to be studied systematically. Meanwhile, epitaxial growth of the thin films could be controlled to enhance the electrical and EO properties.

The poling conditions on the as-developed thin films and the resultant ferroelectric domain patterns can be studied to enhance the EO properties. The EO response time could also be further investigated.

Appendix

Publication list

Journal papers

1. **Z.H. Du**, J. Ma, The Effect of PVP on the Critical Thickness and Properties of PLZT Ceramic Films, *J. Electroceram* 16, 565–569 (2006)
2. **Z.H.Du**, T.S. Zhang, and J. Ma, Effect of polyvinylpyrrolidone on the formation of perovskite phase and rosette-like structure in sol-gel–derived PLZT films, *J.Mater. Res.*, 22, 2195–2203 (2007)
3. **Z. H. Du**, J. Ma, and T. S. Zhang, Densification of the PLZT Films Derived from Polymer–Modified Solution by Tailoring Annealing Conditions, *J. Am. Ceram.Soc.*, 90, 815–820 (2007)
4. **Z.H. Du**, T.S.Zhang, H.M.Shang, X.L.Chen, J.Ma, Growth of PLZT Thick Films by Polymer Modified Sol-gel Processing for Optical Shutting, *Solid State Phenomena*, 136, 67–74 (2008)
5. **Z.H.Du**, T.S.Zhang, M.M.Zhu, J.Ma, Perovskite crystallization kinetics in the PMN-PT thin films prepared by polymer modified sol-gel processing, *J.Mater.Res.*, **24**, 1576–84, (2009)
6. **Z.H.Du**, T.S.Zhang, M.M.Zhu, J.Ma, Growth mode of sol-gel derived PLT seeding layers on glass substrates and its effect on templating the oriented growth of PLZT thin films, *J.Appl.Phys.*, 105, 061612, (2009)
7. **Z.H.Du**, T.S.Zhang, M.M.Zhu, J.Ma, Direct formation of perovskite phase in PMN-PT thin films by modified sol-gel processing and their electrical and optical properties, *J.soli.stat.chem.*, DOI: 10.1016/j.jssc.2009.04.021, (2009)
8. **Z.H.Du**, T.S.Zhang, M.M.Zhu, J.Ma, Formation of core-shell like gel particles in polymer-modified PMN-PT sol-gel solutions and its effect on perovskite crystallization, under review, (2009)

Conference paper

1. **Z.H. Du**, J. Ma, Effect of Polyvinylpyrrolidone Molecular Weight on the Critical, Thickness, Crystallization, Densification and Properties of PLZT Films, *Mater. Res. Soc. Symp. Proc.* San Fransisco, Vol. 928, GG14–19 (2006)