Nano-crystalline ceramic laser materials and lasers

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Nano-crystalline Ceramic Laser Materials and Lasers

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Summary

Polycrystalline transparent yttrium aluminum garnet (YAG) ceramics is an excellent host material for high-power solid-state lasers. Compared to its single crystal form, polycrystalline YAG transparent laser ceramics have the advantages of faster production times, ease fabrication of large size, high dopant concentration, mass production and multifunctionality. It is well accepted that the high quality YAG transparent ceramics will replace the YAG single crystals as the solid-state laser materials and will also give rise to new potential applications where single crystals cannot compete. Therefore, recently, YAG transparent ceramics becomes a very active research topic in the field of advanced materials.

In this work, YAG, rare-earth ions doped YAG and Y_2O_3 nanosized powders have been synthesized by general and modified sol-gel combustion process, co-precipitation assisted with freeze-drying, and high-energy ball milling method, respectively. Highly transparent Nd:YAG ceramics with good lasing quality have been fabricated. Phase evolution, morphology and microstructure of the nanopowders and transparent ceramics were investigated. Key effects on optical properties of the fabricated ceramics were also systematically studied.

Our results show that solvent has an important effect on the phase transformation temperature of sol-gel precursor. Ethanol-deionized water (volume ratio of 1:1) mixture solution adopted as solvent can effectively decrease activation energy, leading to YAG formation at lower calcination temperature. However, the residue carbonates is difficult to be removed completely. As a result, there are many pores trapped in the sintered YAG ceramics.

It was found that high energy ball milling can significantly promote YAG phase transformation by solid-state reactive sintering using Y_2O_3 and Al_2O_3 nanosized powders as starting materials. Our results indicate that the formation of YAG at lower temperature is attributed to the formation of the non-equilibrium phase and the improved activity of the powders by the high-energy ball milling process. Nevertheless, the sintered samples show gray to pink color, probably due to the contamination from WC milling jar and milling balls.

Freeze-drying plays an important role in controlling grain size, morphologies and agglomeration of the powders prepared by co-precipitation. The results show that the powders are spherical and well-dispersed with high reactivity and sinterability. Transparent ceramics have been fabricated using Nd:YAG powders from freeze-drying precursor, with 0.5 wt% TEOS added as a sintering aid.

Lasing quality of Nd:YAG transparent ceramics have been fabricated by solid-state reactive sintering, applying commercial Al_2O_3 powders and synthesized $\text{Nd:Y}_2\text{O}_3$ powders from freeze-dried precursor as raw materials. The in-line transmittance of the 4 at.% Nd:YAG sintered ceramics reaches higher than 84.3% at 1064 nm with 3.1 mm thickness. The slope efficiency of the ceramic lasers has been improved from 36.5% using the coated samples to 40% using un-coated samples.

Based on the optimum fabrication process, other rare-earth ions (RE = Er, Ho, Tm, Tm/Ho) doped YAG transparent ceramics for eye-safe laser applications have been prepared and the optical properties were studied.

Chapter 1 Introduction

1.1 Background and motivations

Since the world's first working ruby laser was reported by T.H. Maiman in 1960 [1-2], many attentions have been attracted on the host media for solid-state lasers. There are a lot of materials have been developed, although relatively few types are widespread for practical applications. In 1964, continuous-wave (CW) laser oscillation using Nd-doped yttrium aluminum garnet (Nd:YAG) single crystal at room temperature was demonstrated by Geusic et al., and then designs of solid-state lasers using single crystal have continually progressed [3]. The fast progress of solid-state lasers also stimulated intensive researches on laser materials. Solid-state host materials must have good optical, mechanical, and thermal properties to withstand the severe operating conditions of practical lasers. Desirable properties include hardness, chemical inertness, and absence of internal strain and refractive index variations, resistance to radiation-induced color centers.

Ten years later, owing to the successful growth of Ti:sapphire single crystal, solid-state laser stepped into the new stage of ultrashort laser [4], which has been widely applied due to its tunability and ability to generate ultrashort laser. In 1990s, Nd:YVO₄ single crystal was grown successfully, leading to a new innovation era of solid-state lasers. At this time, diode pumped microchip solid-state laser attracted great attentions because of their advantages such as compactness, reliability, high efficiency, high power, and the small numbers of longitudinal and low order transverse mode. The very large absorption coefficient (31.2 cm^{-1} for 1.0 at.% Nd:YVO₄) and emission cross-section ($25 \times 10^{-19} \text{ cm}^2$) of Nd: YVO₄ made it a suitable laser gain media for this application. However, its poor

mechanical toughness, inferior thermal properties and small saturation fluency make it unsuitable for high power applications [5].

It is well known that high efficiency and high power solid-state lasers are very important for many technologically important applications, such as remote sensing, laser machining (cutting, drilling and etc.), and target recognition. Besides favorite optical properties, host material for this kind of solid-state lasers applications, must possess mechanical and thermal properties that will permit high-average-power operation. The most important parameters are thermal conductivity, hardness, and fracture strength.

Compared to Nd:YVO₄, YAG has excellent thermo-mechanical properties, good chemical stability, and unique optical properties to sustain the high-power laser operation. YAG has been widely used as a high-temperature structure material in various industries, and an ideal fluorescence phosphor and a laser host in the field of medicine, military and scientific research [6-7]. Traditionally, YAG single crystal, grown by Czochralski (Cz) method, is a popular host for solid-state laser. However, it is extremely difficult to grow large size single crystals with good optical quality. Because the effective segregation coefficient of Nd for the host material is very low (~ 0.2), it is extremely difficult to grow the single crystal Nd:YAG with the doping concentration higher than 1.1 at.%, which also limited its application for high power and highly efficient solid state lasers.

As a polycrystalline material, Nd:YAG transparent ceramics as a laser host has been extensively investigated since 1980s [8-9]. Contrast to its popular single crystal form, polycrystalline YAG transparent ceramics are easy to be fabricated into large size at potentially very low cost and readily to be doped with high rare-earth ion concentrations. Moreover, mass production of YAG ceramics is possible because no sophisticated

technique and expensive equipment are needed, compared with what are involved in the single-crystal growth and subsequent fabrication. In 1995, the first successful laser oscillation was demonstrated by A. Ikesue et al. [10]. After that, Nd:YAG transparent ceramics were widely recognized as a promising laser host. With the development of nano-technologies and ceramics technique, the quality of YAG transparent ceramics has been greatly improved. The remarkable breakthrough in polycrystalline YAG transparent ceramics brought a new hope to the development of high-efficiency high-power lasers and microchip lasers. Recently, various Nd:YAG ceramics lasers such as microchip lasers [11], composite Q-switched lasers [12], mode-locked lasers [13], high-power CW lasers [14-16] have been demonstrated in succession. These achievements strongly stimulated a still-growing wave of research in ceramic-laser materials. It is well accepted that highly transparent Nd:YAG ceramics will replace its single crystal forms as the solid-state laser material and will compete for new applications where single crystals cannot be used [17]. Currently, fabrication of high quality Nd:YAG transparent ceramics has become a highly active area of advanced ceramics [18-20].

However, there remain big challenges to fabricate “real” lasing quality YAG transparent ceramics, because transparent ceramics used as solid-state laser materials must face the stringent requirements on phase purity, low porosity, and clean grain boundaries, which are essential for high optical quality of YAG ceramics. Therefore, intensive investigations have been carried out to improve the quality of YAG transparent ceramics. There are three crucial stages in the fabrication of transparent ceramics: (1) synthesis of high purity nanopowders of a given composition with good dispersion, (2) preparation of highly green dense compacts with near-net shape from the nanopowders, and (3) sintering of the

compacts to fully dense ceramics. In this case, the technological conditions of each subsequent stage depend on the quality of the products of the previous stage.

1.2 Objectives and scope

The present work focuses on fabrication of lasing quality rare-earth ions doped YAG transparent ceramics. The objectives and scope of this project are summarized as follows:

➤ **To synthesize high quality nanopowders leading to transparent YAG ceramics**

YAG and rare-earth ions doped YAG nanopowders with desirable properties are aimed to be prepared at low temperatures. The targeted powder characteristics are high purity, uniform particle size, narrow particle size distribution, high reactivity and sinterability.

➤ **To study phase evolution, morphology, and sinterability of the powders**

Different wet-chemical methods will be applied to prepare nanopowders. The effects of several essential factors, such as solvent, calcination conditions, and drying method on the properties of the powders will be studied. The mechanism behind the low crystallization temperature will be investigated by thermal analysis. The sinterability of the powders by different methods will be investigated. An effective method will be explored to control the agglomeration of the powders.

➤ **To fabricate YAG-based transparent ceramics**

YAG-based transparent ceramics will be fabricated from the high quality synthesized powders. Several key parameters, such as sintering temperature, holding time, and doping concentration, effect on the microstructure and optical properties of the ceramics will be

systemically studied. Optimized fabrication process of transparent ceramics will be developed.

➤ **To investigate the optical properties of YAG-based transparent ceramics**

The optical properties of the transparent ceramics, including transmittance, absorption, emission, and decay time will be studied. Properties by using fabricated laser ceramics will be tested.

1.3 Major contributions of the thesis

The contributions of this research work are summarized as followings:

1. A modified sol-gel combustion process has been carried out, and YAG powders have been synthesized at as low as 800 °C. By study the crystallization kinetics, it is found that the precursor from ethanol-deionized water solvent has lower activation energy than that of precursor from water solvent. This result can be applied to synthesize nanopowders at lower temperature with controlled particle size and narrow particle size distribution.
2. A modified co-precipitation process assisted with freeze-drying has been employed to prepare YAG nanopowders. For this method, only inorganic raw materials were involved, which is the first report in the world by using this method to synthesize YAG powders. Compared with the powders prepared from conventional oven drying, YAG powders prepared from freeze-drying process are well-dispersed with uniform particle size. Freeze drying is an effective way to control the agglomeration occurred in the drying process. As

a result, the powders from freeze-dried precursor have high sinterability, which are suitable for transparent ceramics fabrication.

3. Well-dispersed Nd:Y₂O₃ powders with uniform particle size have been obtained by co-precipitation assisted with freeze-drying. By applying the prepared Nd:Y₂O₃ powders and commercial Al₂O₃ powders, Nd:YAG was obtained at 1300 °C. This temperature is 300-400 °C lower than that of conventional solid-state reactive process.
4. Highly transparent Nd:YAG ceramics were fabricated by reactive sintering method under vacuum conditions. The laser output was demonstrated successfully. Some key processing factors have been identified. By optimizing the processing, the laser output efficiency has been improved from 36% to 40%.
5. Other rare-earth ions, Er, Tm, Ho and Tm/Ho doped YAG transparent ceramics for eye-safe laser applications have been fabricated. Optical properties of the ceramics were studied.

1.4 Organization of the thesis

In Chapter one of the thesis, a brief introduction on laser materials and lasers development are presented. The motivation and objectives of this study are also discussed.

In Chapter two, a literature review on the YAG transparent ceramics and its applications is presented. The fabrication methods of YAG transparent ceramics are introduced. The challenges for powders synthesis and ceramics fabrication process are emphasized.

Chapter three presents YAG nanopowders synthesis process by general and modified sol-gel combustion and co-precipitation methods. Phase transformation mechanism, morphology, and microstructure of the samples were studied. Crystallization kinetics of the precursor from different solvent by sol-gel combustion was discussed. The effect of drying process on the powder properties was explored. The sinterability of the powders was also investigated.

In Chapter four, transparent ceramics were fabricated by solid-state reactive sintering method. Microstructure and morphology of the samples were studied. Effects of different parameters on the optical properties of the ceramics were investigated. Finally, the laser performance was demonstrated.

By optimized the fabrication process, various rare-earth ions ($\text{RE} = \text{Er}, \text{Ho}, \text{Tm}$, and Tm/Ho) doped YAG transparent ceramics have been fabricated in Chapter five. Optical properties of the ceramics were investigated.

A summary of the work as well as the conclusions and directions for future research are presented in Chapter six.

Chapter 2 YAG transparent laser ceramics

2.1 Transparent ceramics

Traditional ceramics have served society for thousands of years. It is an important milestone for advancement of human civilization. According to the C^{14} age determination and calibration curve from C^{14} era to calendar era, it seems that the oldest ceramics were made about 16500 years ago [21]. Today, because of their formability, electrical insulating quality, and thermo-mechanical properties, ceramics are used not only for domestic such as cookware, white-ware or construction materials, but also for industry ranging from golf clubs to rocket nozzles. Even the medical industry has embraced ceramics as prostheses for bones and teeth [22-28].

Generally, ceramics can be defined as a kind of hardened material, which are made by shaping and then firing at a high temperature in a furnace, using inorganic-nonmetallic powders as raw materials [29-30]. The fabrication process of ceramics is shown in Fig. 2.1 [31]. Ceramics are an aggregate of polycrystals and multiphase. The properties of ceramics mainly depend on the chemical component, crystal structure and microstructure. Conventionally, most ceramics are opaque or translucent because they are laden with internal flaws that act as scattering centers in the body shown in Fig. 2.2 [18], such as (a) the grain boundaries, (b) residual pores or inclusions, (c) second phases, (d) double refraction, and (e) surface roughness. However, with care to decreasing or eliminating most of these scattering flaws, optical properties of the polycrystalline ceramics can be improved greatly even to be transparent.

Fig. 2.1. Schematic diagram of ceramics process.

Fig. 2.2. Schematic microstructure of a ceramics and of light-scattering sources, (a) Scattering by grain boundary, (b) Scattering by inclusions or pores, (c) Scattering due to secondary phase, (d) Reflection and double refraction at boundary, (e) Scattering by surface roughness.

In recent years, transparent ceramics have acquired intensive research interests due to wide applications in high power lasers, transparent armors, nose cones for heat seeking missiles, radiation detectors for non-destructive testing, high energy physics, space

exploration, security and medical imaging applications [32-35]. The recent development of transparent ceramic laser materials with dense microstructures and performance exceeding single crystals is a paradigm shift in the field of laser materials. As one of dominant laser host materials, yttrium aluminum oxide compound with the garnet structure has received considerable attentions because of its interesting properties when doped with rare-earth ions [36]. Neodymium-doped YAG (Nd:YAG) has proven to be one of the best solid-state laser materials. Its indisputable dominance in a broad variety of laser applications is determined by a combination of high light emission cross section with long spontaneous emission lifetime, large laser damage threshold, good mechanical strength, and high thermal conductivity. Large YAG ceramic laser elements can be produced at a relatively low cost. These components are free of internal stress or intrinsic birefringence, and allow relatively large doping levels or optimized custom-designed doping profiles. This makes YAG ceramic laser elements particularly important for high-power laser applications.

2.2 YAG transparent laser ceramics

2.2.1 Properties of YAG ceramics

2.2.1.1 Phase diagram

YAG is one of the artificial garnets from the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ system. Since Schneider's research group reported one of the early phase diagrams for the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ system [37], many phase diagrams for the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ binary system were proposed [38-40]. Before 1974, the phase diagrams of the binary system were based mainly on high-temperature sintering of mechanical mixtures of the oxide starting materials. At that time, YAG was

believed to be the only stable phase while YAP and YAM are the metastable phases [38]. Cockayne [41] also reviewed the chronological development of the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ phase diagram. The main differences among the proposed phase diagrams are the solubility of Y_2O_3 in Al_2O_3 and vice versa, the melting temperatures of the binary compounds, the stability and melting behavior of YAP and YAM, the eutectic composition and the eutectic temperatures.

Fig. 2.3 shows the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ phase diagram accepted by most researchers [40]. There are three compounds such as $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG), YAlO_3 (YAP) and $\text{Y}_4\text{Al}_2\text{O}_9$ (YAM) exist in the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ system. Also, three eutectic congruent compositions and temperatures exist in the three phases of YAG, YAP and YAM. The ratios between Y_2O_3 and Al_2O_3 for YAG, YAP and YAM phases are 3:5, 1:1 and 2:1, respectively [42]. Among them, YAG is a stable compound and exists in a cubic form with garnet structure. YAP is a metastable compound and has an orthorhombic, distorted perovskite structure while the YAM has a monoclinic structure [43-45].

The YAG is a line compound and its exact melting point is still under debate. For example, Olds et al., Warshaw et al. and Abell et al. reported that the melting point of the YAG was 1970 °C [38, 46-47]. Toropov et al. and Mizuno et al. reported that the melting point of the YAG was 1930 °C [40, 48]. However, Caslavsky [39] et al. recently suggested the melting point of 1940 ± 7 °C using optical differential thermal analysis.

Fig. 2.3. Phase diagram of the Y_2O_3 - Al_2O_3 system.

2.2.1.2 Crystal structure

YAG is a member of the garnet family which belongs to the cubic space group O_h^{10} - $\text{Ia}3\text{d}$. In general, structure of a garnet is $\text{A}_3\text{B}_2(\text{CO}_4)_3$. The C atoms are at the Wyckoff's position d in tetrahedrons, surrounded by the four O atoms which are at the Wyckoff's position h , and have S_4 symmetry. The B atoms are at the Wyckoff's position a in the octahedrons, surrounded by the six O atoms, and have C_{3i} symmetry. The A atoms are at the Wyckoff's position c in the dodecahedrons, surrounded by the eight O atoms, and have D_{2d} symmetry. In the unit cell, there are the 24 c positions, 16 a positions, 24 d positions and 96 h positions [49].

In YAG crystal structure, the unit cell is large and contains eight formula units, part of which is shown in Fig. 2.4. The Al^{3+} ions occupy two types of sites with different oxygen coordination: 16 octahedrons a positions and 24 tetrahedrons d positions. The octahedron

joins the tetrahedron together to form a dodecahedron space, namely a distorted cube, and the Y^{3+} ions lie in the dodecahedrons c positions. Then in a YAG crystal structure, Al^{3+} ions occupy the center of octahedrons and tetrahedrons; and the O^{2-} ions are at the corner of octahedrons and tetrahedrons; and the Y^{3+} ions are at the center of the distorted cube, surrounded by eight oxygen ions which form the corners of the distorted cube [50]. The unit cell properties of YAG crystals are listed in Table 2.1 [51].

Fig. 2.4. The coordination of tetrahedron, octahedron and dodecahedron in YAG structure.

Table 2.1. YAG unit cell properties.

Crystal structure	Space group	Point group	Lattice parameter, a (Å)	Number of atoms/cell	Melting temperature (°C)	Density (g/cm ³)
cubic	Ia3d	m3m	12.005	160	1970	4.55

2.2.1.3 Properties of YAG

YAG is colorless and an optically isotropic material that possesses a cubic structure characteristic of garnets. In Nd:YAG, generally about 1 at.% of Y^{3+} is substituted by Nd^{3+} , and solid solubility of Nd^{3+} dopant is affected by the size difference between the dopant and the Y^{3+} ions. Some of the important physical properties of Nd:YAG are listed in Table 2.2 [52] together with optical and laser parameters.

Table 2.2. Physical and optical properties of 1 at.% Nd:YAG.

Chemical formula	Nd:Y ₃ Al ₅ O ₁₂
Weight % Nd	0.725
Atomic % Nd	1.0
Nd atoms/cm ³	1.38×10^{20}
Melting point	1970 °C
Knoop hardness	1215 kg/mm ²
Density	4.55 g/cm ³
Rupture stress	$1.3\text{-}2.6 \times 10^6$ kg/cm ²
Modulus of elasticity	3×10^6 kg/cm ²
Thermal expansion coefficient	
[100] orientation	8.2×10^{-6} °C ⁻¹ , 0-250 °C
[110] orientation	7.7×10^{-6} °C ⁻¹ , 10-250 °C
[111] orientation	7.8×10^{-6} °C ⁻¹ , 0-250 °C
Linewidth	120 GHz
Stimulated emission cross section	
R ₂ - Y ₃	$\sigma = 6.5 \times 10^{-19}$ cm ²
⁴ F _{3/2} - ⁴ I _{11/2}	$\sigma = 2.8 \times 10^{-19}$ cm ²
Fluorescence lifetime	230 μs
Photon energy at 1.06 μm	$h\nu = 1.86 \times 10^{-19}$ J
Index of refraction	1.82 (at 1.0 μm)

2.2.2 Lasing mechanism

When trivalent rare-earth (RE^{3+}) ions are doped into YAG, the RE^{3+} ions substitute for the Y^{3+} ions and occupy the c positions in dodecahedrons, forming the optically active centers when excited by an appropriate excitation source. Nd^{3+} , with the configuration of $\text{Nd}^{3+}: \dots 4f^3 5s^2 5p^6$, was the first of the trivalent rare-earth ions to be used in a laser, and it remains by far the most important element in this group. The fluorescence spectra of Nd^{3+} arise from electronic transitions between levels of the partially filled $4f$ shell. Electrons present in the $4f$ shell can be raised by light absorption into unoccupied $4f$ levels. Stimulated emission is obtained at a number of frequencies within three different groups of transitions centered at 0.90, 1.06, and 1.35 μm . Radiation at these wavelengths results from ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$, ${}^4I_{11/2}$, and ${}^4I_{13/2}$ transitions, respectively.

Fig. 2.5. Energy level diagram of Nd:YAG.

Fig. 2.5 shows a energy level diagram of Nd:YAG, a 4-level laser [49]. The nomenclature of the energy levels may be illustrated by a discussion of the Nd^{3+} ion. This ion has three electrons in the $4f$ subshell. In the ground state their orbits are so aligned that the orbital angular momentum adds up to $3 + 2 + 1 = 6$ atomic units. The total angular momentum $L = 6$ is expressed by the letter I . The spins of the three electrons are aligned parallel to each other, providing an additional $\frac{3}{2}$ units of angular momentum, which, when added antiparallel to the orbital angular momentum, gives a total angular momentum of $6 - \frac{3}{2} = \frac{9}{2}$ units. According to the quantum rules for the addition of angular momenta, the vector sum of an orbital angular momentum of 6 and a spin angular momentum of $\frac{3}{2}$ may result in the following four values of the total angular momentum: $\frac{9}{2}$, $\frac{11}{2}$, $\frac{13}{2}$, and $\frac{15}{2}$. The levels corresponding to these values are $^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, and $^4I_{15/2}$. The first of these, which has the lowest energy, is the ground state; the others are among the first few excited levels of Nd^{3+} .

