Fabrication and characterization of transparent sesquioxide laser ceramics

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2019

Yin, D. (2019). Fabrication and characterization of transparent sesquioxide laser ceramics. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/137215>

<https://doi.org/10.32657/10356/137215>

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FABRICATION AND CHARACTERIZATION OF TRANSPARENT SESQUIOXIDE LASER CERAMICS

YIN DANLEI

School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarized materials, and has not been submitted for a higher degree to any other University or Institution.

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Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journals in which I am listed as an author.

Chapter 4 is published as D. Yin, J. Wang, P. Liu, D. Luo, L. B. Kong, Z. Dong, and D.Y. Tang. Ytria nanopowders with low degree of aggregation by a spray precipitation method. *Ceramics International* **44**, 20472-20477 (2018). DOI: 10.1016/j.ceramint.2018.08.042.

The contributions of the co-authors are as follows:

- A/Prof Tang provided the initial project direction.
- I prepared the manuscript drafts. The manuscript was revised by Dr Wang.
- I conducted the experiments in A/Prof Dong's and A/Prof. Kong's research focus labs at the School of Materials Science and Engineering.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr Liu assisted in the hot isostatic pressing of the samples.
- Dr Luo assisted in the experimental result discussions.

Chapter 5 is published as D. Yin, J. Wang, P. Liu, H. Zhu, B. Yao, Z. Dong, and D.Y. Tang. Fabrication and microstructural characterizations of lasing grade Nd:Y₂O₃ ceramics. *J Am Ceram Soc* **00**, 1–7 (2019). DOI: 10.1111/jace.16671.

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- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr Liu assisted in the hot isostatic pressing of the samples.
- A/Prof Zhu assisted in the measurement and interpretation of CW laser performance.
- Ms Yao conducted transmission electron microscope and field-emission scanning electron microscope energy dispersive X-ray analysis.

Chapter 6 is published as D. Yin, J. Ma, P. Liu, B. Yao, J. Wang, Z. Dong, L. B. Kong, and D.Y. Tang. Submicron-grained Yb:Lu₂O₃ transparent ceramics with lasing quality. J Am Ceram Soc **102**, 2587– 2592 (2019). DOI: 10.1111/jace.16105.

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- A/Prof Tang provided the initial project direction.
- I prepared the manuscript drafts. The manuscript was revised by Dr Wang.
- I conducted the experiments in A/Prof Dong's and A/Prof. Kong's research focus labs at the School of Materials Science and Engineering.

- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr Ma assisted in the continuous-wave laser measurement.
- Dr Liu assisted in the hot isostatic pressing of the samples.
- Ms Yao conducted the analysis of the X-ray diffraction data.

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Acknowledgements

Firstly, I would like to express my special respect and gratitude to my supervisor, Prof. Tang Dingyuan, for his excellent guidance and encouragement in my study, and care for my life. His style of advising inspired me to have many creative ideas. Special thanks also go to my co-supervisor, Prof. Dong Zhili, for his generous support and valuable suggestions for my project.

I would like to express my sincere thanks to Dr. Wang Jun for his selfless help in every way. His mentoring gave me an easier start and the valuable discussions with him pushed me forward.

I would like to thank my dear friends and group members, Dr. Ma Jie, Dr. Liu Peng, Dr. Luo Dewei, Ms. Chen Geng, and Ms. Yao Bingqing, for their collaboration. It is a great honor to work with them.

I am particularly grateful for my parents and all of my family members, who have been loving and supporting me unconditionally. Their accompany gave me courage to overcome all the difficulties.

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Summary

Sesquioxide transparent ceramics such as Y_2O_3 , Lu_2O_3 , and Sc_2O_3 , have received a great attention as promising host materials for high powder solid-state lasers. To meet the laser applications requirements, porosity of the ceramics must be minimized to less than 0.01%. Densification of ceramics is closely related to quality of powders, sintering additives and sintering techniques.

In the present research, comprehensive studies regarding to the powder synthesis, sintering additive behavior and sintering controls were conducted. It was found that dispersants have great influence on the morphology and dispersity of both precursors and calcined powders in the chemical co-precipitation process. The utilization of spraying technique provided another way to reduce agglomerations and enhance the sinterability of the powders. At the optimized calcination temperature and sintering conditions, the transparency of sesquioxide ceramics were greatly improved by using the well dispersed powders. Moreover, the role of aliovalent sintering additives, CaO and CaO-ZrO_2 , in the Y_2O_3 ceramic densification were explored.

By optimizing the powder quality and sintering strategy, lasing grade rare-earth doped sesquioxide ceramics like $\text{Yb:Lu}_2\text{O}_3$ and $\text{Nd:Y}_2\text{O}_3$ with high lasing efficiency were realized.