Exciting light that is generated by exciting medium of Nd:YAG by LD is absorbed to medium, transiting Nd^{3+} from ground level to the highest energy level. And then, they were relaxed and the energy level immediately transited down to upper level in several picoseconds. When laser operation starts, Nd^{3+} transits to lower level resulting in radiation of light corresponding to the amount of the energy level. The strongest transition is the $^4F_{3/2} \rightarrow ^4I_{11/2}$ at 1064 nm. After locating at the lower level, they will be transited to ground level in several hundreds picoseconds. This process is continuously repeated during laser

operation. In the process, the transition from pump band to upper level and another one from lower level to ground level are non-radiate and occur without light.

2.2.3 Advantages of Nd:YAG transparent ceramics as a laser medium

Generally, single crystal and glass are used as solid-state laser host materials. The essential requirements on the media used as gain host in solid-state lasers are high thermal conductivity, chemical stability, and ease of machining. In addition, (a) a large product of σ (cross section of stimulated emission) and τ (fluorescence lifetime), (b) lower lasing threshold and stable operation at both continuous and pulse oscillation modes, and (c) excellence in laser energy-conversion efficiency are also crucial and indispensable factors. However, glasses have poor chemical stability, low melting point and are easy to deliquesce. The thermal conductivity of glasses is about one order of magnitude lower than that of single crystals, which makes it seldom used in high power industrial lasers [19, 53]. On the other hand, YAG single crystals, synthesized from a molten precursor by the Czochralski method shown in Fig. 2.6, satisfy all these requirements, and are the main host of solid-state lasers. However, this method has some technical and economical issues. The growth of large Nd:YAG single crystal usually takes long time about 30-40 days. Nd concentration, that affects the performance in laser applications, is limited to 1 at.% because of the segregation distribution coefficient. Thus, efficient absorption of the excitation light is limited [54]. Moreover, the Nd concentration in the grown crystal varies in the axial direction, which results in a highly strained core region and other symmetrical inhomogenities [55]. These defects lead to optical birefringence and wave front distortion. As a result, less than 25% of the grown ingot can be used as laser media.

Fig. 2.6. Fabrication of Nd:YAG single crystal by Czochralski method.

These disadvantages stimulated tremendous efforts to explore alternative fabrication methods. The pioneering research work began on fabricating Nd:YAG ceramics for laser applications in the mid-1990s. With ceramics fabrication process, it is possible to achieve an order of magnitude increase in the concentration of active ions over single crystals, window-pane size laser materials, and engineered dopant profiles. It is impossible to be achieved in single crystal growth. Although forming a ceramic slab requires careful process control, it takes on the order of only several days of processing time. Ceramic slabs have much higher fracture toughness than single crystals, and they are much less likely to shatter or undergo catastrophic breakage when thermally shocked compared with single crystals. Crack growth is inhibited by the numerous grain boundaries and little or no residual stress exists in the ceramic slabs from the manufacturing process. Benefits of YAG ceramics versus its single crystals form for laser gain media include:

- 1) **Much larger dimensions—limited mainly by size of furnace hot zone.**

One of the disadvantages of single crystal growth method is that it is too difficult to get large size of samples, because of the economical limitation. For single crystal with high melting point, expensive Ir crucible has to be used and the cost will increase almost exponentially with the size of single crystal. However, there are no physical limitations on size of ceramics, even the samples with size of about 1 m in diameter are available [56].

2) Relatively less time required and easy for mass production.

Usually it takes tens of days to grow large size single crystals using Czochralski growth process, whereas only several days are required to fabricate large size ceramics. What's more, ceramics fabrication requires lower temperature than melt growth. Yttria is an example of a material that can be fabricated in transparent ceramics at a temperature (sintered at 1700 °C) much lower than its melting point (~2430 °C) [57]. The power required is drastically reduced during the sintering process. Because of the short period of fabrication process and low sintering temperature, the total amount of energy consumed greatly lowers. Moreover, owing to the nature of ceramics fabrication process just like the iron assembly line, it is relative easy for mass production. Potentially the cost of the ceramic laser materials could be much lower than that of the single crystals because of the short period of fabrication process and mass production.

3) Highly concentration doping with controlled uniform distribution.

Dopant concentration in ceramics can be made higher and more homogenous than that in single crystal because of the advanced ceramics process. For example, the maximum Nd ions dopant concentration in YAG single crystal is limited to 1.4 at.%,

as a result of fluctuations in the axial direction for the grown crystal [58]. Such a crystal also presents a drawback of concentration quenching. However, the dopant concentration can be up to 9 at.% in YAG ceramics [17].

4) High optical quality.

There are no optically heterogeneous regions such as facets and core structure in the ceramics. The absorption and emission properties for transparent ceramics are nearly equivalent to those of single crystals.

5) Better mechanical properties.

There is low or no residual stress birefringence in transparent ceramics. Owing to the polycrystalline nature of ceramics, the fracture toughness and shatter resistance is much higher than those of single crystals. The fractures do not propagate through the bulk of the ceramics material as easily as a fracture might propagate in a single crystal. Instead, the fracture will encounter a grain boundary and a different crystal orientation before it propagates very far. However, fractures in a single crystal can travel a longer distance along a crystalline plane before encountering a defect that may stop it.

6) Composite and multi-functional ceramic structure.

Composite ceramics with complicated structures offer a new paradigm in solid-state laser engineering. Ceramics processing techniques provide flexibility in the design of laser system with high performance laser (high quality beam, high output power and high efficiency etc.). Larger sizes and unique composite designs of ceramics at different dopant levels can be produced, and its profile and structure can be engineered before the sintering process, making the whole production process more

flexible and cost-effective [59]. However, it is impossible for single crystal growth to achieve this.

2.2.4 The state of art of YAG laser ceramics

Since the world's first working ruby laser was reported by T.H. Maiman in 1960 [2], the solid-state lasers have been rapidly developed. Especially in recent years, solid-state lasers have been applied with remarkable success in various fields. They have been utilized for micromachining in the semiconductor industry; for welding, cutting, and drilling in the automotive, heavy machinery, and steel industry; for X-ray and laser-beam generation in medical applications [2, 60-61], and as a light source in nuclear fusion [62]. Along with the fast progress of solid-state lasers, transparent ceramics applied for laser host materials have also been explored intensively for long time.

The first translucent Al_2O_3 polycrystalline ceramics reported in 1957, created a new era and this is a starting point of transparent ceramics. Since then, many researchers have speculated that a theoretically dense polycrystal of an isotropic, pure material would be transparent and optically indistinguishable from a single crystal of the same material. The researchers in GE concluded that there are four key requirements for fabrication of highly translucent ceramics: (a) high purity raw materials, (b) suitable starting particle size, (c) uniform particle size distribution without hard agglomeration, and (d) sintering aids [63]. These four conclusions are the important theoretical foundations for fabrication of transparent ceramics.

Since the 1980s, much of the pioneering efforts have been devoted to fabrication of high quality undoped YAG and rare-earth ions doped YAG transparent ceramics for high-temperature's window, arc tubes for lamp, and laser materials [64]. In 1984, G.D. With [8]

successfully fabricated fully dense YAG transparent ceramics using SiO_2 and MgO as sintering aids. In 1990, M. Sekita [65] reported the optical properties of Nd:YAG ceramics fabricated from a urea precipitation method. Optical properties of the sample are almost the same as those of single crystals grown by the Czochralski method and floating-zone method, but the background absorption is up to $2.5\text{--}3.0\text{ cm}^{-1}$. In 1991, Sekita [66] reported the optical spectra of undoped and rare-earth ions (Pr^{3+} , Nd^{3+} , Eu^{3+} and Er^{3+}) doped YAG transparent ceramics. The scattering loss of Nd:YAG ceramics is reduced from 1.7 cm^{-1} to 0.25 cm^{-1} , but the threshold was about 25 times higher than that of single crystals.

In 1995, the first laser oscillation using transparent Nd:YAG ceramics was reported by A. Ikesue, and it is a significant milestone for transparent ceramics used as laser host materials. The ceramics were fabricated by solid-state reactive sintering technology using high-purity powders ($>99.99\text{ wt.}\%$ purity) as starting materials. The fabrication process is shown in Fig. 2.7 [18]. Laser output of the ceramics was about 70 mW obtained with a slope efficiency of 28% under an end-pumping scheme using a 600 mW laser diode. By this time, transparent YAG ceramics had gained wide acceptance as a laser host material. The development of pump diodes was allowing lasers to scale to very high powers.

Fig. 2.7. Fabrication process of Nd:YAG ceramics by solid-state reactive sintering.

Since 1999, Ueda's group in University of Electro-communication and Yagi's group in Konoshima Corp. Ltd, began to fabricate highly transparent ceramic laser materials by a different way from that of Ikesue's group shown in Fig. 2.8 [17].

Fig. 2.8. Fabrication process of Nd:YAG ceramics by Ueda's group.

Aqueous solutions of aluminum, yttrium, and neodymium chlorides were adopted as source materials to prepare high quality of YAG powders first. Then the compact pellets were sintered under high vacuum conditions. Scattering losses were greatly reduced by using the improved wet-chemical powder synthesis and casting formation technique. As a result of this method, great breakthrough has been made on the development of Nd:YAG ceramic lasers during the last several years. Some optical properties of the ceramics are even better than those of the YAG single crystal, especially for large size samples. Lu et al. succeed in demonstrating laser oscillation with it in 2000 and demonstrated the potential of power scaling up to the kilowatt-level in 2002 by using a Nd:YAG ceramic rod [67-68]. High slope efficiency ceramic lasers and high powers ceramic lasers were successful developed in the recent years. Tsunekane et al. demonstrated high power density laser operation using an edge-pumped Yb:YAG/YAG composite ceramic microchip configuration [20, 69]. This structure provided an efficient high-power laser action such as > 300-W CW operation in a 300- μ m-thick laser medium. By using Nd:Y₃ScAl₄O₁₂, the first mode-locking operation in RE³⁺-ion-doped ceramic material was reported in 2003 [18, 70]. Solid-state laser is at the dawn of a new laser era: high-efficiency and high-power lasers.

Indeed, Nd:YAG ceramics is particularly promising for very high-efficiency and high-power lasers because of its good thermo-mechanical properties and high thermal conductivity. In 2006, the Lawrence Livermore National Laboratory (LLNL, Livermore, CA) used ceramic Nd:YAG amplifiers to generate a record average power of 67 kW from its Solid State Heat Capacity Lasers (SSHCL). In September 2008, a National Research Council review panel from USA, called ceramic slab lasers “the most promising near-term

technical approach for solid-state lasers” usable as weapons to counter rockets, artillery, and mortars. It was just reported on the 5th Laser Ceramics Symposium that 105 kW laser had been achieved by using the Nd:YAG ceramics made by Konoshima Corp. Ltd in Dec. 2009. The progress of Nd:YAG ceramic laser accompanied with the improvement of Nd:YAG ceramics is summarized in Fig. 2.9 [17].

Fig. 2.9. Progress of Nd:YAG ceramic laser.

2.3 Fabrication methods of YAG transparent ceramics

Usually, according to the state of starting materials, fabrication methods for YAG transparent ceramics can be classified into two groups:

(a) “wet” method developed by Yanagitani [71-73], which is based on wet-chemical synthesis of a precursor material that is subsequently decomposed to form a powder with the final composition;

(b) “dry” method developed by group of Ikesue [74], which is based on solid-state mixing and reaction of the primary oxides Al_2O_3 , Y_2O_3 or other oxide dopants as starting materials.

2.3.1 Wet-chemical process

In this process, YAG powders are firstly synthesized by different wet-chemical process, then the powders are sintered by various techniques, such as hot press [75-76], spark plasma sintering [77-78], hot isostatic press [79] and vacuum sintering [80-81].

Conventionally, YAG powder is produced by a solid-state reaction using individual component oxides. The method generally requires repeated mechanical mixing and extensive heat treatment at temperatures as high as 1600 °C to achieve the desired composition [82-83]. Unfortunately, the reaction-ability of the YAG powders is degraded greatly during the heating period. Moreover, these processing conditions do not permit facile control of microstructure, grain size, grain size distribution, or shape of the resulting powders. In order to overcome the disadvantages of this process, various wet-chemical processes for powders synthesis have been explored extensively for long time.

The wet-chemical process was previously used to fabricate transparent YAG ceramics by G.D. With, et al. [8]. In his work, single-phase YAG were yielded at 1300 °C for 6 h, using sulphate salts as starting materials. Finally, the ceramics were obtained at as high as 1850 °C under vacuum about 10^{-5} torr. Recently, the development of nanotechnology

offers new innovation for powder synthesis process. As well known, nanopowders have a very high surface area to volume ratio, which provides a tremendous driving force for diffusion, especially at elevated temperatures. Sintering can take place at lower temperatures, over shorter time scales than for larger particles. In this respect, many wet-chemical processes have been explored for nanopowders in recent years, including sol-gel process [84-88], combustion process [89-91], sol-gel combustion [92-94], hydrothermal synthesis [95], glyco-thermal process [96], spray-pyrolysis synthesis [97-98], and co-precipitation method [99-100]. These chemical processes offer intimate mixing of reactant cations on the atomic level, leading to an increase in reaction rate and lowering synthesis temperature.

(a) Sol-gel process.

The sol-gel process generally involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel), and the sol/gel transition controls the particle size and shape. Calcination of the gel produces the oxide. Sol-gel method of synthesizing nanopowders is very popular amongst chemists and is widely employed to prepare high purity oxide materials. Especially for multi-component composition, this process allows for a more homogenous distribution of dopant in the final product [101]. For example, Manalert' group [102] synthesized YAG powders at 900 °C from metal-organic precursor. Nearly full density of pellet was obtained after sintering at 1600 °C in O₂. Pereira et al. [103] synthesized YAG phosphors from yttrium and aluminum chloride by non-hydrolytic sol-gel route assisted with microwave irradiation to heat-treat the oxide mixture.

(b) Combustion process.

Combustion process is the sequence of exothermic chemical reactions between a fuel and an oxidant accompanied by the production of heat and conversion of chemical species. Pabhakaran et al. [104] synthesized YAG nanopowders by sucrose self-sustained combustion using aluminium nitrate and yttrium nitrates as starting materials. This method is quite simple and the combustion reaction lasts only a few seconds. However, its reaction is too violent to control, and the powders are too difficult to collect [105].

(c) Sol-gel combustion process.

Sol-gel combustion process is developed for synthesis of nanopowders at lower temperature in recent years. This method perfectly combines the advantages of sol-gel process and low-temperature combustion processes. In the sol-gel stage, it provides the composition with the precise control stoichiometry and homogeneity at atomic level. In the combustion of redox stage, it prevents the gel precursor from severe agglomeration during drying. By calcination the fluffy precursor, YAG powders can be obtained. For example, Zhang et al. [106] fabricated transparent YAG ceramics by vacuum sintering with synthesized powders by sol-gel combustion. The transmittance at wavelength of 1064 nm is about 75%.

(d) Hydrothermal synthesis.

This process includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures. It is one of the best methods to produce pure fine oxide powders. Li et al. [107] used nitrate salts as raw materials and ethanol as a solvent to synthesize YAG powders at 290 °C and 10 Mpa pressure. However, it needs a special autoclave to withstand high temperatures and pressures for prolonged periods of time.

(e) Glyco-thermal process.

This method embodies in hydrothermal processing can be extrapolated to nonaqueous system, leading to a simple low temperature route. However, just same as hydrothermal process, the process conditions such as pH, reaction temperature and time, have significant effects on the formation, phase component, morphology and particle size [108].

(f) Spray-pyrolysis synthesis.

Spray-pyrolysis process is carried out by subjecting the precursor solution to temperatures at which pyrolysis of the solute will occur. The rapid evaporation of the solvent from an aerosol would contribute to produce spherical nanoparticles. However, this method is complex and some intermediate phases may be formed because of the high heating rate and short heating time [109-110].

(g) Co-precipitation process.

This method is a facile and convenient way to synthesize nanopowders from salt solutions. For multi-component composition, chemical precipitation is preformed by the reverse-strike technique, namely, the solution of nitrate salts is added dropwise into the precipitant solution. This technique has the advantage of higher cation homogeneity in the precursor [111]. Lu et al. [34] prepared YAG powders with a given composition by co-precipitation and applied casting technique to produce the first large-scale kilowatt-level Nd:YAG ceramic rod, with diameter of 8 mm and length of 203 mm under vacuum. Since then, researchers at Konoshima [112-113] and Li et al. [82-83] used ammonium hydrogen carbonate as a precipitant and succeeded in producing transparent YAG without sintering aid additives.

As shown above, many wet-chemical methods have been developed to synthesize YAG nanopowders for ceramics recent years. Among these chemical routes, sol-gel combustion and co-precipitation process are the most widely used because of simple process, good mixing of the starting materials and considerable chemical homogeneity of the final product.

2.3.2 Solid-state reactive sintering

As we mentioned the process above in Section 2.2.4, high-purity, sub-micrometer oxide powders are used as starting materials and ethanol is used as solvent. Tetraethyl orthosilicate (TEOS) is added as a sintering aid. The mixture was ball-milled using high-purity alumina media in ethanol solvent. After well mixed, the slurry is dried in oven. Then the powder is pressed into various shapes. The near-net shaped sample is cold isostatically pressed at 200 MPa, and a green body with a packing density of 50-55% of theoretical density is obtained. After calcined at about 800 °C to remove the organic component, the powder compact is sintered under vacuum conditions. During the sintering, YAG phase crystallite is formed and fully dense ceramics will be obtained with the grain growth as well as density increase. This process resulted in laser quality material with ~50 µm grain size. The optical quality of the ceramics is comparable to that of sing crystal. Later on, E. Zych and C. Brecher [114-115] prepared YAG transparent optical ceramics using the mixture of Y_2O_3 and Al_2O_3 powders by hot-press at 1750 °C for 4 h under a pressure of about 300 atm.

2.4 Freeze drying

Whatever process is used for ceramics fabrication, the quality of raw material is the most essential for the whole stage. Although the powders synthesized by wet-chemical have many advantages, agglomeration-control is still the most common concern, especially for multi-component composition. In wet-chemical process, water is usually used as both the reagent and rinse solution. During drying after synthesis from an aqueous solution, liquid bridges between particles (as shown in Fig. 2.10) are not avoided forming because of the surface tension of the water [116].

Fig. 2.10. Liquid bridge formed between particles due to capillary force.

The residual liquid at the contact region between particles exerts a capillary pressure, leading to an attractive force between the two particles, required for the bridge to form, is given by r_k , the Kelvin radius:

$$r_k = \frac{\gamma V}{RT \ln(p/p_s)} \quad (2.1)$$

where r_k is the radius of the droplet, γ is the surface tension, V is the molar volume, R is the universal gas constant, T is temperature and p/p_s the relative vapor pressure of the liquid phase.

If $p_s > p$, $r_k < 0$, then the gas condenses onto the droplets increasing their volumes, so a concave meniscus (negative curvature) is expected. This gives rise to a negative Laplace pressure:

$$\Delta P = \gamma / r_k \quad (2.2)$$

If $p_s < p$, then liquid evaporates from the droplets. If the vapor is cooled, then T decreases, but so does p_s . This means p / p_s increases as the liquid is cooled. We can treat γ and V as approximately fixed, which means that the critical radius r_k must also decrease. The further a vapor is supercooled, the smaller the critical radius becomes. Ultimately it gets as small as a few molecules and the liquid undergoes homogeneous nucleation and growth [117].

Solid bridges usually are formed by two different ways: one due to drying the precipitate, crystalline bridges may be formed at the close neck between two particles as the liquid evaporates. The evaporation reduces the proportion of liquid, producing high strength pendular bridges before crystals form. The other one is due to calcination the precipitate to crystal particles. As the temperature elevated, neighboring crystals contact at the neck region by the transport of material. During powder synthesis process, in order to alleviate solid bridges to control agglomeration, the best solution is to remove the water between the precursor particles, and reduce the surface tension as low as possible.

Freeze drying technology is an advanced process used for agglomeration-free powders fabrication [118]. Freeze-drying process consists of freezing the water solution of desired materials and subsequent sublimation. In the freezing process, it is important to cool the

material below its triple point, the lowest temperature at which the solid and liquid phase of the material can coexist. This ensures that the frozen water in the material to sublime directly from the solid phase to the gas phase, rather than melting occurrence, shown in Fig. 2.11.

Fig. 2.11. Drying phase diagram: (a) freeze drying, and (b) normal drying.

Freeze drying has two promising advantages: (1) the steric stabilization of the precursor after frozen becomes no longer active, and the cations hardly have enough mobility to segregate, resulting higher cations homogeneity; (2) the frozen water is directly removed by sublimation, preventing from forming solid bridges during drying and calcination of the precursor. Moreover, the powders made from freeze-drying process normally own higher sinterability, leading to a lower sintering temperature and decreasing the shrinkage and defects [119]. It has proved to be a unique and simple method for making nanopowders with good chemical homogeneity and narrow particle size distribution. Yan et al. [120] synthesized Ce:YAG powders from freeze-dried precursor by using sulphate salts and further calcinating in molten Li_2SO_4 salt. Rabinovitch et al. [121] also

synthesized Nd:YAG powders from organic complex precursors by using freeze-drying process in their recent work. The Nd:YAG powders synthesized by them showed hard agglomerations and a small amount of YAlO_3 (YAP) intermediate phase was produced during the calcination.

2.5 Current problems and challenges

In practice, highly transparent YAG ceramics have needed to be sintered under very stringent conditions, and fabrication of YAG with high quality is more challenge for two principle reasons. First, the large and complex nature of the unit cell results in a large Bueger's vector for this material as well as low diffusion rates for the cations. It results in YAG's large creep resistance at high temperatures, and the pores are prone to be entrapped during sintering process. Pores can not only scatter light but also make the ceramic too brittle and ruin the flow of electrons and/or heat through the material. The second one is how to synthesize YAG phase with precisely defined stoichiometry. Stoichiometry is crucial since YAG is a line compound, and any deviation from a molar ratio of $3\text{Y}_2\text{O}_3:5\text{Al}_2\text{O}_3$ results in scattering from second phases. Moreover, the complex crystal structure of YAG does not offer much solubility for secondary phase, and any impurity in the sintered body will result in the scattering.

It is well known that the important practical properties of a ceramics strongly depend on not only its intrinsic properties, but also its microstructure. Because the latter is a direct consequence of the sintering, it is important to synthesis an easily sinterable powder for developing a new high-performance ceramics under ordinary sintering conditions. The sinterability of a powder depends on the powder characteristics, including the purity, particle average size, size distribution and particle shape. These characteristics depend

strongly on the method used to synthesize the powder, and these, in turn, influence the subsequent processing of the ceramics. So, the starting powders must meet the following severe requirements:

(a) High purity powders, even above 99.99%.

For multi-component optical material, any impurity can degrade optical quality in different ways. Some impurities can transition into a liquid phase at the sintering temperature and increase the grain growth rate (liquid-phase sintering). High grain-growth rates lead to a large number of trapped pores in the grains, which are very difficult to remove. Other impurities can segregate into secondary phases at the grain boundaries or in grains. The secondary phases have different refractive indices than the surrounding primary phase, which results in scattered light.

(b) Particles with suitable average size.

The driving force for densification during sintering is proportional to the curvature of particle surface. Fine powders result in small vacancy migration distances as well as a high dangling bond density, which promotes shrinkage of the ceramics. According to Herring's scaling law [122],

$$t_2 = (r_2 / r_1)^n t_1 \quad (2.3)$$

where t_i and r_i are sintering time and grain size, and n is a constant depending upon the sintering mechanism (for volume diffusion, $n = 3$). It can be clearly concluded that, as the particle size is reduced, so is the sintering time.

(c) Particles with narrow size distribution and good dispersion.

Hard agglomerates are chemically bonded clusters of nanoparticles that have a fixed structure, rather than being held together by Van der Waals forces. Agglomerated particles lead to heterogeneous packing on the green body, which in turn lead to different shrink rate. This can cause serious defects such as pores, differential stress and crack-like voids in the sintered body [123]. Uniform and equiaxed shape facilitate the forming process that are necessary to achieve uniform packing. The particles are as close as possible to each other result in short distance for material transport during sintering. Moreover, uniform packing contributes to isotropic linear shrinkage and higher densification rate.

(d) Dopant with uniform distribution in the host material.

The dopant with a small amount has to be as well distributed as possible inside the host matrix. Otherwise, the laser properties will be affected. Lupei et al. indicated that the neighbouring ions were responsible for the formation of characteristic features in the spectral lines [124].

Currently, the raw oxide powders, Al_2O_3 , Y_2O_3 and YAG are available on the market. However, except Al_2O_3 powders, high quality of Y_2O_3 and YAG powders are limited commercial available for fabrication of transparent laser ceramics. Moreover, the price is much higher than the cost of synthesis process.

In the project, we will fabricate YAG-based transparent ceramics by two methods. One is wet-chemical process, namely, the YAG powders synthesized by wet-chemical process are used as starting materials. The other one is solid-state reactive sintering using commercial Al_2O_3 powders, synthesized $\text{Nd}:\text{Y}_2\text{O}_3$ powders as starting materials. Vacuum sintering technique was applied for transparent ceramics. Compare with the vacuum

sintering technology, although it takes shorter sintering time for hot press, hot isostatic press and spark plasma sintering, they usually need graphite die and high pressure. As a result, there is some carbons inleakage in the sintered sample. Moreover, it results in both high running costs and difficulties with mass production because of the use of high pressure. Vacuum sintering technology without high pressure and graphite die, is an economical, effective, clean and flexible method for different size and form of the sample. All the ceramics in this project were sintered in a high vacuum furnace. The heating element consists of a tungsten mesh assembly that supplies $\Phi 70 \text{ mm} \times 100 \text{ mm}$ hot zone. Vacuum is achieved with a mechanical pump followed by a turbo pump. The temperature is monitored by a type C thermocouple and a calibrated optical pyrometer. The pyrometer looks directly at the surface of the sample through an optical view port. The system can reach 1900°C under a vacuum of 10^{-3} Pa .

Just as we mentioned above, in this work, homogenous distribution of the small amount of rare-earth elements in the matrix is a great challenge. This is critical for the fabrication of high quality laser ceramics. In our work, in order to distribute the little of rare-earth element homogenously, we employed three ways to increase the homogenous distribution of the rare-earth dopant in the YAG ceramics. First, rare-earth elements doped yttrium oxide nanopowders were synthesized by co-precipitation process as source materials. Second, freeze drying was employed to suppress the ion mobility and thus increase the uniformity of rare-earth dopant. Third, long soaking time at high sintering temperature was applied to promote the sufficient reaction and diffusion of rare-earth ion into the YAG ceramics.

Base on the optimized process, other rare-earth elements doped YAG ceramics will be fabricated. Optical properties of the doped YAG ceramics will be investigated.

Chapter 3 Fabrication of YAG ceramics by wet-chemical process

As mentioned in Chapter two, wet-chemical processes have been developed and successfully used for nanopowders synthesis in recent years. For YAG transparent ceramics, fine and agglomerate-free powders with high purity are essential to achieve a full density and transparency at lower temperature and for a shorter sintering time. In this chapter, YAG nanopowders have been prepared by general sol-gel combustion from nitrates-citrate deionized water solvent, modified sol-gel combustion from nitrates-citrate ethanol-deionized water solvent, general co-precipitation process, and modified co-precipitation assisted with freeze-drying. Phase evolution, morphologies, microstructure, and sinterability of the powders have been studied. YAG transparent ceramics have been fabricated applying the powders synthesized by modified co-precipitation assisted with freeze-drying. Optical properties of the ceramics were also analyzed.

3.1 YAG powders prepared by general sol-gel combustion

3.1.1 Introduction

Sol-gel combustion is one of the dominate wet-chemical processes for nanopowder synthesis. It has been claimed that this route can produce pure phase powders at lower temperature with good composition homogeneity, good crystallinity, fine particle, and high reactivity [125-126]. YAG powders have been synthesized from aqueous solution by various chelating agent derived sol-gel combustion, such as citric acid [127], triethanolamine [94], and ethylene glycol [128].

In this work, YAG powders have been synthesized from a mixed solution of aluminum nitrate and yttrium nitrate by general sol-gel combustion. Aluminum nitrate and yttrium nitrate dissolved in deionized water were used as cations sources. As a chelating agent and a fuel, citrate acid can effectively chelate metal ions of varying ionic sizes, helping in preventing their selective precipitation to maintain compositional homogeneity among the constituents. Crystallization behavior of amorphous YAG has been analyzed via X-ray diffraction and differential thermal analysis. Morphology, microstructure and sinterability of the powders have been studied.

3.1.2 Synthesis of the YAG powders

Yttrium nitrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.999%, sinopharm, China) and aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99.999%, sinopharm, China) were used as starting materials. Solid citrate monohydrate ($\text{C}_6\text{H}_8\text{O}_7$, 99.999%, Sinopharm, China) was used as a chelating agent and a fuel for the combustion process. The Al and Y reactants were combined to yield a composition with the general formula of $\text{Y}_3\text{Al}_5\text{O}_{12}$. The ratio of nitrate to citrate used is 1:1. The synthesis process is shown in Fig. 3.1. Stoichiometric amounts of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in deionized water ($18.2 \text{ M}\Omega \cdot \text{cm}$) under mild magnetic stirring. The concentration of the solution was 0.09 M for Y^{3+} and 0.15 M for Al^{3+} . $\text{C}_6\text{H}_8\text{O}_7$ was then added to the mixture to yield a 1:1 nitrate/citrate molar ratio and allowed to dissolve whilst stirring. The precursor was heated at 60°C by a hot plate, with continuously stirring for several hours till the solution formed yellowish sol. Then, the sol temperature was increased to 80°C with unceasing agitation. After the sol was gelled, it was transferred into an oven preheated at 200°C and the gel was burned by this auto-

combustion process. The resulted yellowish, fluffy precursor was then calcined at 700-1100 °C with a heating rate of 3 °C/min for 2 h in a muffle furnace in air.

Fig. 3.1. Synthesis of YAG powders by general sol-gel combustion process.

Differential thermal (DTA) and thermal gravimetric analysis (TGA) of the precursors were performed on a DSC/DTA-TGA analyzer (NETZSCH STA 449C, Gebrüder, Germany) in flowing air atmosphere from the room temperature to 1200 °C with a heating rate of 5 °C/min, using $\alpha\text{-Al}_2\text{O}_3$ powders as the reference. Fourier transform infrared spectroscopy (FTIR) of both the precursor and the powders in KBr discs were measured in the range of 4000-400 cm^{-1} by a PerkinElmer Spectrum GX spectrometer. Phase identification, morphologies and microstructure of the samples were studied by XRD (Shimadzu, Kyoto, Japan) and FESEM (Leo 1550, Cambridge, Cambridgeshire, UK).

3.1.3 Phase evolution of the precursor

The thermal decomposition and the crystallization temperature of the precursor were studied by DSC-TGA, as shown in Fig. 3.2. The thermo-gravimetry curve shows that the mass decreased rapidly below 500 °C due to removal of hydroxyl/ester/carboxylic and

other organic groups of the polymeric precursor [129]. The endothermic peak at 100 °C is assigned to the removal of absorbed water and an exothermic peak at 428 °C can be attributed to the decomposition of citric acid and nitrate ions in the precursor [130]. The exothermic peak at 800 °C can arise from the decomposition of carbonates or carboxylates as well as the start of crystallization and accompanying structure transformations. This result is also confirmed by FTIR spectrum shown in Fig. 3.3b. About 4 % of further mass loss observed between 800 and 900 °C is due to the removal of trapped carbonaceous residues. The exothermic peak at 918 °C corresponds to the crystallization of YAG phase. The total mass loss is up to 75 wt% during the entire calcination process.

Fig. 3.2. DSC-TGA curves of the YAG precursor from the general sol-gel combustion.

Fig. 3.3. FTIR spectra of (a) the precursor and YAG powders from the general sol-gel combustion calcined at (b) 800 °C and (c) 900 °C for 2 h.

Fig. 3.3 shows the FTIR spectra of the precursor after calcined at 800 °C and 900 °C for 2 h in the wave number range between 400 and 4000 cm^{-1} . The spectra of the precursor powder clearly shows a broad absorption around 3418 cm^{-1} (Fig. 3.3a), which is characteristic of the stretching vibration of hydroxyl groups (O-H) [131] including water and yttrium/aluminum hydroxyl groups. The broad peak in the calcined powders becomes weaker with the increase of calcination temperature due to the decomposition of the precursor. The peak at 1610 cm^{-1} is attributed to the bending mode of the O-H bands of the absorbed water. Other peaks at 1432, 1081 and 854 cm^{-1} correspond to asymmetrical and symmetrical stretching vibrations of the carboxylate group (O-C=O) [132]. Those peaks are minimized as the heating temperature increased to 800 °C. The weak peak at about 2416 cm^{-1} is attributed to the absorbed carbon dioxide from the atmosphere [133]. After calcined at 900 °C, new peaks at 769, 723, 683, 559 and 457 cm^{-1} appear. These

peaks represent the characteristic metal-oxygen vibrations, indicating the formation of crystalline YAG [134], which is confirmed by the XRD patterns shown in Fig. 3.4.

Fig. 3.4. XRD patterns of the YAG powders by the general sol-gel combustion calcined at (a) 700 °C, (b) 800 °C, (c) 900 °C, (d) 1000 °C, and (e) 1100 °C for 2 h.

Fig. 3.4 shows the XRD patterns of the powders calcined at 700-1100 °C for 2 h with a 1:1 molar ratio of citrate to nitrate. No obvious diffraction peaks are observed for the sample calcined at 700 °C (Fig. 3.4a), indicating that the as-synthesized powders are amorphous below this temperature. At 800 °C, a small peak of [420] centered at 33.42° is clearly seen in Fig. 3.4b, indicating the onset of crystallization of the YAG. All the peaks of the sample calcined above 900 °C for 2 h can be indexed by cubic YAG (PDF: 33-0040), and no other intermediate phases such as YAM or YAP are detected, indicating that YAG directly crystallize from the amorphous precursor (Fig. 3.4c-e). This result is also consistent with the FTIR results (Fig. 3.3). Both XRD and IR spectra results illustrated that the YAG crystallized well at 900 °C. This crystallization temperature is a

little lower than that measured by DSC (Fig. 3.2), which is because the exothermic peak in the DSC often lags behind crystallization due to the hysteresis of temperature [135]. Moreover, in the case of DSC analysis, the samples were heated at a rate of 5 °C/min. Whereas for XRD analysis, the samples were calcined at a rate of 3 °C/min and held for 2 h at the setting temperature [128].

Fig. 3.5 shows the XRD patterns of the powders calcined at 900 °C for 2 h with different ratio of citrate to nitrate. All of the powders had crystallized completely. There is no evidence of any crystalline phase other than YAG (PDF: 33-0040) when the molar ratio of citrate to nitrate is lower than 1:1. With increase of the ratio to 1.5:1, the intensity of the peaks becomes sharpen and three peaks of YAM phase appear (Fig. 3.5c). This result can be attributed to the excessive citrate acid. The main function of citrate acid is not only to provide a potential heat source during calcination but also to provide a polymeric network which maintains local stoichiometry and hinder cation mobility. Previous work [136] found that high concentration of citrate acid that inhibits carbon oxidation, can retard crystallization of the desired oxide phase from polymeric precursor. Veitch [137] studied the combustion process of synthesis YAG, and he believed that the residual Al_2O_3 co-existed with YAG phase in the system when YAM phase occurred. With the calcination temperature increased up to 1000 °C, the residual Al_2O_3 reacted with YAM and only YAG phase was obtained, shown in Fig. 3.6. The result is consistent with that of Veitch.

Fig. 3.5. XRD patterns of the YAG powders from the general sol-gel combustion calcined at 800 °C for 2 h with different molar ratio of citrate to nitrate: (a) 3:4, (b) 1:1, and (c) 1.5:1.

Fig. 3.6. XRD patterns of the YAG powders by the general sol-gel combustion calcined at 1000 °C with citrate to nitrate ratio of 1.5:1.

3.1.4 Morphology of the powders

Fig. 3.7 shows the SEM images of the YAG powders synthesized with citrate to nitrate ratio of 1:1, which were calcined at different temperatures between 900 and 1200 °C for 2 h. The powders are severely agglomerated. With the increase of calcination temperature, the grains grow up from 20 nm to 60 nm and form cross-connected skeleton microstructures (Fig. 3.7c and d). The cross-connected structures may be resulted from the high reactivity of the powders that led to particle sintering to form neck link during the calcination.

Fig. 3.7. SEM images of the YAG powders by the general sol-gel combustion calcined at (a) 900 °C, (b) 1000 °C, (c) 1100 °C, and (d) 1200 °C for 2 h.

For fabrication of transparent ceramics, the agglomerated powder is undesirable for green body forming and ceramics sintering. These aggregates inhibit the densification of the

powders compact. During sintering, agglomerates with low-pore coordination numbers shrink first and locally causing porous regions with high coordination number to develop between agglomerates. These highly coordinated regions are then kinetically unlikely to disappear, unless the particle rearrangement occurs [138]. Any residue porosity is unacceptable for optical applications, because it will cause light scattering. Therefore, severe agglomeration in the synthesized powders must be avoided.

3.2 YAG powders synthesized by modified sol-gel combustion

3.2.1 Introduction

It is well known that sol-gel combustion combines the advantages of sol-gel process and combustion process. About the essential of reaction, it is complex. The chemical reactions and explanations for the whole processing are described as following: first, cations are hydrolyzed and formed M-OH species shown in Fig. 3.8 [139], where M is the metal.

Fig. 3.8. Reaction of hydrolysis.

Then, the hydroxyl species of M-OH are chelated by citric acid (shown in Fig. 3.9) [140]. Condensation reactions occur on the M-OH complex by removal of the water (Fig. 3.10). After ignited the complex at 200 °C, the gel burns to form fluffy precursor. Finally, oxides are produced when the precursor is calcined at higher temperature.

Fig. 3.9. Reaction of chelating.

Fig. 3.10. Reaction of condensation.

From the above reactions, it is noticed that many hydroxyls are produced in the sol-gel process. During calcination, the hydroxyls can result in the formation of solid bridges between two particles, causing irreversible hard agglomeration. These hard agglomerations are detrimental for reaching fully dense structure during sintering, since they cause non-uniform packing densities in the green body and subsequent differential sintering.

In order to control the hydroxyls forming by sol-gel combustion, we modified the synthesis process to prepare YAG powders in this section. Ethanol-deionized water mixture solution was used instead of deionized water as a solvent in the same way described in Fig. 3.1. In the process, the ethanol reacts with citric acid at first and replaces parts of hydroxyl to form a network structure. Aluminum nitrate and yttrium nitrate were used as starting materials. These reactants were combined to yield a composition with the general formula of $\text{Y}_3\text{Al}_5\text{O}_{12}$.

3.2.2 Synthesis of the YAG powders

Stoichiometric amounts of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in the mixed solution of ethanol and deionized water. The concentration of the solution was 0.15 M for Al^{3+} . The flow chart for preparation of the YAG powders by modified sol-gel combustion is shown in Fig. 3.11. The resulted yellowish, fluffy precursor was then calcined at 750-1100 °C with a heating rate of 3 °C/min for 2 h in a muffle furnace in air.

Fig. 3.11. Synthesis of YAG powders by the modified sol-gel combustion process.

Differential thermal and thermal gravimetric analysis of the precursors were performed on the DSC/DTA-TGA analyzer in flowing air atmosphere from the room temperature to 1200 °C with a heating rate of 5 °C/min, using $\alpha\text{-Al}_2\text{O}_3$ powders as the reference for the DSC/DTA. Fourier transform infrared spectroscopy (FTIR) of both the precursor and the powders in KBr discs were measured in the range of 4000-400 cm^{-1} by a PerkinElmer Spectrum GX spectrometer. Solvent effect on crystallize kinetics of the amorphous YAG has been analyzed via thermal analysis. Phase identification, morphologies and microstructure of the samples were studied by XRD, FESEM and TEM. The density of the samples was measured by the Archimedes method.

3.2.3 Phase evolution of the powders

XRD patterns of the precursor and powders calcined at various temperatures for 2 h are shown in Fig. 3.12. No obvious diffraction peaks are observed for the sample calcined at 750 °C (Fig. 3.12a), indicating that the as-synthesized powders are still amorphous. At 800 °C, the characteristic peaks of YAG phase appear. This temperature is 100 °C lower than that of powder from deionized water solvent. Above 900 °C, only the defined peaks with stronger intensities are observed, indicating promoted crystallite growth of the YAG powders with the increase of calcination temperature. The phase evolution shown by XRD indicates that YAG is the only phase detected during calcining. It can be concluded that YAG crystallizes directly from the amorphous precursor, indicating higher cation homogeneity of the precursor.

Fig. 3.12. XRD patterns of the YAG powders by the modified sol-gel combustion calcined at (a) 750 °C, (b) 800 °C, (c) 900 °C, (d) 1000 °C, and (e) 1100 °C for 2 h.

Fig. 3.13 shows the FTIR spectra of the YAG powders calcined at different temperatures in the wave number range between 400 and 4000 cm^{-1} . In the YAG precursor powder spectrum, a broad absorption around 3418 cm^{-1} can be assigned to the stretching vibration of hydroxyl bands (O-H), due to the crystal water and absorbed water, as well as yttrium/aluminum hydroxyl groups [99, 141]. The peaks at about 1591, 1410, 1079 and 864 cm^{-1} correspond to the characteristic asymmetrical and symmetrical stretching vibrations of carboxylate group (O-C=O). As calcination temperature increases, all the above peaks become weaker because of the decomposition of the precursor. After calcined at 750 $^{\circ}\text{C}$ for 2 h, a weak peak at around 2376 cm^{-1} appear due to the absorption of atmospheric CO_2 [128]. The peaks between 764 and 557 cm^{-1} , which exist above 800 $^{\circ}\text{C}$, correspond to the formation of crystalline YAG. This result is consistent with that of XRD analysis shown in Fig. 3.12.

Fig. 3.13. FTIR spectra of the precursor (a) and powders by the modified sol-gel combustion calcined at different temperatures: (b) 750 $^{\circ}\text{C}$, (c) 800 $^{\circ}\text{C}$, and (d) 900 $^{\circ}\text{C}$ for 2 h.

The weight loss of the precursor as a function of temperature in air was measured by DSC-TGA. The curves for the crystallization of YAG precursor obtained at a heating rate of 5 °C/min in air are presented in Fig. 3.14. The sample weight decreases with increasing temperature continuously from room temperature to 600 °C, and the total weight loss is about 76 wt%. The peak at around 110 °C can be ascribed to water evaporation. An abrupt weight loss appears at the range of 300-550 °C, results from the decomposition of citric acid, carboxylate and nitrate ions. The exothermic DSC peak at 817 °C can be ascribed to the crystallization of YAG from the amorphous precursors.

Fig. 3.14. DSC-TGA curves of the YAG precursor from the modified process.

3.2.4 Crystallization kinetics study by DTA and TG

It is noticed that the crystallization temperature of YAG by general sol-gel combustion is higher than that by modified sol-gel combustion. We believe that the solvent plays an important role in the phase formation of the precursor.

In general, an amorphous substance will crystallize upon heating if sufficient thermal energy is provided to allow the atoms to rearrange themselves. This is because an ordered, crystalline arrangement of atoms has a lower free energy than does a random configuration of atoms found in an amorphous state. This transformation is accompanied by a concomitant release of energy as the atoms rearrange themselves into the lower free energy state. This release of energy can be observed and measured using thermal analysis equipment such as a differential thermal analyzer (DTA). The rate of this transformation typically varies with temperature and heating rate. Hence, the kinetics of crystallization can be studied using both non-isothermal and isothermal method. Non-isothermal experiment is conducted by heating the specimen at various rates and observing the shift in the crystallization temperature with heating rate (higher heating rates result in higher crystallization temperatures). Isothermal experiment is carried out by rapidly heating the specimen up to a specified temperature and holding the specimen at that temperature while measuring the exothermic release of energy during crystallization. Several different hold temperatures are used to determine how the rate of crystallization varies as a function of temperature.

There are several different kinetic models for characterization the amorphous to crystalline transformation [142-143]. Kissinger's method is one of the most efficient methods to estimate the activation energy for crystallization. In the modified Kissinger's equation shown as below:

$$\ln \frac{T_p^2}{\Phi} = C + \frac{E_a}{RT} \quad (3.1)$$

where Φ is the heating rate (deg/min), T_p (K) corresponds to the crystalline peak temperature in the DTA curve, E_a ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) is the activation energy for crystallization, R is the gas constant (8.3143 KJ/mol), and C is a constant.

After performing a series of non-isothermal DTA experiments at several different constant heating rates, a table of peak crystallization exotherm temperatures (T_p) vs. heating rates (Φ) can be created. The values can then be plotted using the Kissinger's equation and the data should produce a graph with a straight line. The activation energy (E_a) corresponding to relative peaks could be calculated from the slopes of the lines.

In this study, the crystallization kinetics for preheated precursor to form YAG phase were characterized using a non-isothermal experiment. The crystallization kinetics of the sol-gel combustion synthesized YAG precursor from different solvents was performed by DTA scan at heating rates of 10 °C/min, 15 °C/min, and 20 °C/min, respectively. The effect of heating rate on the DTA crystallization peak is shown in Fig. 3.15. The precursor crystallization exothermic peak shifts to higher temperatures with increasing heating rate, as have been observed by Chen et al. in thermal analysis of the metal-organic precursor [94]. Specifically, the crystallization exothermic peak at 1005 °C with the heating of 10 °C/min shifts to higher temperature of 1015 °C with the heating rate of 15 °C/min. When the heating rate is 20 °C/min, the crystallization exothermic peak locates at 1024 °C (Fig. 3.15A). Similar phenomena have been found in the thermal analysis of the precursor from modified sol-gel combustion. The crystallization exothermic peak at 975 °C with the heating rate of 10 °C/min moves to 988 and 999 °C with the heating rate increasing to 15 and 20 °C/min (Fig. 3.15B).

Fig. 3.15. DTA analysis scans of YAG precursor observed at various heating rate by (A): general sol-gel combustion, and (B): modified sol-gel combustion.

With different heating rates, the change trends of weight loss in TG curves as a function of heating temperature are similar to each other. However, the temperature corresponding to the complete most decomposition of the precursor (sharp weight loss occurred) increases with the increasing of the heating rate. For precursor from general sol-gel

combustion, 613 °C is for the heating rate of 10 °C/min, and 643 °C is for 15 °C/min. When the heating rate increased to 20 °C/min, the peak shifts to 678 °C (Fig. 3. 16A). So does the peaks of the YAG precursor from modified sol-gel combustion (Fig. 3.16B). The peak is 613 °C with the heating rate of 10 °C/min. When the heating rate increased to 15 °C/min and 20 °C/min, the peaks shifts to 673 and 697 °C, respectively.

Fig. 3.16. TG curves of the YAG precursor from (A): general sol-gel combustion, and (B): modified sol-gel combustion with various heating rates.

Fig. 3.17. Kissinger plot of the YAG precursor from (A): general sol-gel combustion, and (B): modified sol-gel combustion.

According to Kissinger's formula, a straight line can be obtained by plotting $\ln(T_p^2/\Phi)$ vs. $1/T_p$. The activation energy relative to the peaks could be estimated from the slope of the straight line as shown in Fig. 3.17. From the slope of the Kissinger plot, the activation

energy for crystallization of the YAG by general sol-gel combustion is 480.6 KJ/mol, which is much higher than 361.7 KJ/mol determined from that by modified sol-gel combustion. According to the mechanism of crystallization, activation energy must be overcome so that a chemical reaction can occur. Due to the low activation for modified sol-gel combustion using ethanol-water mixed solvent, the crystallization temperature is 800 °C (Fig. 3.12), which is lower than 900 °C (Fig. 3.4) for that by general sol-gel combustion. This result is consistent with those analyzed by the XRD (Fig. 3.4 and 3.12) and DSC (Fig. 3.2 and 3.14).

We believe that the low activation energy and low crystallization temperature in the modified system are closely related with the usage of ethanol-deionized water solvent. In the sol-gel process, ethanol can first react with citric acid to replace parts of hydroxyl as a chelate agent [144] and forms numerous tiny enclosures that trap the constituent cations at the molecular level, leading to a reduction of the diffusion length and an enhancement of the reactivity of the precursors. It helps to lower the crystallization temperature of YAG.

3.2.5 Structure and microstructure characterization

Fig. 3.18 shows the morphologies of the powders calcined at different temperatures from 900 to 1200 °C for 2 h. Compared with the general sol-gel combustion, the powders from modified sol-gel combustion are less agglomerated. The grain size increases with increasing calcination temperatures, while the particles are still well-dispersed (Fig. 3.18d). Regular shape YAG grains with size of 55 nm can be clearly observed at high magnification SEM images (Fig. 3. 19a), which is nearly equal to the grain size value calculated from the Scherrer equation.

Fig. 3.18. SEM images of the YAG powders by the modified process calcined at (a) 900 °C, (b) 1000 °C, (c) 1100 °C, and (d) 1200 °C for 2 h.

Fig. 3.19. (a) Bright field TEM image of YAG powder by the modified process calcined at 1100 °C for 2 h, and (b) Lattice image of a YAG grain.

The lattice images were observed by HRTEM (Fig. 3.19b). The clear lattice fringe shown in Fig. 3.19b indicates a good crystallization of the powder. The interfacial spacings are 3.0 Å and 2.5 Å, corresponding to (400) and (332) planes of cubic crystal structure of YAG ($a = 10.400$ Å), respectively.

3.2.6 Sintering of the YAG powders

The YAG powders were milled in ethanol solvent with high purity ZrO_2 balls. 0.5 wt% tetraethyl orthosilicate (TEOS) added as a sintering aid. The YAG powder mixtures were dried in an oven and pressed into pellets in a stainless steel die at about 30 MPa. The green body was further cold-isostatically pressed at 200 MPa, and the green body density was about 49% of the theoretical value. The compact pellets were sintered at 1750 °C for 5 h under vacuum at about 10^{-3} Pa in a furnace with a tungsten mesh as the heating element. Finally, the YAG ceramics were annealed at 1550 °C for 10 h in a muffle furnace in air.

The relative density of the YAG ceramics is higher than 99%. But unfortunately, the YAG ceramics are not transparent and show gray to black color, which cannot be improved even by long time annealing in air. The gray color in the YAG ceramics results from the residue carbon in the YAG powders. It is very difficult to remove completely during vacuum sintering and the following annealing at 1550 °C. Therefore, fully oxidation to remove the residue carbon after the combustion is quite important for the following sintering process to increase the transparency of the YAG ceramics.

3.3 Nd:YAG powders synthesized by general co-precipitation

3.3.1 Introduction

Co-precipitation process is one of the most promising techniques for nanopowder synthesis, because of the inexpensive starting materials, a simple synthesis process, good mixing of the starting materials at molecular level, excellent chemical homogeneity, and commonly available apparatus. It is well recognized that characteristics and sinterability of the wet-chemically derived powders depend on the type of salts and precipitator as well as synthesis conditions. In co-precipitation process, chemical composition and physical properties of the precursor could be manipulated by varying the starting materials and the precipitation conditions. For the synthesis of multi-component YAG powders, metal chlorides or metal nitrates are usually chosen as metal sources, and urea, ammonia or ammonium hydrogen carbonate is used as a precipitator. In our work, nitrates were used as the metal salts, since the nitrate anion is typically easier to completely remove by thermal decomposition than the chloride anion. Based on our previous work, ammonium hydrogen carbonate (NH_4HCO_3) was chosen as a precipitator.

In the carbonate derived co-precipitation process, composition of this precursor depends on the present anions and the solubility of metal cations in solution. The chemical reactions during the precipitation are listed below:

In these chemical reactions, the solubility products (K_{sp}) of amorphous $\text{Al}(\text{OH})_3$, $\text{Y}(\text{OH})_3$ and $\text{Y}_2(\text{CO}_3)_3$ are 1.3×10^{-33} , 8.0×10^{-23} and 2.5×10^{-31} , respectively. In a multicomponent precipitation system, individual particles of the different metal salts might precipitate separately and therefore segregate, owing to the different of solubility products K_{sp} . If the particles are colloiddally unstable, they can hetero-coagulate together into a mixed aggregate particle. Therefore, suitable precipitation operation is necessary In order to avoid forming aggregate particle.

Generally, chemical precipitation can be performed by the normal-strike method (adding precipitant solution to the salt solution) or by the reverse-strike technique (adding salt solution to the precipitant solution). Reverse-strike technique has proved efficiently to improve the component homogeneity.

In this work, we synthesized YAG nanopowders by reverse-strike process, using nitrate metal salts and ammonium hydrogen carbonate as starting materials.

3.3.2 Synthesis of the Nd:YAG powders

Yttrium nitrate hexahydrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.999%, sinopharm, China), aluminum nitrate hydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99.999%, sinopharm, China), neodymium nitrate hexahydrate ($\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.999%, sinopharm, China), and ammonium hydrogen carbonate (NH_4HCO_3 , 99.95-100.05%, Sinopharm), were used as the raw materials.

$(\text{NH}_4)_2\text{SO}_4$ was used as a dispersant. The synthesis process by general co-precipitation is shown in Fig. 3.20.

Fig. 3.20. Synthesis of YAG powders by general co-precipitation process.

Starting solutions were prepared by dissolving the metal nitrates into deionized water ($18.2 \text{ M}\Omega \cdot \text{cm}$). The concentration of the solution was 0.15 M for Al^{3+} and the quantity of Nd^{3+} was taken for 1 at.% doping in YAG. 1.5 M precipitant solution was prepared by dissolving NH_4HCO_3 into deionized water. A small amount of $(\text{NH}_4)_2\text{SO}_4$ was added into the precipitant solution used as a dispersant. The reverse strike method was used in which the 240 ml mixed metal salt solution was added into 480 ml of the NH_4HCO_3 solution under mild agitation at a speed of 2 ml/min. The pH value was kept about 8 during the whole process by adding NH_4HCO_3 into the precipitates. After aging for 2 h, the resultant suspensions were filtered using a suction filter, washed with deionized water to remove the byproducts of the precipitation reaction, such as NO_3^- or CO_3^{2-} . Then the filtered

precipitate was washed with absolute ethanol for several times to remove the absorbed water. The precursor was obtained after dried at 80 °C for 12 h. The dried precursors were calcined in air at 800~1300 °C for 2 h with a heating rate of 3 °C/min.

Differential thermal analysis and thermal gravimetric analysis of the precursors were performed on the DTA-TGA analyzer in a flowing air atmosphere with a heating rate of 10 K/min. Phase identification was performed by a XRD with CuK α radiation. The morphologies of the samples were observed by FESEM and TEM.

3.3.3 Microstructure of the synthesized YAG powders

The thermal decomposition and the crystallization temperature of the precursor were studied by simultaneous DTA-TGA analysis (as shown in Fig. 3.21). The endothermic peak centred at 138 °C is assigned to the evaporation of absorbed water and the release of molecular water. Major mass loss of the precursor takes place below 600 °C, corresponding to about 82% of the total weight loss (43%). The weight loss at lower temperatures is mainly due to the release of hydroxyl and partial carbonate. While the weight loss at higher temperatures almost completed around 1000 °C, is mainly caused by the further decomposition of carbonate species into oxide. There are two small exothermic peaks at 940 and 1050 °C, respectively. The exothermic peak at 940 °C is attributed to the crystallization of YAG. This conclusion is further supported by the results of XRD (Fig. 3.22). The latter exothermic peak at 1050 °C is accompanied by a small mass loss of 2.4%, and the XRD analysis of the samples (Figs. 3.22d and e) does not allow relating it to a new phase appearance. Therefore, it is attributed to the further decomposition and oxidization of the intermediate phase of carbonates, which was also reported by Hinode et al. [145] and Li et al. [146].

Fig. 3.21. DTA-TGA curves of the general co-precipitation precursor.

Fig. 3.22. XRD patterns of the YAG powders from the general co-precipitation calcined at

(a) 800 $^{\circ}\text{C}$, (b) 900 $^{\circ}\text{C}$, (c) 1000 $^{\circ}\text{C}$, (d) 1100 $^{\circ}\text{C}$, and (e) 1200 $^{\circ}\text{C}$ for 2 h.

Fig. 3.23 shows the morphologies of the precursor and YAG powders calcined at different temperatures between 1000 and 1200 °C. The carbonate precursor (Fig. 3.23a) is composed of extremely fine primary particles with loose and good dispersion. After calcination, the particle is almost spherical and the size is uniform. However, the powders show some agglomerations which are unable to be dispersed by ultrasound dispersion (Fig. 3.23b and c). When the temperature increased up to 1200 °C, neck links form between neighboring particles (Fig. 3.23d).

Fig. 3.23. SEM images of the Nd:YAG powders by the general co-precipitation: (a) the precursor, (b) calcined at 1000 °C, (c) 1100 °C, and (d) 1200 °C for 2 h.

3.3.4 Sintering of the powders

The Nd:YAG powders calcined at 1000 °C, 1100 °C, 1200 °C, and 1300 °C were milled in ethanol for 4 h, with 0.5 wt% TEOS added as a sintering aid, respectively. The powder mixtures were dried in an oven and pressed into pellets in a Φ 10mm stainless steel die at about 30 MPa. The green body was further cold-isostatically pressed at 200 MPa. The compacted pellets were sintered at 1750 °C for 5 h under vacuum at about 10^{-3} Pa in a furnace with a tungsten mesh as the heating element and then finally annealed at 1550 °C for 10 h in a muffle furnace in air. The densities of green body and the sintered ceramics were measured by the Archimedes method shown in Table 3.1.

Table. 3.1. Relatively density of the samples.

Calcination temperature (°C)	Relatively density of green body (%)	Relatively density of ceramics (%)
1000	52.5	94.3
1100	57.8	97.2
1200	56.7	98.5
1300	55.8	96.6

The sintered ceramics from the powders calcined at 1000 °C, 1100 °C, 1200 °C, and 1300 °C densified to about 94.3, 97.2, 98.5 and 96.6 of the theoretical, respectively. Although the green body from the powders calcined at 1100 °C show high density, there are small

cracks in the sintered ceramics after vacuum sintering. This is resulted from the high reactivity of the powders. During sintering, rapid shrinkage may cause the pellet to crack.

The microstructure of the polished YAG ceramics with the highest density was observed by SEM after being thermally etched at 1600 °C for 1 h in an air furnace. Fig. 3.24a shows photograph of the vacuum sintered YAG ceramics with 2 mm thickness. It is semitranslucency, because there are many pores both in the grain and at the grain boundary as scattering centers (Fig. 3.24b). The YAG powders with linked bridges and agglomerates cannot be compacted homogenously, so pore-grain boundary separation does not occur and the pores are difficult to be removed during sintering and finally entrapped in the sample.

Fig. 3.24. (a) Photograph of the YAG ceramics and (b) SEM microstructure of the YAG ceramics after thermal etching.

As we know, in the carbonate derived co-precipitation system, the carbonates precipitates decompose during calcination. The released gas favors to break the links between the particles and prevent forming agglomeration. As we discussed in Chapter 2, liquid bridges present from the start between particles likely to result in the formation of neck links

between particles during the calcination. On the other hand, surfaces with hydroxyl groups of the powders undergo condensation reaction when they are heated up, leading to solid bridges. The resultant product shows hard agglomeration, which are especially undesirable in powders for fabrication of transparent ceramics as they do not disintegrate into primary particles by simple means. In the following work shown in Section 3.4, we will modify the co-precipitation process and decrease the solid bridges as few as possible.

3.4 Nd:YAG ceramics fabricated by modified co-precipitation

3.4.1 Introduction

In the general co-precipitation process for YAG, agglomeration still is the big challenge and many efforts have been made to improve it during the whole process. In the starting precipitation period, some additives, such as $(\text{NH}_4)_2\text{SO}_4$ [83], hydroxypropyl cellulose [135], and OH-scavenging reagent [147] were used as a dispersant to control the powders agglomeration. During washing the precursor, ethanol is used to replace deionized water in order to reduce hydrogen bond formation as possible as we can.

The precursor drying is also critical. Many important properties of the powder, such as the homogeneity, the size of the agglomerates and the extent of agglomeration are closely related with the drying process. When a solvent is removed by evaporation, capillary effects force the particles in contact with each other due to liquid bridges. As mentioned above, surface with hydroxyl groups will undergo condensation reaction when they are calcined, leading to solid bridges. The skeleton of precursor particles is retained in most cases after calcination [148]. Thus, the hard agglomerates generated in the precursor

during drying are inherited by the calcined powders. These hard agglomerates are detrimental for reaching full density, since they cause non-uniform packing densities in the green body and subsequent differential sintering [138].

Recently, freeze drying has proved to be an effectively drying technology for nanopowder synthesis with desirable homogeneity and narrow particle size distribution. As water is directly removed by sublimation, the influence of surface tension does not exist because the gas-liquid interface does not exist [149-151]. No liquid bridges are involved in the later stages of drying, leading to well-dispersed powders after calcination.

In our work, we modified the general co-precipitation process by adopting freeze-drying to dry the precipitate. Well-dispersed Nd:YAG nanopowders have been synthesized without any dispersant and intermediate phase transformation from the freeze-dried precursor. Phase evolution of the precursor, morphologies, and microstructure of the powders were studied. Nd:YAG transparent ceramics were fabricated from the freeze-dried nanopowders under vacuum sintering. The spectroscopic properties of the Nd:YAG powders and the resultant Nd:YAG transparent ceramics were also investigated.

3.4.2 Agglomeration control of the Nd:YAG nanopowders by freeze-drying

The synthesis process is similar with general co-precipitation, shown in the following (Fig. 3.25):

Fig. 3.25. Synthesis procedure by modified co-precipitation assisted with freeze-drying.

In this process, yttrium nitrate hexahydrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), aluminum nitrate hydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), neodymium nitrate hexahydrate ($\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), and ammonium hydrogen carbonate (NH_4HCO_3), were used as raw materials. Starting solutions were prepared by dissolving the metal nitrates into deionized water ($18.2 \text{ M}\Omega \cdot \text{cm}$). The concentration of the solution was 0.15 M for Al^{3+} and the quantity of Nd^{3+} was taken for 2 at% doping in YAG. 1.5 M precipitant solution was prepared by dissolving NH_4HCO_3 into deionized water. The precipitate for freeze-drying process was made by adding 240 ml of the mixed solution at a speed of 2 ml/min into 480 ml of the NH_4HCO_3 solution under mild agitation. Based on the principle of freeze-drying, the precursor after washing with deionized water, was first frozen to immobilize the ions under -20°C for 20 h. Then, the frozen precursor was transferred to a vacuum dryer which operates at about 0.05 torr

and -80 °C. The fluffy precursor obtained from freeze-drying process was calcined in air at 800-1300 °C for 2 h with a heating rate of 3 °C /min.

3.4.3 Characterization of the powders

Differential thermal analysis and thermal gravimetric analysis of the original precursors were performed on a DTA-TGA analyzer in flowing air atmosphere with a heating rate of 10 °C /min. IR spectra in KBr discs were measured in the range of 4000-400 cm^{-1} by a PerkinElmer Spectrum GX FTIR spectrometer. Phase identification was performed by a Shimadzu X-ray diffractometer (XRD) with Cu K_{α} radiation. The morphologies of the samples were observed by a Leo 1550 field emission type scanning electron microscope (FESEM) and JEOL JEM-2010 transmission electron microscope (TEM). The specific area of the powders was measured by the BET method (ASAP, 2020) with N_2 adsorption using a Monosorb. Before the BET analysis, the powders were degassed at 120 °C for more than 2 h to eliminate the absorbed moisture. The emission spectra were obtained by exciting the sample at room temperature with a 808 nm GaAlAs diode laser on a fluorescence spectroscope (Jobin-Yvon, Fluorlog-3, Edison, USA), and the emission spectra were recorded from 850 to 1200 nm.

The thermal decomposition and crystallization temperature of the freeze-dried precursor were studied by simultaneous DTA-TGA analysis (as shown in Fig. 3.26). The endothermic peak centered at 74 °C is assigned to the release of the adsorbed molecular water. It is noted that there are no obvious endothermic peaks at around 100 °C, implying that there is no water remained in the precursor after freeze-drying. Major mass loss of the precursor takes place below 500 °C, corresponding to about 71% of the total weight loss (47%). The weight loss at lower temperatures is mainly ascribed to the release of

molecular water and the partial decomposition of carbonate, whereas the weight loss at higher temperatures, almost completed at around 900 °C, is mainly caused by the further decomposition of carbonate species into oxide, and thus the successive weight loss is small. The exothermic peak at 918 °C is attributed to the crystallization of YAG. The peak is very small because the mass left after decomposition and removal of carbonaceous matter is very small, less than 5 % shown in Fig. 3.26.

Fig. 3.26. DTA-TG analysis curve of the precipitate precursor from freeze-drying.

Fig. 3.27 shows the FTIR spectra of the precipitate precursor after calcination at 900 °C and 1000 °C for 2 h. The peaks at around 3440 cm^{-1} and 1638 cm^{-1} are assigned to the stretching of O-H bands of the absorbed water, which become weaker with the increase of calcination temperature due to the decomposition of the precursor. Other peaks at 1522, 1426 and 854 cm^{-1} correspond to NH_4^+ , CO_3^{2-} and HCO_3^{-1} ions in the bond-stretching mode, respectively. After calcination at 900 °C and above, new peaks at 769, 723, 683, 559 and 457 cm^{-1} appeared. These peaks represented the characteristic metal-oxygen

vibrations of Nd:YAG structure, indicating the formation of Nd:YAG [152]. Thus, it is certain that the precursor precipitant prepared by the co-precipitation is compound carbonate, which is partially decomposed at lower temperature of 900 °C.

Fig. 3.27. FTIR spectra of (a) the precursor and YAG powders by the modified co-precipitation calcined at (b) 900 °C and (c) 1000 °C for 2 h.

Fig. 3.28 shows the XRD patterns of the precursor and powders calcined at 800-1300 °C for 2 h. No obvious diffraction peaks are observed for the sample calcined at 800 °C (Fig. 3. 28b), indicating that the as-precipitated powders are still amorphous below this temperature, which is consistent with the DTA-TGA results (Fig. 3.26). The powder calcined at 900 °C reveals peaks of crystalline YAG (PDF: 33-0040) and without any detectable intermediate phase or other crystallized phase, which is consistent with the results of FTIR analysis (Fig. 3. 27). With the increase of calcination temperature, the peaks become sharper and stronger, indicating growth of the YAG crystallites. The

addition of 2 at.% neodymium, understandably, does not cause any shift in the peak positions or additional new peaks due to neodymium oxide (Fig. 3.28c to g).

For a multication precursor, it is common for an intermediate phase to be generated from the inhomogeneous area of the components during calcination if the drying process is not controlled correctly [153], but this was not detected by XRD in our YAG powders prepared by freeze drying. Because of the poor mobility of the cations immobilized in the frozen precursor, the freeze drying process can preserve the high cations homogeneity obtained by co-precipitation.

Fig. 3.28. XRD patterns of (a) the precipitate precursor and the YAG powders by the modified co-precipitation calcined at (b) 800 °C, (c) 900 °C, (d) 1000 °C, (e) 1100 °C, (f) 1200 °C, and (g) 1300 °C for 2 h.

The XRD results also confirm that the crystallization of Nd:YAG starts at around 900 °C as shown in Fig. 3.28c. This crystallization temperature is lower than that detected by DTA, because the exothermic peak in the DTA often lags behind crystallization as a result

of the hysteresis of temperature. On the other hand, the difference in the crystallization temperature observed by DTA and XRD analysis is possibly due to the fact that the different heating condition. The heating rate for DTA analysis is 10 °C/min, whereas the heating rate of powder calcination for XRD is 3 °C/min and holds for 2 h at the calcination temperature.

Fig. 3.29. SEM images of the YAG powders by the modified co-precipitation calcined at different temperatures for 2 h: (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, and (d) 1300 °C.

Fig. 3.29 shows SEM images of the YAG powders by modified co-precipitation calcined at different temperatures. The crystallites in Fig. 3.29a-d are fairly uniform and spherical in shape. The mean grain size of the powders calcined at 1000 °C (as shown in Fig. 3.29a) is ~35 nm and increases to ~55 nm at 1100 °C (Fig.3.29b), which is consistent with the

grain size value calculated from the Scherrer's formula. When the calcination temperature is increased to 1300 °C, rapid crystal growth occurs but the particles are still well-dispersed (Fig. 3.29d). The result shows that the freeze-drying process of the wet precipitate has a significant effect on the dispersion of the resultant powders. Thus, high-quality YAG powders have been synthesized with freeze-drying, which is vital for the following fabrication of YAG ceramics.

Fig. 3.30 shows TEM images of YAG particles calcined at 1200 °C for 2 h. Fig. 3.30a clearly indicates that the powders are well dispersed with average grain size of 80 nm. The clear lattice fringe shown in Fig. 3.30b reveals good crystallization of the powder. The interfacial spacing is 3.2 Å and 3.0 Å, corresponding to (321) and (400) plane of cubic crystal structure of YAG ($a = 10.400$ Å), respectively.

Fig. 3.30. (a) TEM and (b) HRTEM micrographs of the YAG powders by the modified co-precipitation calcined at 1200 °C for 2 h.

Fig. 3.31 shows the analysis of particle size calculated according to the BET surface area data of the Nd:YAG powders calcined at different temperatures. The relationship between equivalent BET diameter (particle size) D and BET surface area is:

$$D_{\text{BET}} = 6 / (\rho * S_{\text{BET}}) \quad (3.9)$$

where ρ ($= 4.55 \text{ g/cm}^3$) is the theoretical density of Nd:YAG crystal and S_{BET} is the relative surface area determined by BET measurement. The relationship indicates that the BET surface area of the Nd:YAG particles will decrease rapidly with the increase of calcination temperature due to the grain growth in the process of calcination, which is consistent with the XRD analysis (Fig. 3. 28). Rapid crystallite growth is observed from 1300 °C. According to the principle of BET measurement, the particle size depended on the adsorption of liquid nitrogen gas and the test value is close to the “true” size of 3D diameter of the grains. According to ASTM [154], the “true” size equals to 1.5 times of the 2D diameter observed by SEM, then the particle size calculated from BET and SEM is very close.

Fig. 3.31. BET surface area and crystalline size of the Nd:YAG particles by modified co-precipitation as a function of calcination temperature.

For Nd^{3+} , the four lower-lying levels provide a condition favorable to the formation of population inversion. For this reason, Nd^{3+} is used as the active ion in many high-power, solid-state lasers (at 1.06 μm wavelength). The relative emission intensity of Nd^{3+} in $\text{Y}_3\text{Al}_5\text{O}_{12}$ has been found to be as follows [155]:

$^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ (0.87-0.95 μm)	: 0.25
$^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ (1.05-1.12 μm)	: 0.60
$^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}$ (~ 1.34 μm)	: 0.15
$^4\text{F}_{5/2} \rightarrow ^4\text{I}_{9/2}$ and others ($\tau=230$ μs)	: 0.010

Fig. 3.32. Luminescence emission spectra of Nd:YAG nanopowders by the modified co-precipitation calcined at (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, and (d) 1300 °C for 2 h.

Fig. 3.32 illustrates the fluorescence spectra of Nd:YAG nanopowders calcined at 1000-1300 °C. The emission spectra between 850 and 1200 nm were excited at 808 nm using a diode laser at room temperature. All the spectra consist of two characteristic bands

assigned to the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ (850-955 nm) and ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ (1045-1080 nm) transitions, and the maximum peak is at around 1064 nm. The intensity of ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition increases with the growth of crystallites at elevated temperature (Fig. 3.32a-b), but it becomes weaker when the temperature is increased to 1300 °C (Fig. 3.32d). The relative intensity of ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition compared to ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition increases with the size of crystallites.

3.4.4 Fabrication of Nd:YAG ceramics

The Nd:YAG powders by modified co-precipitation calcined at 1200 °C were milled in ethanol for 4 h, with 0.5 wt% tetraethyl orthosilicate (TEOS) added as a sintering aid. The powder mixtures were dried and pressed into pellets in a $\Phi 10$ mm stainless steel die at 30 MPa. The green body was further cold-isostatically pressed at 200 MPa. The compacted pellets were sintered at 1750 °C for 5 h under vacuum of about 10^{-3} Pa in a furnace and finally annealed at 1550 °C for 10 h in air.

Densities of the sintered ceramics were measured by the Archimedes method. Microstructure of the polished surface was observed by FESEM after thermally etched at 1600 °C for 1 h in air furnace. Transmittance of the transparent ceramics was measured over the wavelength region from 200 to 900 nm using a UV-VIS spectrometer (UV-VIS, Varian Cary-5000).

Fig. 3.33a shows the photographs of the Nd:YAG ceramics sintered at 1750 °C after thermal etching and polishing. The ceramics fabricated from freeze-dried powders calcined at 1200 °C, is transparent with 3 mm thickness and the word under the sample can be clearly read. FESEM observation (Fig. 3.33b) of the ceramics from freeze-dried

powders reveals that the sample consisted of a well-defined microstructure and there were no pores or other defects observed. The homogenous microstructure of the sintered sample can be attributed to the well-dispersed powders from freeze-dried precursor, which is prone to compacted homogenously leading to high density green body.

Fig. 3.33. (a) Photograph of the sintered Nd:YAG ceramics and (b) SEM microstructure of the Nd:YAG ceramics after thermal etching.

Fig. 3.34. The transmittance spectrum of 2 at.% Nd:YAG ceramics.

Fig. 3.34 shows the optical transmission spectra of 2 at.% Nd:YAG ceramics with the thickness of 3 mm in the wavelength range from 200 to 900 nm. The representative spectrum of Nd³⁺ ion in the YAG ceramics is illustrated in Fig. 3.34. In the measured wavelength region, the optical transmittance increases with increasing wavelength and the highest transmittance is about 40% in visible wave length.

We know that when light traverses a transparent medium, it is attenuated through three loss mechanisms: absorption, reflection, and scattering. It can be readily shown that the transmittance of a given specimen is expressed by the equation

$$I/I_0 = \frac{(1-r-s)^2 \exp(-\alpha x)}{1-r^2(1-s)^2 \exp(-2\alpha x)} \quad (3.10)$$

$$r = (n-1)^2 / (n+1)^2 \quad (3.11)$$

where I/I_0 is the transmittance of the specimen, r is the reflectivity at each surface, s is the fractional scattering loss at each surface, x is the sample thickness in centimeters, and α is the absorption coefficient (cm⁻¹). This last term includes not only absorption but also losses due to distributed scattering throughout the bulk. It can be expressed as

$$\alpha = \mu + S_{in} + S_{op} \quad (3.12)$$

where μ is the absorption term characteristic of electron transition, S_{in} is the scattering due to structural inhomogeneities (e. g., pores and second phase), and S_{op} is the scattering due to optical anisotropy (birefringence). In order to get the higher transmittance, the terms in formula (3.12) should be as less as possible.

The drop off in transmittance at < 350 nm indicates that there are some scattering sources in the ceramics such as pores, inclusions and grain boundaries, which could result in a different index of refraction. When the scattering center is significantly smaller than the wavelength of the radiation, the scattering intensity can be determined by Rayleigh's equation. According to the Rayleigh's equation, the scattering intensity is proportional to d^6/λ^4 , where d and λ are radius of the scattering body and the measuring wavelength. Therefore, the scattering intensity increases proportionally with λ^{-4} , where λ is the wavelength [156]. It can be seen that the scattering intensity will increase with decreasing wavelength.

3.4.5 Transmittance improvement of the sintered ceramics

In order to optimize the fabrication process by the modified co-precipitation to improve the transmittance of the ceramics, we also study the main parameters effect on transmittance of the sintered ceramics.

3.4.5.1 Effect of sintering temperature

The influence of sintering temperature on optical transmittance of non-doped YAG ceramics with 1 mm thickness prepared by co-precipitation method was investigated. The samples were sintered at 1650 °C, 1700 °C, 1720 °C, 1760 °C and 1800 °C for 4 h, respectively. With increasing the sintering temperatures from 1650 °C to 1760 °C, the porosity of the YAG ceramics decreased continuously due to the growth of grains, leading to continuous increase of the transmittance of the ceramics. When sintered at 1760 °C, transmittance of the ceramics reached the highest, and then the transmittance decreased with further increase of the sintering temperature to 1800 °C, shown in Fig. 3.35. The

possible reason was that high sintering temperature led to the generation of grain-boundary phase and more pores were formed by the vaporization of silica rich-secondary phases at high sintering temperature [157].

Fig. 3.35. Dependence of transmittance of YAG transparent ceramics on sintering temperature.

3.4.5.2 Effect of sintering aid

Fig. 3.36 shows the photo of the YAG transparent ceramics doped with different amount of TEOS. The liquid phase produced by adding 0.1 wt% TEOS in the YAG ceramics is not enough to remove the pores trapped in grain or at boundaries [158], so the YAG ceramics shown in Fig. 3.36a is translucent with lots of scattering centres. With increasing amount of TEOS to 0.5 wt%, the YAG ceramics shows the highest transmittance of around 60~70% (as shown in Fig. 3.37). The grain boundary of the 0.5 wt% TEOS doped sample was observed by HRTEM as shown in Fig. 3.38. The grain boundary is clear and sharp and no other phase such as SiO_2 was observed in the grain boundary. However, when the amount of TEOS increased further to 2 wt%, the YAG ceramics become

translucent again (as shown in Fig. 3.36c) and the transmittance of the sample also decreases. Maître and Boulesteix [159-160] reported that silica grain-boundary phase was formed when 0.3 wt.% SiO_2 (corresponding to 1.1 wt. % TEOS) doped in the YAG ceramics. Therefore, when the TEOS amount increased to 2 wt%, silica grain-boundary phase was formed, thus the transmittance of the sample decreased.

Fig. 3.36. The photos of YAG transparent ceramics doped with (a) 0.1 wt%, (b) 0.5 wt%, and (c) 2.0 wt% TEOS.

Fig. 3.37. The transmittance spectra of YAG transparent ceramics doped with different amount of TEOS.

Fig. 3.38. HRTEM image of the ceramics with 0.5 wt.% TEOS.

3.5 Summary

1. YAG nanopowders have been successfully synthesized by general sol-gel combustion, modified sol-gel combustion, general co-precipitation process, and modified co-precipitation process assisted with freeze-drying.
2. YAG powders were synthesized at 900 °C by general nitrate-citrate sol-gel combustion process. The desirable ratio of nitrate to citric acid is contributed to preparation of YAG at lower temperature. The suitable ratio of nitrate to citric acid is 1:1. The as-synthesized powders are cross-connected and form agglomerates, indicating poor dispersion and poor sinterability.
3. Solvent has a significant effect on YAG phase transformation and morphology. Well-dispersed YAG powders were synthesized at lower calcination temperature of 800 °C using ethanol-deionized water mixture solution as solvent. From Kissinger's formula, the activation energies relative to the YAG phase

transformation were calculated. The activation energy of crystallization of YAG by general sol-gel combustion is higher than that derived from modified sol-gel combustion. According to the mechanism of crystallization, the lower activation energy for modified sol-gel leads to YAG forming at lower temperature. This result is further certified by XRD and DSC analysis.

4. The YAG powders synthesized by modified sol-gel combustion show well-dispersed and narrow particle size distribution. The sintered YAG ceramics have high relative density of more than 99%. But unfortunately, the YAG ceramics are not transparent and show gray to black color. This kind of color even cannot be changed by long time annealing in the air. Fully oxidation of the residue carbon after the combustion is quite important for the sintering of transparent ceramics.
5. YAG powders from general co-precipitation show good uniform particle size, but with some hard agglomerates and neck links. The best calcination temperature for the precursor is 1200 °C. The YAG powders obtained at this temperature is of high sinterability and densified. However, the YAG ceramics with 2 mm thickness are semi-translucent and there are some pores trapped both in the grain and at the grain boundary.
6. Homogenously well-dispersed 2 at.% Nd:YAG powders were synthesized by co-precipitation assisted with freeze drying without any intermediate phase, which are spherical with narrow particle sized distribution. The YAG powders from freeze-dried precursor are high reactivity and more beneficial to obtain transparent ceramics. The vacuum-sintered ceramics with 3 mm thickness are transparent and

the highest transmittance is about 40 % in the wavelength range from 200 to 900 nm.

7. Key parameters effects on optical transmittance have been studied. Our research result shows that the suitable sintering temperature is 1760 °C. 0.5 wt% TEOS is used as a sintering aid to accelerate densification of the YAG ceramics.

Chapter 4 Fabrication of YAG ceramics by solid-state reactive sintering

Solid-state reactive sintering, namely, “dry” method is starting from the powder mixtures of Al_2O_3 , Y_2O_3 and other oxide dopants. The YAG phase is formed during the sintering. In this chapter, YAG ceramics were fabricated by high-energy ball milling, using the commercial available high-purity nanosized oxide powders as raw materials presented in section one. In the other section, laser-quality of Nd:YAG transparent ceramics was fabricated by solid-state reactive sintering, applying the commercial high-purity Al_2O_3 powders and as-prepared Nd: Y_2O_3 powders as starting materials. The key parameters for fabricating YAG-based transparent ceramics were studied.

4.1 YAG ceramics fabricated by high energy ball milling

4.1.1 Introduction

High-energy ball milling, also known as mechanical attrition or mechanical alloying, is an industrial-important solid-state reaction powder preparation method and can be operated at a large scale. Coarse source material powders are crushed mechanically in rotating jars by tungsten carbide balls. This repeated deformation can cause large reduction in grain size to obtain nanoparticles. Furthermore, through mechanical activation, chemical reactions may also take place among the as-milled solids and new nanostructure compounds can be synthesized. A number of nanostructure metal oxides and their solid solutions such as $\text{ZrO}_2\text{-Fe}_2\text{O}_3$ [161], SrTiO_3 [162], $\text{Pb}_{0.52}\text{Zr}_{0.48}\text{TiO}_3$ [163] and hydroxyapatite/titania [164] have been prepared by high-energy ball milling method.

In this work, pure-phase YAG powders were prepared at low temperature of 1200 °C from the mixture of nanosized Al_2O_3 and Y_2O_3 powders activated by high-energy ball milling process. The calcination temperature is significantly lower than that required by the conventional solid-state reaction process (>1600 °C) and comparable with the crystallized temperature required by most of the wet-chemical methods.

4.1.2 Experiment procedure

Commercial high-purity nanosized Al_2O_3 powders (99.99%, 10-20 nm, Sinopharm, China) and Y_2O_3 powders (99.99%, <50 nm, Sinopharm, China) were used as starting materials. Morphologies of the powders were shown in Fig. 4.1. The starting powders were weighted according to the stoichiometry of YAG and were dry-milled in a Retsch RM400 planetary ball milling system at the speed of 200 rpm for up to 20 h. Tungsten carbide milling jar and balls were used as high-energy ball milling medium. After formed by Cold Isostatical Press (CIP) under 200 MPa pressure, the green pellets with 45-52% of theoretical density were calcined at 900-1500 °C for 2 h in an air furnace with a heating rate of 3 °C/min. Phase identification, morphologies and microstructure of the samples were studied by XRD (Shimadzu, Kyoto, Japan), FESEM (Leo 1550, Cambridge, Cambridgeshire, UK) and TEM (JEOL JEM-2010, Kyoto, Japan). The density of the samples was measured by the Archimedes method.

Fig. 4.1. SEM morphologies of the raw materials: (a) Al_2O_3 , Sinopharm, China; (b) Y_2O_3 , Sinopharm, China.

4.1.3 Mechanical alloying effect of Y_2O_3 - Al_2O_3 nanopowders

Fig. 4.2 shows the SEM images of the Al_2O_3 - Y_2O_3 powders ball milled for 5 h and 20 h. The powders milled for 5 h are still fairly dispersed with loose agglomeration (Fig. 4.2a) [165]. After ball milling for 20 h, large agglomerated particles were formed (Fig. 4.2b and Fig. 4.3a). Fig. 4.3b shows the HRTEM images of the powders ball milled for 20 h. The boundaries of the particles are indicated by the dash line. Some defects such as lattice mismatch and nanocracks caused by high energy applied into the crystal lattice during milling process can be observed (marked with arrows in Fig. 4.3b). According to the interfacial spacing of cubic Y_2O_3 (PDF 43-1036) and hexagonal α -phase Al_2O_3 (PDF 26-0031), the component of the particles are also labeled (marked with Y for Y_2O_3 and A for Al_2O_3 in Fig. 4.3b). In the boundary area of adjacent Y_2O_3 and Al_2O_3 particles, a thin layer with disordered lattice formed by the high-energy mechanical crush and attrition can

be observed. This layer was confirmed as the non-equilibrium and disordered phase of Y-Al-O.

In order to evaluate the effect of ball milling process on the sintering activity of the powders, the powders milled for 5 h and 20 h were pressed into pellets respectively and were calcined at 900 °C for 2 h. The pellet made from the 5 h-milled powders is still powder-like without obvious sign of sintering (Fig. 4.4a). With the increasing ball milling time to 20 h, the pellet is densified into porous ceramics and the particles also grow larger (Fig. 4.4b). It indicates that high-energy ball milling can increase the sintering activity of powders and the longer milling time favors to lower the sintering temperature of the powders.

Fig. 4.2. SEM images of the powders ball milled for (a) 5 h and (b) 20 h.

Fig. 4.3. (a) TEM and (b) HRTEM images of the powders ball milled for 20 h (A for Al_2O_3 and Y for Y_2O_3).

Fig. 4.4. SEM images of 900 °C annealed pellets made from ball milled powders for (a) 5 h and (b) 20 h.

4.1.4 Sintering study of the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ nanopowders

The as-milled powders for 20 h were pressed into pellets and the green pellets were calcined at 900-1500 °C for 2 h. Fig. 4.5 shows the XRD patterns of the as-milled

powders before and after calcination at different temperatures. After milling for 20 h, the main XRD peaks belong to Y_2O_3 and Al_2O_3 (Fig. 4.5a), but the peaks become broad and weak compared to that of the starting mixture of Y_2O_3 and Al_2O_3 powders, suggesting a microstructure change after high-energy ball milling. No YAG phase is found in the as-milled powders (Fig. 4.5a). It indicates that there are no chemical reactions between Y_2O_3 and Al_2O_3 during the ball milling process. It is known that multi-components reactions can be easily initiated during the high-energy ball milling process. However, due to the chemical inert property of Y_2O_3 and Al_2O_3 , the activation energy is not enough for the synthesis of YAG, which was also reported by Kong [166] et al. Only disordered non-equilibrium phase were obtained by Sakurai [167] et al. when they synthesized $Y_{1-x}Ce_xAlO_3$ by high-energy ball milling process using Y_2O_3 and $Al(OH)_3$ as starting materials.

Fig. 4.5. XRD patterns of (a) the as-milled powders calcined at (b) 900 °C, (c) 1000 °C, (d) 1100 °C, (e) 1200 °C, (f) 1300 °C, (g) 1400 °C, and (h) 1500 °C for 2 h.

After calcination at 900 °C for 2 h, the main characteristic peaks of the sample can match perfectly with those of cubic YAG database (PDF 33-0040), indicating that YAG phase is formed (Fig. 4.5b). Some intermediate YAP phase is found in the samples calcined below 1200 °C (Fig. 4.5b-d). Raising the calcination temperature to 1200 °C and higher, the peaks of the YAP intermediate phase disappeared (Fig. 4.5e-h).

Conventionally, many earlier studies reported that there are three phases monoclinic YAM phase, perovskite YAP phase, and cubic YAG in the solid-state reaction of Al₂O₃-Y₂O₃ system [168-170]. The phase evolution at elevated calcination temperature is shown as below.

According to the solid-state reaction process, pure phase YAG is generally formed when the calcination temperature increased up to 1450 °C. In our work, the formation temperature of YAG is much lower than that required by the conventional solid-state reaction process (>1600 °C) and is comparable with those required by most of the wet-chemical method (900-1200 °C), which can be attributed to the formation of the non-equilibrium phase and the improved activity of the powders by the high-energy ball milling process. It is known that high-energy ball milling process can introduce an excess of energy into the crystal lattice during ball milling process. The as-milled material contains a very high defect density and it is in meta-stable state. Thermal energy provided by calcination seems to lower its internal energy and attain equilibrium rapidly, so

transformations and reactions between the as-milled raw materials can be initiated easily. Intensity of those new peaks increases gradually with the increase of calcination temperatures, which is attributed to the grain growth of YAG (Fig. 4.5c-h). No impurities of the milling medium are found in the powders.

Fig. 4.6 shows the SEM images of the ball milled powders calcined at different temperatures. It shows that the grain size is fairly homogeneous (Fig. 4.6a-c) and the crystal grow up obviously when the temperature increased up to 1300 °C (Fig. 4.6d). The sample sintered at 1300 °C is confirmed by XRD (Fig. 4.5) to be YAG phase. With the sintering temperature increased, the pores are further eliminated and the grains start to link each other at 1400 °C (Fig. 4.6e). The pellet densified to dense ceramics at 1500 °C with rapid crystallite growth (Fig. 4.6f). It is obvious that the average grain size of the pellets increases with the increasing of calcination temperature. It indicates that the powders show high reactivity and sinterability, which benefits from the high-energy ball milling.

YAG powders calcined at 1200 °C were cold isostatical pressed and sintered at 1700 °C for 5 h in vacuum furnace of about 10^{-3} Pa. The density of the sintered ceramics is around 98.7%. The color of sintered samples show gray to pink color, probably due to the contamination from WC milling jar and milling balls. The contamination is vital and must avoid for transparent ceramics. On the other hand, the nanopowders after high energy ball milling exhibit a high reactivity during the sintering process but are difficult to manipulate. This feature may lead to the contamination with undesired impurities or to the mixture of powders in a different ratio with respect to the desired stoichiometry. So, to choose the

powders with suitable particle size and particle match is very important for fabricating multi-component transparent ceramics.

Fig. 4.6. SEM images of the samples calcined at (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C, (e) 1400 °C, and (f) 1500 °C for 2 h.

4.2 Nd:YAG ceramics fabricated by modified reactive sintering process

4.2.1 Introduction

As we mentioned above, solid-state reactive sintering for fabricating transparent ceramics has been explored extensively last decade years. It is well known that the qualities of the starting powders have a significant effect on fabricating process as well as optical properties of the resultant product. The challenge has been and remains to be the control of good mixture of the starting powders, particle size, morphology, and doping homogenous distribution. Al_2O_3 powders, with desirable quality, are relatively easier available from the market (shown in Fig. 4.7). Compare with Al_2O_3 powders, it is difficult to choose commercial available Y_2O_3 powders with satisfied quality on the market directly used as a starting material.

Fig. 4.7. SEM morphology of the commercial Al_2O_3 powders (AKP-30, Sumitomo Chemical Co., Ltd, Japan).

We have demonstrated that freeze-drying is an effective method for nanopowders synthesis with controlled agglomeration and particle size in Chapter 3. Moreover, its

lower temperature contributes to restrict segregation for the multi-component material, especially for a small amount of dopant. As a result, the calcined powders will remain initial stoichiometry.

In this work, well-dispersed Nd:Y₂O₃ nanopowders with high reactivity have been synthesized from freeze-dried precursor. 2 at.% Nd:YAG transparent ceramics were fabricated by vacuum reactive sintering technology using the as-synthesized Nd:Y₂O₃ powders and commercial Al₂O₃ powders as starting materials. Phase evolution, morphologies and microstructure of the powders and the sintered transparent ceramics were investigated. The key effects on the sintering process and quality of the ceramics were investigated. Optical properties of the transparent ceramics were also studied.

4.2.2 Nd:Y₂O₃ powders synthesized by freeze-drying assisted co-precipitation

The Nd:Y₂O₃ powders synthesis process and characterizations are almost the same as that of YAG detailed in section 4 of Chapter 3. The synthesis process for Nd:Y₂O₃ powders is shown in Fig. 4.8.

Fig. 4.8. The synthesis process of Nd:Y₂O₃ powders from freeze-dried precursor.

Yttrium nitrate hexahydrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.99%, Sinopharm), neodymium nitrate hexahydrate ($\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.99%, Sinopharm), and ammonium hydrogen carbonate (NH_4HCO_3 , 99.95-100.05%, Sinopharm) were used as the raw materials. Starting solutions were prepared by dissolving the metal nitrates into deionized water ($18.2 \text{ M}\Omega \cdot \text{cm}$). 0.25 M Y^{3+} and $2 \text{ at.}\% \text{ Nd}^{3+}$ aqueous solution were prepared by dissolving the metal nitrates into deionized water. Then, $2 \text{ M NH}_4\text{HCO}_3$ aqueous solution was dripped into the above solution under mild agitation at room temperature and the Y^{3+} and Nd^{3+} were precipitated into white precipitate. After aging for 2 days, the precipitate was washed repeatedly with deionized water and then was frozen and dried by freeze-drying (Telstar cryodos-80, Telstar industrial, Spain) at -80°C under 0.03 torr . Finally, $\text{Nd}:\text{Y}_2\text{O}_3$ powders were crystallized by calcining the fluffy precursor in air at $500\text{-}1100^\circ\text{C}$ for 4 h with a heating rate of $3^\circ\text{C}/\text{min}$.

Differential thermal analysis and thermal gravimetric analysis of the original precursors were performed on a DTA-TGA analyzer in flowing air atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$. IR spectra in KBr discs were measured in the range of $4000\text{-}400 \text{ cm}^{-1}$ by a PerkinElmer Spectrum GX FTIR spectrometer. Phase identification was performed by a Shimadzu X-ray diffractometer (XRD) with $\text{Cu } K_\alpha$ radiation. The morphologies of the samples were observed by a Leo 1550 field emission type scanning electron microscope (FESEM) and JEOL JEM-2010 transmission electron microscope (TEM). The distribution of Y and Nd was observed by energy-dispersive spectroscopy. The specific area of the powders was measured by the BET method (ASAP, 2020) with N_2 adsorption using a Monosorb. Before the BET analysis, the powders were degassed at 120°C for more than 2 h to eliminate the absorbed moisture.

4.2.3 Characterization of the Nd:Y₂O₃ powders

Thermal decomposition process of the as-prepared precipitate precursor was studied by simultaneous DTA-TGA analysis and the results are shown in Fig. 4.9. The broad endothermic peaks centered at 120 °C and 304 °C are assigned to the removal of absorbed and molecular water, respectively. The exothermic peak at 660 °C is caused by the decomposition of yttrium carbonate and crystallization of Y₂O₃. It is found that thermal decomposition of the carbonate precipitate into yttria oxide is almost completed at about 700 °C since there is no significant weight loss at temperature higher than 700 °C.

Fig. 4.9. DTA-TGA analysis of the yttrium carbonate precursor.

Fig. 4.10 shows the FTIR spectra of the precipitate precursor before and after calcination. Yttria powders bought from Merck was used as reference (Fig. 4.10e). In Fig. 4.10a, the peaks centered at 3410 cm⁻¹ and 1630 cm⁻¹ of the absorption bands can be attributed to OH stretching vibration and the presence of absorbed water, respectively. The absorption bands appearing at 1518, 1430 and 1131 cm⁻¹ correspond to C-O asymmetric stretching

vibration and bending. Furthermore, the peaks at 848 cm^{-1} and 763 cm^{-1} are also apparent in the FTIR, which can be assigned to N-O stretching origin from the NO_3^- remains. The relative intensities of O-H, C-O and N-O groups decrease with the increasing calcination temperature (as shown in Fig. 4.10b-d). After being calcined at $500\text{ }^\circ\text{C}$ and higher, the peaks at low frequency assigned to the stretching of N-O bonds have disappeared owing to the decomposition and the most prominent bands appeared at 563 cm^{-1} are assigned to the Y-O vibration of cubic Y_2O_3 . But the peak at 3410 cm^{-1} and peaks in the region of $1518\text{--}1131\text{ cm}^{-1}$ are still observed even the calcination temperature reached up to $1100\text{ }^\circ\text{C}$, which is attributed to the absorption of CO_2 and H_2O by yttria powders and the KBr substrate. This is further confirmed by the FTIR spectrum of commercial yttria powders (shown in Fig. 4.10e).

Fig. 4.10. FTIR spectra of (a) yttrium carbonate precursor and powders calcined at (b) $500\text{ }^\circ\text{C}$, (c) $700\text{ }^\circ\text{C}$, (d) $1100\text{ }^\circ\text{C}$ for 4 h and (e) yttria powders bought from Merck.

The XRD patterns of the freeze-dried precursor calcined at different temperatures from 500-1100 °C for 4 h are shown in Fig. 4.11. The precursor powders are found to exhibit low crystallinity after aging for 2 days (Fig. 4.11a). Yttria phase is formed after calcined at 500 °C (Fig. 4.11b). Further calcining of the precursor over 700 °C, an increase of the peak intensity indicates the growth of grains (Fig. 4.11c-e). All the peaks of the powders calcined at 1100 °C can be indexed by cubic yttria (PDF: 41-1105).

Fig. 4.11. XRD patterns of the yttrium carbonate precursor and powders calcined at various temperatures for 4 h.

Fig. 4.12 shows SEM images of the Nd:Y₂O₃ powders from freeze-dried precursor calcined at different temperatures for 4 h. The Y₂O₃ crystallites from the freeze-dried precursor shown in Fig. 4.12a-d are fairly uniform and spherical in shape. The mean particle size of the powders calcined at 900 °C is ~25 nm (Fig. 4.12a) and it increases to ~40 nm after calcined at 1000 °C (Fig. 4.12b). When temperature is increased over 1100 °C, a significant grain growth takes place and some particles have clearer profile (Fig.

4.12d). The result shows that freeze drying process has a significant improvement on the dispersion and size of powders.

Fig. 4.12. SEM images of the Nd:Y₂O₃ powders from freeze-dried precursor calcined at different temperatures for 4 h: (a) 900 °C, (b) 1000 °C, (c) 1100 °C, and (d) 1200 °C, and (e) EDX of spectra of the powders calcined at 1000 °C.

Chemical composition of the powder calcined at 1000 °C was valued by EDX as shown in Fig. 4.12e. The detected content of Nd is 2.36 wt%, nearly constant to the theoretical value of 2.53 wt%.

Fig. 4.13 shows the TEM micrograph of the Nd:Y₂O₃ powders calcined at 1100 °C. It is found that some particles are single crystals while others are formed by conglomeration of several single crystals (Fig. 4.13a). The result indicates that the precursor forms primary crystallites after calcination. Fig. 4.13b shows HRTEM micrograph of a typical Y₂O₃ grain. The clear lattice fringes of HRTEM image (Fig. 4.13b) indicate a single crystal structure of the grain.

Fig. 4.13. (a) TEM images of Y₂O₃ powders calcined at 1100 °C for 4 h and (b) HRTEM image of a typical Y₂O₃ grain.

It is known that the calcination conditions have big effects on the specific surface area (SSA). Table 1 summarized the SSA value of co-precipitates calcined at different conditions. From results shown in Table 1, we can find that the SSA decreased with increasing the calcination temperature. By increasing the holding time, the SSA will also

decrease. For reactive sintering, generally we need uniform powder mixtures for homogenous compact. The particle size of Y_2O_3 should match that of the Al_2O_3 powders we used. By adjusting the calcination conditions, the particle size can be easily controlled.

Table. 4.1. Specific surface area calcined at different conditions.

Sample	Calcination temperature/ $^{\circ}\text{C}$	Dwelling time/h	SSA/ m^2/g (made by BET method)
2.0 at.% Nd: Y_2O_3 precursor	---	---	37.2
2.0 at.% Nd: Y_2O_3	800	2	18.5
2.0 at.% Nd: Y_2O_3	900	2	16.7
2.0 at.% Nd: Y_2O_3	1000	2	13.1
2.0 at.% Nd: Y_2O_3	1100	2	11.8
2.0 at.% Nd: Y_2O_3	1200	2	10.5
2.0 at.% Nd: Y_2O_3	1300	2	7.3
2.0 at.% Nd: Y_2O_3	1000	4	12.6
2.0 at.% Nd: Y_2O_3	1000	6	11.7
2.0 at.% Nd: Y_2O_3	1100	4	11.4

4.2.4 Effect of parameters on the optical properties of Nd:YAG ceramics

For solid-state reactive sintering process, quite a lot of parameters such as particles size, particle size distribution, the sintering temperature, holding time, sintering aid, and its doping concentration will affect the microstructures of the sintered ceramics, which will have the further influence on the optical properties of fabricated ceramics. In this section, we have studied the key parameters effect on the ceramic sintering.

4.2.4.1 The effects of calcination conditions

In order to investigate the effect of calcination condition of Nd:Y₂O₃ powders on the sintered ceramics by solid-state reactive sintering, we used commercial Al₂O₃ powders (AKP-30, Sumitomo Chemical Co., Ltd, Japan) and the synthesized Nd:Y₂O₃ powders calcined at various temperatures as raw materials. Two groups of experiments shown in Table 2 were designed. For group A, specimen labeled A1 through A4, the calcination temperatures of Nd:Y₂O₃ powders were varied from 800 °C to 1300 °C but the holding time was kept at 2 h. For group B, the calcination temperature of the samples labeled B1 through B4 is kept at 1000 °C, but the holding time is changed from 2 h to 6 h. In order to make these data comparable, all of the experiment conditions were kept exactly the same.

Table. 4.2. Two groups of experiments designed to study the effects of Nd:Y₂O₃ powders.

Specimen	A1	A2	A3	A4	B1	B2	B3	B4
2%Nd:Y₂O₃ Powder calcination conditions	800 °C/2h	1000 °C/2h	1100 °C/2h	1300 °C/2h	1000 °C/2h	1000 °C/4h	1000 °C/5h	1000 °C/6h
SSA (m²/g)	18.5	13.1	11.8	7.3	13.1	12.6	12.3	11.7
Al₂O₃	Commercial powders, AKP-30, 99.99%, 300 nm							
TEOS	0.5 wt%							
Milling and Forming conditions	The powders were mixed at 220 rpm for 18 h (Fritsch, planetary ball milling, P5). The mixtures were dried at 80 °C for 12 h. Dry pressed at 30 MPa with a Φ20 mm stainless steel die, and followed by CIP at 200 MPa.							
Sintering conditions	1720 °C for 6 h in vacuum furnace of 10 ⁻³ Pa.							

The fabrication procedure was shown in Fig. 4.14. The Nd:Y₂O₃ powders and Al₂O₃ powders were blended together according to the stoichiometric ratio of 2 at.% Nd:Y₃Al₅O₁₂ and were ball-milled with high-purity Al₂O₃ balls in ethanol solvent, with 0.5 wt% tetraethyl orthosilicate (TEOS) added as a sintering aid. The powder mixtures

were dried and pressed into Φ 20 mm pellets in a stainless steel die at 30 MPa, and then the green body was further cold-isostatically pressed at 200 MPa. The compressed pellets were sintered at 1720 °C for 6 h under vacuum of around 10^{-3} Pa in a furnace with tungsten as the heating element. The ceramics were further annealed at 1550 °C for 10 h in a muffle furnace in air.

Fig. 4.14. Fabrication of Nd:YAG transparent ceramics by solid-state reactive sintering.

Phase identification of the Nd:YAG ceramics was performed by a X-ray diffractometer (XRD, Shimadzu, Kyoto, Japan) with Cu K_{α} radiation. Densities of the sintered Nd:YAG ceramics were measured by the Archimedes method and deionized water was used as the immersion medium. Microstructure of the polished transparent ceramics on both surfaces was observed by FESEM after thermally etched at 1600 °C for 1 h in air. Transmittance of the sintered ceramics was measured by Cary-5000 UV-VIS-NIR spectrometer. The emission spectra from 850 to 1200 nm were obtained by exciting the sample at room temperature with an 808 nm diode laser and recorded on a fluorescence spectroscopy (Jobin-Yvon, Fluorolog-3, Edison, USA).

After CIP processing, the green body density is in the range of 48-55% of their theoretical value. Fig. 4.15 shows that all the peaks of the samples whether group A or group B can be characterized by cubic YAG (PDF: 33-0040) after vacuum-sintered at 1720 °C for 6 h.

Fig. 4.15. XRD patterns of the sintered Nd:YAG ceramics.

After polished on both surfaces, optical transmittance was measured by Cary-5000 UV-VIS-NIR spectrometer. Fig. 4.16 shows the optical transmittance at 1064 nm for 1.7 mm thickness of 2 at.% Nd:YAG. From Fig. 4.16A, we can find that the transmittance increases when the calcination temperature increases from 800 °C to 1000 °C, and then decreases sharply with the further increasing of the calcination temperature. From Fig. 4.16B, it can be found that the longer calcination time results to the better optical quality. However when the calcination time increased to 6 h, slightly decreasing of the transmittance is observed.

Fig. 4.16. The dependence of transmittance on SSA value (A1: 800 °C/2h; A2: 1000 °C/2h; A3: 1100 °C/2h; A4: 1300 °C/2h; B1: 1000 °C/2h; B2: 1000 °C/4h; B3: 1000 °C/5h; B4: 1000 °C/6h).

Fig. 4.17 shows microstructures of the 2 at.% Nd:YAG ceramics after thermal etched at 1600 °C for 1 h. From the SEM pictures, there are quite a lot of pores are trapped in the grains as well as on the grain boundaries (Fig. 4.17a, c and d).

Fig. 4.17. The SEM morphologies of the A1-A4 samples made from the 2 at.% Nd:Y₂O₃ powders with different calcination temperatures (The polished samples were thermal etched at 1600 °C for 1 h).

For co-precipitated powders, lower calcination temperature results to smaller crystallite size of the particles. Generally speaking, smaller crystallite size of the powder owns higher sintering activity. However, if the calcination temperature is too low and the holding is not long enough, the precursors cannot be completely decomposed. Even little of residue will cause serious scattering in the as-prepared ceramics. It is very obviously that the 800 °C of the calcination temperature is not high enough for completely decomposition of the precursors. If the calcination temperature is too high or the holding

time is too long, the grain size grows rapidly and the sintering activity of the powder will degrade, which is undesirable for solid-state reactive sintering.

From the above results, we can conclude the best calcination conditions for Nd:Y₂O₃ powders should be in the range of 1000 °C for 4-5 h.

4.2.4.2 The effects of sintering temperature and holding time

From the literatures, fabrication of Nd:YAG by reactive sintering from oxides powders, the best sintering temperature should be in the range of 1700 °C to 1850 °C. Normally the prolonged heating time is preferred. In some reports, 50 h of holding time was even reported. However, it is not easy for measuring such high temperature very accurately, especially when sintered under high vacuum. Moreover, according to the ceramic sintering theory, if we can get the pore-free microstructure of ceramics, the longer holding time will result in bigger of the average grain size. In order to investigate the effect of sintering temperature and holding time on the sample, we fabricated the specimen by the same fabrication process mentioned in Fig. 4.14, using Nd:Y₂O₃ powders calcined at 1000 °C for 4 h and Al₂O₃ (AKP-30) as starting materials. In the follow section, the raw materials are the same if there are not specified.

Fig. 4.18 shows the phase evolution of the ball-milled starting materials after calcined at various temperatures from 1100 to 1500 °C. After being milled for 5 h, the main peaks belong to Y₂O₃ and Al₂O₃ (Fig. 4.18a) and no YAG phase is found. After calcination at 1100 °C and 1200 °C, Y₄Al₂O₉ (YAM), YAlO₃ (YAP) and a small amount of YAG phase are detected, co-existing with little unreacted Al₂O₃ and Y₂O₃ (Fig. 4.18b and c). Further calcination at higher temperature, the intermediate phases of YAM and YAP continue to react with the unreacted Al₂O₃. Pure YAG phase is formed at 1300 °C, and the main peaks

of the sample can match perfectly with those of cubic YAG database (PDF 33-0040) (Fig. 4.18d). Due to the high reactive ability of the Nd:Y₂O₃ powders synthesized with freeze-drying, the crystallization temperature of YAG is much lower than that required by the conventional solid-state reaction process (>1600 °C).

Fig. 4.18. XRD patterns of the 2 at.% Nd:Y₂O₃-Al₂O₃ milled powders calcined at different temperatures for 3 h: (a) mixture before calcination, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C, and (e) 1500 °C. Y: Y₂O₃; A: Al₂O₃; P: YAP; M: YAM; G: YAG.

Fig. 4.19 shows the grain growth behavior of 2 at.% Nd:YAG specimens sintered at various temperatures from 1100 to 1650 °C for 6 h. It shows that the grain size is fairly homogeneous (Fig. 4.19a-d) and the average grain size of the pellets increases from 0.15 μm to 7 μm with the increase of sintering temperature. The YAG grains show initial linkage each other at 1300 °C in Fig. 4.19b. XRD results confirm that there is only YAG phase formed after sintering at 1300 °C. With further increasing the sintering temperature, YAG crystals grow and the density of the sintered body gradually increases. Rapid

crystallite growth with clear crystal face is observed at 1500 °C (Fig. 4.19c). The grains combined compactly and the pellet densified to dense ceramics with nearly pore-free microstructure at 1650 °C (Fig. 4.19d). It indicates that the powders show high reactivity and sinterability.

Fig. 4.19. SEM images of the samples sintered at different temperatures for 6 h: (a) 1100 °C, (b) 1300 °C, (c) 1500 °C, and (d) 1650 °C.

Fig. 4.20 shows the dependence of the relative densities on different sintering temperatures for 6 h. The 55 % relative density of the pellet sintered at 1100 °C is almost the same as that of the green body. The onset temperature of shrinkage is ~ 1300 °C, which corresponds to the complete transformation of the only YAG phase confirmed by

XRD (Fig. 4.18d). The density of the pellet is about 65%, indicating that it is the initial densification stage.

For solid-state reactive sintering, the solid grains undergo solid-state sintering during heating. Depending on the solid-liquid solubility relations, new microstructure develops by the liquid wetting the solid. In this case, the newly formed liquid penetrates between the solid grains, dissolves the sinter bonds, and induces grain rearrangement. Further, because of solid solubility in the liquid, the liquid improves transport rates responsible for grain coarsening and densification [171]. Therefore, the density of the samples increases with increasing the sintering temperatures. When sintering temperature increased to 1700 °C, the density increases to nearly full density and transparent YAG ceramics are obtained.

Fig. 4.20. The dependence of relative density of Nd:YAG ceramics on sintering temperature.

Fig. 4.21. Dependence of optical transmittance of the 2.0 at.% Nd:YAG ceramics sintered at different temperatures for 6 h. The samples thickness is 3.1 mm. Both faces were polished down with 3 μm diamond paste.

Fig. 4.21 shows the effects of the sintering temperature on the optical transmittance of the 2.0 at.% Nd:YAG ceramics. The ceramics were sintered at different temperatures for 6 h. With the sintering temperature increased from 1650 °C to 1700 °C for 6 h, a sharp increasing of the transmittance can be found in the figure. With further increasing sintering temperature to 1780 °C, the transmittance is slightly increased. When sintering temperature increased to 1800 °C, partly melting area in the samples can be observed, leading to the decrease of optical transmittance. Fig. 4.22 shows the SEM picture of one of the samples sintered at this temperature. We think that the localized partial melting of some areas may be caused by the inhomogenous chemical distribution or defects. However, when EDX was used to measure the composition of these areas, no obvious composition difference was detected because the composition variation is too small and

beyond the detection limit of EDX. Furthermore, the melting area can be observed throughout the sample when the temperature is increased up to 1800 °C. Therefore, the high sintering temperature close to the melting point of YAG should be the main reason for the localized partial melting of the YAG ceramics sintered at 1800 °C.

Fig. 4.22. The party melting phenomenon happened when sintering temperature increased to 1800 °C.

Fig. 4.23 shows the relationship between the holding time when sintered at 1720 °C and the transmittance of the ceramics with 3.1 mm thickness. The transmittance improves with prolonged the holding time. After sintered for 12 h, the transmittance of the sample increases to the theoretical value of 94 %. To further decrease the scattering losses of the ceramics to optical grade, it is necessary to sinter the samples for longer time because grain growth to a critical size relative to the pore size is essential to remove the larger pores in the final sintering stage [168, 170].

Fig. 4.23. Dependences of optical transmittance of the 2.0 at.% Nd:YAG ceramics sintered at 1720 °C for different holding time.

Fig. 4.24. SEM morphologies of the 2.0 at.% Nd:YAG ceramics sintered at 1720 °C (a) for 4 h; and (b) for 30 h.

Fig. 4.24 shows the SEM images of two samples sintered at 1720 °C for 4 h and 30 h, respectively. The average grain size is increased from 5.0 μm to 13.5 μm . It is expected that the further prolonging the holding time results to the bigger average grain size. However, it is not meaningful for doing the sintering at such a long time if we cannot

fabricate the Nd:YAG ceramics with pore-free structures. Once residual pores are trapped inside the grains, they are difficult to be removed by increasing the sintering time since the lattice transport required is extremely slow.

4.2.4.3 The effects of doping concentration of SiO₂

From literatures, it is well known that TEOS is a very effective sintering aid for YAG based transparent ceramics by inducing the forming of secondary liquid phase. Owing to the presence of a liquid phase, the particle rearrangement becomes easier and mass transport by grain boundary diffusion could take place at a lower temperature, leading to enhanced densification kinetics.

Many studies have also reported that the SiO₂ addition would be linked to a solid solution formation by substitution of Al³⁺ by Si⁴⁺ in the tetrahedral sites [158-159, 172]:

The formation of Y³⁺ vacancies enhances the lattice diffusion and could improve the YAG densification rate. Fig. 4.25 shows the relationship between the relative transmittance and the doping concentration of TEOS. All the samples are sintered at 1700 °C for 8 h in this case, and all other processing parameters are kept the same. We can see that the transmittance of the sample is greatly improved with the increase of TEOS. However, when the quantity of TEOS is increased up to 1.2 wt%, transmittance of the sample decreases.

As it is well known that Si⁴⁺ ions are slightly smaller than Al³⁺ ($r_{Si}^{4+} = 0.026$ nm, $r_{Al}^{3+} = 0.039$ nm), leading to elastic distortions in YAG lattices. As a consequence, only a small quantity of silica can be expected to dissolve in pure YAG during the sintering: its

quantities below 0.28 wt% dissolve in the YAG matrix at 1973 K [173-174]. If excessive TEOS is added, the optical transmittance degrades because the silica rich-secondary phases vaporizes to form gaseous species such as $\text{SiO}_{(g)}$, leading to pores formation [158].

Fig. 4.25. Dependence of the optical transmittance on TEOS doping amount. 4 mm thickness samples were used for this measurement.

Fig. 4.26 shows the microstructures of the fabricated 2.0 at.% Nd:YAG ceramics sintered at 1720 °C for 8 h with different TEOS doping amount. All other processing parameters were kept as same. For un-doped samples, there are many pores entrapped in the sample. There is no obvious grain growth and the grain size is quite small. The small grain size could be attributed to the low volume fraction of liquid phase that would be formed during sintering. Only 0.2 wt% of TEOS greatly increased the grain growth, owing to the diffusion of grain boundary droved by liquid phase. With the further increasing of TEOS doping amount to 0.5 wt%, the average grain size is around 20 μm and there are no

heterogeneous microstructures observed in Fig. 4.26c. Few pores can be observed in the SEM picture. The results we observed are very similar to the literature reports [168].

Fig. 4.26. SEM pictures of the thermal etched surfaces with various TEOS doping contents.

In SiO₂-YAG system, a previous study has indicated that the liquid-phase sintering is operative between 1400 and 1550 °C. The computed phase diagram of the SiO₂-YAG in Fig. 4.27 [67] shows that the secondary liquid phase begins to form around 1400 °C [170]. The corresponding invariant equilibrium can be written as follows [174]:

The grain growth kinetics of SiO₂ doped YAG sintered at 1720 °C fit the grain growth model [175]:

$$G^n - G_o^n = kt \quad (4.6)$$

where G is the average grain size, G_o is the initial grain size, k is a rate constant, and t is time. In SiO₂ doped YAG system, it fits an $n = 3$ dependence. As described by Brook, a exponent of 3 indicates that liquid phase mass transport is the dominant mechanism for coarsening in the sample [176].

Fig. 4.27. SiO₂-YAG phase diagram.

4.2.5 Fabrication of Nd:YAG transparent ceramics

Based on above investigations, the main processing parameters had been identified and optimized. By using high purity commercial Al_2O_3 powders and co-precipitated Nd:Y $_2$ O $_3$ powders calcined at 1000 °C for 4 h, almost free-pore Nd:YAG ceramics had been fabricated. Fig. 4.28 shows the detail fabrication flow chart of the optimized processing conditions.

Fig. 4.28. Detail fabrication flow chart of the optimized processing conditions.

Fig. 4.29 shows the microstructure and transmittance spectra of a typical 4.0 at.% Nd:YAG sample sintered at 1730 °C for 12 h, with 0.5 wt% doping content of TEOS. The Nd:YAG ceramics is very dense and no pinholes or other defects are observed. The in-line transmittance higher than 84.3% at 1064 nm has been achieved in 3.1 mm thickness

sample. Even at 400 nm wavelength, the transmittance is still higher than 80%, due to the high quality of transparent ceramics with pore-free structure.

Fig. 4.29. The microstructure (left) and transmittance spectra (right) of the typical 4.0 at.% Nd:YAG samples fabricated at optimized processing conditions.

4.2.5.1 Doping concentration effect on the microstructure

Currently, Nd:YVO₄ had been considered as the most efficient laser host crystal for diode-pumped solid-state lasers (DPSSLs) because of its large absorption coefficient (31.2 cm⁻¹ for 1.0 at.% Nd:YVO₄) and high stimulated emission cross section (25×10⁻¹⁹ cm²). However its poor thermal properties and small saturation fluorescence make it unsuitable for high power applications. Compared with Nd:YVO₄, Nd:YAG owns high mechanical strength, good chemical stability, and high thermal conductivity to sustain the high-power laser operation. But its absorption coefficient and cross section is too small, which makes it difficult for DPSSLs applications. It was thought that these drawbacks can be compensated by high concentration doping of Nd³⁺ ions. Compared with its single

crystals, this is one of the main advantages for Nd:YAG ceramics. High concentration Nd:YAG ceramics have much higher absorption coefficients which in turn reduce length of laser materials. High concentration ceramic laser materials can be polished into microchips and used to efficiently generate single-frequency laser output which may compete with microchip Nd:YVO₄ single-frequency laser [177]. Currently it is still a big challenge to grow high quality Nd:YAG single crystals with doping concentration higher than 1.1 at.%.

By adopting above optimized processing, we succeed in making good quality transparent Nd:YAG ceramics with different doping concentration from 0.8 to 6.0 at.%. Fig. 4.30 shows the photographs of the transparent Nd:YAG ceramics with different doping concentration of Nd³⁺. The words below the samples can be clearly resolved, with no any visible distortion.

Fig. 4.30. The Nd:YAG ceramics with different doping concentration (from left to right, the doping concentration is increased from 0.8 at.% to 6.0 at.%. The sample thickness is 4.0 mm).

Fig. 4.31. The microstructure of Nd:YAG ceramics with different doping concentration.

The samples were thermal etched at 1600 °C for 30 min.

SEM images of the thermal etched surfaces are shown in Fig. 4.31. All of the samples own uniform microstructures. The average grain size decreases with the increasing of

Nd^{3+} doping concentration, which is consistent with the literatures published [168, 178-179]. It seems that the grain growth had been greatly suppressed especially when the doping concentration higher than 4.0 at.%.

In YAG garnet structure, Nd^{3+} ions usually replace Y^{3+} cations placed in twelve dodecahedral sites to form eutectic. However, with the increase of Nd^{3+} concentration, Ramirez's [178] group has demonstrated that Nd^{3+} segregation would take place at grain boundary by two main reasons, namely, the increased atomic mass and ionic radius of Nd^{3+} ion with respect to either Y^{3+} or Al^{3+} [180-181], and the influence of surface morphologies of grain boundaries on the relative concentration of Nd^{3+} ions in YAG [179, 182]. Boulesteix [159] also has indicated that the grain boundary diffusivities of Nd^{3+} are about five orders of magnitude higher than that the respective lattice diffusivities. This result highlights the grain boundaries as preferential paths for the Nd^{3+} ions diffusion. We believe that the relative higher concentration of Nd^{3+} ions at grain boundary increases the potential barrier for surface diffusion, resulting in higher activation energy to prevent grain boundary further diffusion. As a consequence, the grain growth is suppressed.

4.2.5.2 Doping concentration effect on the optical properties

The optical absorption spectra of 1 at.% Nd:YAG ceramics shown in Fig. 4.32 was carried out using Cary-5000 UV-VIS-NIR spectrometer. The highest absorption peak is centered at 808.6 nm. The absorption coefficient is 10.77 cm^{-1} , and the FWHM (full width at half maximum) of absorption peak is 0.78 nm. The results are close to those reported in the literature, as shown in Fig. 4.32b with 1.04 nm for the FWHM of absorption peak [177]. The absorption increases in proportion to the Nd^{3+} concentration, as shown in Fig. 4.33. From the figure, one can see the absorption coefficient almost increases linearly with

increasing Nd^{3+} doping concentration. At the peak absorption wavelength of 808 nm, absorption coefficient of the 5.0 at.% Nd:YAG ceramics reached 50 cm^{-1} , which is large enough for microlasers.

Fig. 4.32. Absorption spectrum of 1 at.% Nd:YAG ceramics from 770 nm to 850 nm; (a) our fabricated ceramics, (b) referenced sample [176].

Fig. 4.33. The dependence of absorption coefficient at 808 nm on Nd³⁺ doping concentration.

Fig. 4.34 shows the emission spectra and fluorescence lifetime measurements of Nd:YAG ceramics with different doping concentration. For emission spectroscopic experiments, a CW diode laser tuned to 808 nm was used as the excitation source inclined 45° to irradiate the centre of the samples. The laser was focused onto the samples and the diameter of the exciting beam was smaller than 0.2 mm. The emission spectra were recorded by a spectrofluorometer (Fluorolog-3, Jobin Yvon Co., Edison, USA) equipped with a Hamamatsu R5509-72 photomultiplier tube. All emission spectra are corrected for the spectral response of the measuring system. The experiments were performed at room temperature. For lifetime measurements, the 808 nm LD was run under pulsed mode.

Fig. 4.34. The emission spectra (a) and decay time spectra (b and c) of fabricated transparent Nd:YAG ceramics with different doping concentration.

The emission spectra show the typical fluorescence spectrum of Nd:YAG ceramics. Emission spectra for 1 at.%, 2 at.% and 5 at.% Nd:YAG ceramics have been measured as shown in Fig. 4.34a. The main emission peak is centered at 1064 nm, which is corresponding to $^4F_{3/2}$ to $^4I_{11/2}$ transition of Nd^{3+} ion. With the doping concentration increased, the emission intensity decreases and a little wavelength red-shift has been observed. Our results are similar with some literatures report [177, 183-184]. Fluorescence lifetime of 284 μs , 274 μs , 206 μs , 163 μs , 102 μs , 75 μs and 65 μs have been measured, respectively, for 0.3 at.%, 1.0 at.%, 2.0 at.%, 3.0 at.%, 4.0 at.%, 5.0 at.% and 6.0 at.% Nd:YAG ceramics, as shown in Fig. 4.34b. With the doping concentration increased from 0.3 at.% to 6.0 at.%, the fluorescence lifetime decreases from 284 μs to 65 μs . Dramatic decrease happened when the doping concentration is higher than 2.0 at.%. This result is attributed to the concentration quenching process activated by direct cross

relaxation and near-field electric dipole interaction between Nd^{3+} - Nd^{3+} [185-187]. The decay curves of all the samples are exponential and well fitted with single exponential function, as shown in Fig. 4.34c.

4.3 Nd:YAG transparent ceramic laser

4.3.1 Optical quality evaluation

By using above optimized fabrication method, several batch of Nd:YAG ceramics with different concentration had been successfully fabricated. The results can be repeated very well. The optimal sintering temperature need to be calibrated by the optical pyrometer through a quartz window on the chamber, which is 1720 °C. Fig. 4.35 shows one of our Nd:YAG transparent ceramic samples, with the doping concentration of 2.0 at.%. The thickness is 4.0 mm. It is found that the objectives can be clearly resolved through the transparent ceramic. No distortion was observed.

Fig. 4.35. The photo was taken through a 2.0 at.% Nd:YAG ceramics with 4 mm thickness.

For optical materials, we know that the scattering loss is always important. Generally, the lower scattering loss is better for the laser results. For laser materials, if the surface is optically polished, the scattering from the surface is very low and can be ignored in most of case. Then, the absorption efficiency at non-absorption band is roughly equal to the scattering loss. There are several different ways to measure the absorption efficiency directly or indirectly, such as laser calorimeter, transmittance and etc. According Lambert-Beer's law, the absorption efficiency can be expressed as

$$\alpha = \frac{1}{l} \ln \left(\frac{(1-R)^2}{2T} + \sqrt{R^2 + \frac{(1-R)^4}{4T^2}} \right) \quad (4.7)$$

$$R = \left(\frac{1-n}{1+n} \right)^2 \quad (4.8)$$

Where α is the absorption efficiency, l is the thickness of the measured sample, and T is transmittance that can be measured directly by UV-VIS-NIR spectrometers. R is the single surface reflectance calculated with Eq. (4.8), which requires knowledge of the index of refraction at specific wavelength (for YAG, $n = 1.815$). Equation is the least accurate, but easiest way to find α for a transparent material. The main problem for this method is that when α is small, a small uncertainty in l gives a large uncertainty in α . If the materials have significant absorption, then Eq. (4.7) is accurate. Another problem with this method is that there is no distinction between scatter losses and absorption losses. The value of α measured in this way includes contributions from both bulk and surface scatter. Although there are some drawbacks by using this way to evaluate the optical quality of the samples, this method will still be useful if we keep all of the measurement conditions at the same.

Fig. 4.36 shows the absorption coefficients of one of our (0.8 at%) Nd:YAG samples (A) and commercial-available Konoshima's sample (B). The thickness of the two samples is 4 mm. A fixed refractive index of 1.8153 was used for the calculation. We can see that the absorption coefficient is 0.048 cm^{-1} at 1064 nm, which is comparable to the scattering loss of the Nd:YAG single crystals produced 15 years ago. Compared with Konoshima's sample, we still need to improve our optical quality. But even for Konoshima's sample, the scattering loss at UV range is still a little high, which will cause the solarisation effects under lamp pump.

Fig. 4.36. The calculated absorption coefficient of 0.8 at.% Nd:YAG ceramics fabricated by (a) NTU and (b) Konoshima, respectively.

4.3.2 Lasing testing

We also did the LD pumping experiments for both samples at the same conditions. Before testing, both samples had been cut to the size of $3 \times 3 \times 7 \text{ mm}$ (shown in Fig. 4.37). No any optical coating was applied on both samples. Fig. 4.38 shows the schematic diagram

of the laser experimental setup. Output coupler is a concave mirror with 100 mm radius and the reflectivity is 90% at 1064 nm.

Fig. 4.37. The photos for laser testing samples.

Fig. 4.38. Pumping scheme diagram of the laser experiments.

Fig. 4.39a and b shows the laser testing results of our sample and Konoshima's sample, respectively. It can be observed that both samples show quite good laser results. The slope efficiency is around 40.0%.

It is well known that the homogenous distribution of the dopant has an important effect on the optical homogeneity of the laser ceramics. EDAX analysis of the 0.8 at.% Nd:YAG ceramics shown in Fig. 4.40 have proved that the microstructures of the Nd:YAG ceramics are chemically homogenous.

Fig. 4.39. The laser testing results on 0.8 at.% Nd:YAG ceramics fabricated by (a) NTU and (b) Konoshima, respectively.

Fig. 4.40. Energy-dispersive spectroscopy of the 0.8 at.% Nd:YAG ceramics.

4.4 Summary

1. Pure phase YAG powders have been synthesized at as low as 1200 °C by high energy ball milling. The reactivity and sinterability of the powders were improved by high-energy ball milling process. However, the ball-milled YAG powders were contaminated by the milling media, tungsten carbide, which is undesirable for fabrication of transparent ceramics.
2. Well-dispersed Nd:Y₂O₃ powders with spherical shape were prepared by carbonate precipitation process assisted with freeze drying. Yttria can be formed at 500 °C, but higher calcination temperature is necessary to decompose the carbonate completely. Our results suggested that freeze drying is contributed to

control morphology of the synthesized powders and the optimum calcination temperature of the yttrium carbonate precursor was 1000 °C for 4 h.

3. Highly transparent Nd:YAG ceramics, with various doping concentration, have been fabricated by vacuum sintering using as-synthesized Nd:Y₂O₃ powders and commercial Al₂O₃ powders as starting materials. With the doping concentration increased, the absorption coefficient increases whereas the emission intensity decreases because of concentration quenching. With the doping concentration increased from 0.3 at.% to 6.0 at.%, the fluorescence lifetime decreases from 284 μs to 65 μs. Dramatic lifetime decrease happen especially when the doping concentration is higher than 2.0 at.%.
4. The effects of the processing conditions had been optimized. Scattering loss is suppressed to 0.048 cm⁻¹ level. The in-line transmittance of the 4 at.% Nd:YAG sintered ceramics reaches higher than 84.3% at 1064 nm with 3.1 mm thickness.
5. Based on our optimized process, we have developed a diode-pumped 2 at.% and 0.8 at.% Nd:YAG ceramics laser, and the slope efficiency have been improved from 36.5% in coated sample to 40% in un-coated sample, respectively.

Chapter 5 Fabrication of eye-safe RE:YAG laser ceramics

5.1 Introduction

During the last decade, numerous YAG-based laser materials have been widely investigated all over the world, owing to its combination of excellent thermo-mechanical properties and favorable spectroscopic properties. Great achievements have been made since the first Nd:YAG ceramic laser was demonstrated by A. Ikesue's group in 1995[10]. Besides Nd:YAG, Er^{3+} , Tm^{3+} , Ho^{3+} and Tm-Ho co-doped YAG ceramics have also been a considerable current interest because of their most attractive laser applications around 2 μm wavelength at room temperature called "eye-safe" wavelength region [188-191].

Er^{3+} :YAG is an attractive laser medium owing to its particular spectra by the $^4I_{13/2} \rightarrow ^4I_{15/2}$ and $^4I_{11/2} \rightarrow ^4I_{13/2}$ transitions. Fig 5.1 shows a typical energy level diagram of Er:YAG. The laser around 3 μm on the $^4I_{11/2} \rightarrow ^4I_{13/2}$ transitions operated at room temperature, couples well into water and body fluids, give potential applications in medicine, biological labels, as well as pulsed and cw regimes. Moreover, although fluid water shows strong absorption at 2.94 μm , water vapor does not. This make the laser suitable for meteorological and some special metrology applications. Emission at 1.6 μm is useful for free space communication, range finding, spectroscopy, LIDAR and remote sensing system, due to high transmission of atmosphere, availability of sensitive photo-detectors and eye-safety aspects [192-194].

Fig. 5.1. Energy level diagram of Er:YAG laser.

Tm³⁺:YAG is an promising 2 μ m laser based on the transition of $^3F_4 \rightarrow ^3H_6$ shown in Fig. 5.2. This laser has higher pulse energy and high-efficient wide tunability about 100 nm widths. Additionally, it has a high quantum efficiency (~ 2), which compensates for its small emission cross section. This laser is advantageous in both CW and Q-switched operations at room temperature. It is an important laser sources for various applications in spectroscopy, range detection, and optical countermeasures. Moreover, Tm³⁺ laser is very efficient for superficial ablation of tissue, with minimal coagulation depth in air or in water. This makes thulium lasers attractive for laser-based surgery. This laser is also useful in environment studies for DIAL (Differential Absorption LIDAR) measurements of CO₂ and H₂O, Doppler velocimetry (wind shear detection, global wind speed measurement both from satellite and ground stations) and coherent Doppler-LIDAR (Light Detection and Ranging) [195-197].

Fig. 5.2. Energy level diagram of Tm:YAG laser.

Ho³⁺:YAG is an attractive laser material in the longer eye-safe 2.1 μm wavelength regime emitted by the $^5I_7 \rightarrow ^5I_8$ transition shown in Fig. 5.3. Due to its eye-safe laser wavelengths in the window of high atmospheric transmission, Ho³⁺ laser is suitable for several important modern applications. Tunable holmium 2.0 μm stimulated emission generation shows great potential for remote sensing and monitoring of atmospheric CO₂ and H₂O laser spectroscopic technologies. The CO₂ gas and water vapour molecules play important roles in global climate change, including the greenhouse effect (global warming). Compare with the small emission cross section of Tm:YAG lasers, Ho:YAG has high peak power. Its attractively long fluorescence lifetimes (about 10 ms) allow large energy storage for high Q-switching operation. Additionally, the unique ability of the Ho:YAG to vaporize, ablate and coagulate soft tissues and extremely hard materials, have made it the most versatile surgical laser available to today's laser surgeon [198-199]. Unfortunately,

owing to its no absorption bands in the 780-790 nm regions, it cannot be pumped directly by commercially available high-power diode laser.

Fig. 5.3. Energy level diagram of Ho:YAG.

In order to overcome the disadvantages of Tm:YAG and Ho:YAG laser, Tm/Ho co-doped YAG laser with a wavelength of 2.1 μm is developed recently. In the system, the Ho^{3+} serves as the active ion emitting at 2.1 μm by the $^5\text{I}_7 \rightarrow ^5\text{I}_8$ transition, while Tm^{3+} is used to enhance the efficiency of energy transfer to the active ion. The laser combines the advantages of Tm:YAG and Ho:YAG. The small laser-transition effective cross-sections ($7 \times 10^{-21} \text{ cm}^2$ at 2.097 μm), and long upper-laser-level lifetimes, in the range 5.5-10 ms, make it suitable for a compact and high power tunable mid-infrared laser with both a high conversion efficiency and a long term stability [190, 200]. The unique optical qualities make Ho-Tm:YAG co-doped lasers appropriate for coherent laser radar applications and atmospheric probing, as well as for medical applications [198].

Fig. 5.4. Energy level diagram of Ho/Tm:YAG laser.

In this chapter, based on the technology we achieved from the fabrication of Nd:YAG ceramics, Er:YAG, Tm:YAG, Ho:YAG and Tm-Ho co-doped YAG transparent ceramics have been fabricated, respectively. The optical properties of the ceramics were studied.

5.2 Fabrication of RE:YAG (RE = Er, Tm, Ho) transparent ceramics

The fabrication process and raw materials are very similar with that mentioned in chapter 4. The as-synthesized RE:Y₂O₃ powders calcined at 1000 °C for 4 h and commercial Al₂O₃ powders were blended together according to the stoichiometric ratio of Y_{3(1-x)}RE_{3x}Al₅O₁₂ and were ball-milled with high-purity Al₂O₃ balls in ethanol solvent, with 0.5 wt% tetraethyl orthosilicate (TEOS) added as a sintering aid. The powder mixtures were dried and pressed into Φ 20 mm pellets in a stainless steel die at 30 MPa, and then the green body was further cold-isostatically pressed at 200 MPa. The relative density of the green bodies is about 54-58 % of the theoretical value. The compressed pellets were sintered at 1730 °C for 12 h under vacuum of around 10⁻³ Pa in a furnace with tungsten

heating element. The ceramics were further annealed at 1450 °C for 10 h in a muffle furnace in air.

Phase identification of the sintered ceramics was performed by an X-ray diffractometer (XRD, Shimadzu, Kyoto, Japan) with Cu K_{α} radiation. Densities of the sintered RE:YAG ceramics were measured by the Archimedes method and deionized water was used as the immersion medium. Transmittance of the sintered ceramics was measured by UV-VIS-VIS method on Varian Cary-5000. A He-Cd laser with 325 nm was used as the PL excitation source and the PL signal was dispersed by a 300 mm monochromator combined with suitable filters and detected by a liquid-nitrogen-cooled InSb photodiode detector using the standard lock-in amplifier technique. All the measurements were performed under room temperature. The spectra were corrected according to the system response.

5.3 Optical properties of the RE:YAG transparent ceramics

All the samples after vacuum sintering can be characterized by cubic YAG (PDF: 33-0040). Fig. 5.5 shows the pictures of the RE:YAG ceramics doped with different concentration of rare earth ions after mirror-polished. The letters can be clearly read through the samples. The relative density of the ceramics reaches about 99.8% of the theoretical value.

Fig. 5.5. The photos of RE:YAG transparent laser ceramics.

The absorption spectrum of 1at.% Er:YAG ceramics with 2.73 mm thickness in the range of 1400-1800 nm are displayed in Fig. 5.6. The band assignments are also indicated in the figure. From the Fig. 5.7, it was found that the absorption increased with the Er^{3+} doping concentration.

Fig. 5.6. The absorption spectrum of 1 at.% Er:YAG ceramics.

Fig. 5.7. The dependence of absorption coefficient at 1532 nm on Er^{3+} doping concentration.

Fig. 5.8. Room temperature absorption and emission spectra of 0.5 at.% Er:YAG.

Fig. 5.8 shows the absorption and emission spectra of the Er:YAG transparent laser ceramics with doping concentration of 0.5 at.% at room temperature. The absorption peak is attributed to the $^4I_{13/2}$ band and the emission spectrum is due to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of the Er^{3+} in YAG-based garnet. From the figure, we can see that the strongest

emission peak centred at 1532 nm matches well the absorption peak, indicating the $^4I_{13/2}$ band suitable for diode pumping.

The transmittance spectrum of 6 at.% Tm:YAG ceramic with 2.87 mm thickness is shown in Fig. 5.9. The in-line transmittances in the visible region and the infrared region are both over 82%. There is no obvious decline of transmittance in the visible region, due to a limited number of scattering centers in the sample. The highest transmittance reaches up 84.4% at 2010 nm.

Fig. 5.9. The transmittance spectrum of the polished 6 at.% Tm:YAG ceramics.

The absorption spectrum of the Tm:YAG ceramics with 6 at.% doping concentration from 200 to 2500 nm at room temperature is shown in Fig. 5.10. We can see that Tm:YAG has seven strong absorption bands, which are associated with the energy level transitions in Tm^{3+} ions from the ground state 3H_6 to the excited states, 3P_2 , 1D_2 , 1G_4 , 3F_3 - 3F_2 , 3H_4 , 3H_5 , and 3F_4 , respectively. The central wavelengths corresponding to the peaks are 261, 357, 460, 681, 783, 1172, and 1622 nm, respectively. Two strong absorption peaks located at 681 nm ($^3H_6 \rightarrow ^3F_3$ - 3F_2) and 783 nm ($^3H_6 \rightarrow ^3H_4$) are consistent with the emission

wavelengths of the near-infrared diode and the infrared diode. The absorption coefficients are 5.65 cm^{-1} at 781 nm and 7.06 cm^{-1} at 1627 nm, respectively. Tm:YAG should be an excellent diode-pumped laser medium [201]. The room temperature emission spectrum from 1500 to 2300 nm by the $^3F_4 \rightarrow ^3H_6$ transition is illustrated in the Fig. 5.11.

Fig. 5.10. The absorption spectrum of 6 at.% Tm:YAG.

Fig. 5.11. Room temperature emission spectrum of 6 at.% Tm:YAG.

In Fig. 5.12, the absorption and emission spectra of 2 at.% Ho:YAG and 8 at.% Tm-2 at.% Ho co-doped YAG at room temperature is given. We can see that the strongest absorption peaks of the two samples all located around 700 nm, and both of them are suitable for near-infrared diode pumping. The emission spectra are shown in the inserted figures. For Ho:YAG, the emission spectrum from 1800 to 2200 nm is by the $^5I_7 \rightarrow ^5I_8$ transition. Compared with Tm:YAG (Fig. 5.10) and Ho:YAG (Fig. 5.12 (left)), the absorption and emission of the Tm/Ho co-doped YAG are both improved. This result can be attributed to the co-doped ions effect. In the co-doped sample, the absorbed pump radiation in the Tm 3H_4 self-quenches to the Tm 3F_4 , producing 2 Tm atoms in the Tm 3F_4 for every photon absorbed into the Tm 3H_4 . Since the Tm 3F_4 and Ho 5I_7 manifolds have energy levels that are partially coincident, energy can be efficiently transferred from Tm to Ho without the need for phonon assistance. In other word, the Tm³⁺ (3F_4) level transfer its excitation to the Ho (5I_7) level followed by Ho ($^5I_7 \rightarrow ^5I_8$) laser emission near 2 μm [202-203].

Fig. 5.12. Room temperature absorption and emission spectra of 2 at.% Ho:YAG (left) and 8 at.% Tm-2 at.% Ho co-doped YAG (right).

5.4 Summary

1. Other rare-earth elements doped RE:YAG (RE = Er, Tm, Ho, and Tm/Ho) transparent ceramics with desirable properties have been fabricate. The relative density of the sintered ceramics reaches about 99.8% of the theoretical value.
2. The absorption spectrum of 2 at.% Er:YAG is attributed to the $^4I_{13/2}$ band and the emission spectrum is by the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition. The strongest emission peak is centered at 1532 nm, matching well the absorption peak.
3. Seven strong absorption bands have been observed in the spectrum of 8 at.% Tm:YAG, which is resulted from the ground state 3H_6 to the excited states of the doped Tm^{3+} ions. The emission spectrum of the sample is attributed to the $^3F_4 \rightarrow ^3H_6$ transition.
4. The absorption and emission spectrum of Ho:YAG have been studied. The strongest absorption peak is located around 700 nm. The emission spectrum is resulted from the $^5I_7 \rightarrow ^5I_8$ transition. After co-doped with Tm^{3+} ions, the optical feature of the sample is improved.

Chapter 6 Conclusions and Future Directions

6.1 Conclusions

Since the first Nd:YAG ceramic laser oscillation was reported by A. Ikesue in 1995, till today, transparent laser ceramics have been a hot research topic of advanced materials. The fabrication process of transparent laser ceramics offer significant advantages over traditional single crystal growth techniques, such as reduced processing time, scaling to large size, design flexibility of doping ions. However, in order to get “real” lasing quality ceramics, it is important to strictly control the quality of the starting powders and the fabrication process and conditions. This project has investigated how to prepare the high quality powders and how to fabricate the lasing quality Nd:YAG transparent ceramics. In summary, rare-earth doped YAG and Y_2O_3 powders have been prepared by sol-gel combustion, co-precipitation and high-energy ball milling method, respectively. Special attentions have been paid on improving the quality of the synthesized powders. It is found that freeze-drying plays an important role on the control of powders agglomeration. Moreover, phase evolution, morphology, microstructure and sinterability of the powders have been studied. Using the prepared powders, rare-earth doped YAG transparent ceramics have been fabricated using the high vacuum sintering technique. The effects of some key parameters, such as calcination conditions, sintering temperatures, holding time, sintering aids, and doping concentration on the optical property of the sintered ceramics have been systematically investigated. The following major conclusions and achievements have been made in the project:

1. YAG nanopowders have been synthesized using the general and modified sol-gel combustion technique, respectively. It was found that solvent had an important effect on the phase transformation and morphology of the powders. Especially, the ethanol-deionized water solvent promoted the formation of YAG phase and lowered the onset crystallization temperature to as low as 800 °C.
2. The YAG nanopowders synthesized from ethanol-deionized water solvent with the modified sol-gel combustion are well dispersed and have a narrow particle size distribution. The sintered YAG ceramics show high relative density of more than 99%. However, the vacuum-sintered YAG ceramics are not transparent and show gray to black color due to carbon contaminations. Full oxidation of the residue carbons after combustion is crucial for the sintering of transparent ceramics.
3. YAG nanopowders prepared by the general co-precipitation method have good uniform particle size, but showed some hard agglomerates and neck links. The optimal calcination temperature of the precursor precipitate is 1200 °C and the YAG nanopowders obtained at this temperature show good reactivity and high sinterability. Due to pores trapped in the sintered ceramics, the fabricated YAG ceramics with 2 mm thickness are semi-translucent.
4. Freeze-drying plays an important role in the agglomeration control of nanopowders. Homogenously dispersed Nd:YAG nanopowders without any intermediate phase are synthesized from inorganic precursor by the modified co-precipitation process assisted with freeze drying for the first time. The prepared nanopowders are spherical and have a narrow particle sized distribution. Benefited from the high sinterability and uniform microstructure of the powders, Nd:YAG

transparent ceramics have been successfully fabricated with vacuum sintering technique.

5. YAG powders have been obtained at as low as 1200 °C applying the solid-state reactive sintering technique from the high-energy ball-milled $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ powders. The reactivity and sinterability of the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ powders are improved by high-energy ball milling activation process. However, the ball-milled YAG powders are contaminated by the milling medium, tungsten carbide, which is undesirable for the fabrication of transparent ceramics.
6. Well-dispersed Nd:Y₂O₃ powders with spherical shape were also prepared by carbonate precipitation process assisted with freeze drying. Pure phase Nd:Y₂O₃ can be formed at 500 °C. The optimal calcination temperature is 1000 °C for 4 h in order to decompose the carbonate completely. By employing the prepared Nd:Y₂O₃ powders and commercial Al₂O₃ powders as starting materials, highly transparent Nd:YAG ceramics have been fabricated by vacuum sintering.
7. The doping concentration has an important effect on the optical property of the fabricated Nd:YAG ceramics. With the doping concentration increased, the absorption efficiency increased whereas the emission intensity decreased because of concentration quenching. As the doping concentration increased from 0.3 at.% to 6.0 at.%, the lifetime decreases from 284 μs to 65 μs.
8. The effects of the processing conditions on the optical property of the Nd:YAG transparent ceramics had been investigated. Lasing quality ceramics have been fabricated. It is found that the scattering loss coefficient of the fabricated ceramics is as low as 0.048 cm⁻¹ and in-line transmittance of a 4 at.% Nd:YAG sintered

ceramics with 3.1 mm thickness is higher than 84.3% at 1064 nm. The slope efficiency of the ceramic lasers constructed with the Nd:YAG ceramic has been improved from 36.5% using the coated samples to 40% using the un-coated samples.

9. Based on our optimized process, various rare-earth ions doped YAG transparent ceramics targeting the eye-safe laser applications have been fabricated. The rare-earth ions doped YAG ceramics have desired optical properties.

6.2 Recommendations for future research

Rare-earth ions doped transparent ceramics as laser materials have main advantages: size scalability, tailored distribution of the active ions, and easy fabrication of composite objects. Although transparent ceramics with high optical transmittance were fabricated in the project, and high laser output had been obtained on the Nd:YAG ceramics, there is still a large space to further improve the optical property of the Nd:YAG ceramics. Several microstructures factors, such as the residue pores, impurities and grain-boundary phase contribute to the large optical loss of the fabricated ceramics. In order to get a thorough understanding on the matter, more detailed studies are needed. To this end, the following future works are proposed:

1. In the current project, it was found that freeze-drying is an effective technique for synthesis multi-component nanopowders with controlled composition. Based on this, we believe that further systematical works on co-precipitation synthesis assisted with

freeze-drying are necessary to thoroughly investigate the effect of processing parameters on the properties of YAG powders.

2. Extended study on the working mechanism of sintering aids should be conducted. For transparent ceramics, sintering aids are required to achieve high optical quality ceramics. Investigation on the working mechanism of sintering aids helps us to better understand the densification and grain growth of the ceramics.
3. Investigation on the correlations between laser property and the optical quality of the fabricated transparent Nd:YAG ceramics. Microstructural properties of ceramics govern their optical properties. For laser applications, defect-free ceramics are required to minimize the light scattering resulted from the residual pores or secondary phases. Ikesue's group reported that optical scattering in YAG transparent ceramics is caused almost solely by pores [204]. It is important to determine the correlations between porosity contents and optical properties.
4. Fabrication of large size transparent ceramics with homogenous composition for highly efficient high-power lasers. It is possible to fabricate large size laser ceramics through a glass-like fabrication process. This will lower the cost of laser materials. Fig. 6.1 shows a large size laser ceramics [205].
5. Development of new ceramic fabrication techniques to manufacture composite structures of transparent ceramics. Composite laser ceramics are promising materials for creation of new laser performance, such as high power, high efficiency, and high quality beam. The advance of modern ceramic fabrication technology allows the fabrication of multi-layered and multi-functional composite ceramic materials, e.g. YAG/Yb:YAG/YAG. Fig. 6.2 shows a continuous fabricating process of multi-

functional ceramics, which is similar to the iron and glass fabrication process. The green-sheet of ceramics is combined in the multi-layered sheets in the rolling mill [205], which highlights a possible future composite ceramic laser material fabrication process.

6. Fabrication of sesquioxides transparent ceramics with high melting temperature. Sesquioxides (such as Y_2O_3 , Sc_2O_3 , Gd_2O_3 , and Lu_2O_3) have proved to be promising laser materials for high-output-power and ultrashort-pulsed lasers due to their superior thermo-mechanical properties, strong Stark-splitting, and low phonon energies [206-207]. However, because of their melting-point is higher than $2000\text{ }^\circ\text{C}$, it is extremely difficult to grow large-size high-quality sesquioxides single crystal by conventional crystal growth methods. The fabrication process of transparent ceramics requires a temperature which is $400\text{-}700\text{ }^\circ\text{C}$ lower than for the melting point. Therefore, the technique enables the fabrication of sesquioxide laser ceramics.

Fig. 6.1. Large size ceramic laser materials.

Fig. 6.2. A future image of the multi-functional ceramics fabrication process.

Author's Publications

Journal papers

- [1] **Hua Gong**, Jian Zhang, Ding-Yuan Tang, Hui Huang, Jan Ma, Fabrication and laser performance of highly transparent Nd:YAG transparent ceramics from well-dispersed Nd:Y₂O₃ nanopowders by freeze-drying, J. Nanopart. Res. (Accepted).
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Conference Papers

- [1] **Hua Gong**, Jian Zhang, Dingyuan Tang, Hui Huang, Jan Ma, Agglomeration control and luminescent properties of Nd:YAG powders synthesized from freeze drying process, 5th Laser Ceramics Symposium, Dec. 9-11, 2009, Bilbal, Spain.
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