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Chapter 1 Introduction

1.1 Motivation

Solid-state lasers are broadly used in industrial manufacturing, RGB light sources, environmental instrumentation, measurements and medical devices. In conventional solid-state lasers, the gain medium hosts are usually made of single crystals or glasses, the first example of which was the ruby laser designed by Maiman in 1960.^{1,2} Using single crystals to design solid-state lasers was progressed with the success in generating continuous-wave laser oscillation in an Nd: YAG single crystal in 1964.³ However, the growth of single crystals is very time consuming and complex facilities are required. Hence the high cost of single crystals leads to expensive solid-state lasers. Moreover, the difficulty of large-scale production and mechanical brittleness also restrain single crystals from being an ideal material of laser gain hosts.

Efforts to use transparent ceramics as a laser gain medium began with Dy: CaF₂ in cryogenic conditions in 1964.⁴ Then, Greskovich and Chernoch achieved the first oxide ceramic laser in 1973, by using Nd-doped yttralox (1 % Nd₂O₃, 89 % Y₂O₃ and 10 % ThO₂) ceramic rods.⁵ Since Ikesue et al.^{6,7} successfully fabricated transparent neodymium-doped yttrium aluminum garnet (Nd:YAG) ceramics and first achieved their laser oscillation in 1995, YAG ceramics have attracted more attentions as an important laser host material. Apart from that it is not unrealistic to fabricate YAG ceramics with the similar optical transmission to YAG single crystals, transparent YAG ceramics also have various advantages over single crystal as laser gain hosts, such as high yield, short fabrication period and ease of making large sizes.^{8,9} Thus specially designed structure can be easily realized and high power solid-state lasers can be achieved. The solid-state lasers with highest power (>100 KW) have already achieved

using the Nd:YAG ceramics produced by the Konoshima corporation¹⁰, showing a great potential of the YAG ceramics for high power solid-state lasers.

Recently, many studies shown that sesquioxide transparent materials, including Y_2O_3 , Lu_2O_3 , and Sc_2O_3 , are another excellent host material for solid-state lasers for their lower thermal expansion, higher thermal conductivity and lower phonon energy than YAG.^{11,12} For instance, thermal conductivity values of undoped Y_2O_3 , Lu_2O_3 , and Sc_2O_3 are 12.8 W/mK, 12.2 W/mK, and 15.5 W/mK respectively, higher than that of the undoped YAG (10.7 W/mK).¹³ For high-power solid-state lasers, the population of the terminal laser level tends to increase along with the rise of temperature and the lasing efficiency will be decreased, so it is significant to remove heat efficiently. In this case, high thermal conductivity of the laser gain media is required for effective heat removal. Therefore, the superior thermal properties of sesquioxides make them more promising laser gain hosts for high-power solid-state laser applications.

However, similar to YAG single crystals, the growth of sesquioxide single crystals is also very difficult and time demanding. For example, both the melting points of Y_2O_3 and Lu_2O_3 crystals are above 2400 °C, the growth of which requires very sophisticate and expensive facilities.^{10,14} In addition, it is difficult to machine and shape single crystals to meet different applications. Furthermore, it is not easy to realize large-scale production. On the contrary, sesquioxide transparent ceramics possess various advantages like cost effectiveness, ease to achieve large scale, feasible shape and good mechanical properties. In this respect, sesquioxide transparent ceramics become very important in terms of replacing single crystals as high-power laser gain hosts.

Currently, the primary challenge for fabricating sesquioxide transparent ceramics is to eliminate all the scattering sources inside the ceramics and to achieve high transparency which could be comparable to single crystals.

1.2 Objectives and scope

The purpose of this research is to fully understand the main factors that cause light scattering in sesquioxide transparent ceramics and to eliminate all the scattering centers during the ceramic fabrication processes. In this case, the optical properties of sesquioxide ceramics would be dramatically improved and qualified for solid-state laser applications. The research is organized to address the following objects:

1. Fabricate sesquioxide nano-powders with low degree of agglomerations and good sinterability.
2. Investigate the microstructure evolution under different sintering conditions to find the most favorable method to achieve fully densified transparent sesquioxide ceramics.
3. Explore the effects of different sintering additives on the densification of sesquioxide ceramics.

1.3 Organization of the thesis

The thesis is organized as following:

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the foundational powder synthesis principle and the classic ceramic sintering theory. In addition, various methods regarding the fabrication of sesquioxide transparent ceramics are reviewed.

Chapter 3 discusses the effects of dispersants on the powder morphology, dispersity and the subsequent sintering behavior of Yb:Lu₂O₃ ceramics.

Chapter 4 compares the novel designed spray co-precipitation method with the traditional dripping method. Yttria nano-powders with low degree of agglomeration are studied.

Chapter 5 introduces the fabrication procedure and microstructural characterizations of lasing grade Nd: Y₂O₃ transparent ceramics. The highest efficiency of Nd: Y₂O₃ solid-state laser is achieved.

Chapter 6 addresses the importance of powder homogeneity and sintering controls on the fabrication of submicron-grained Yb:Lu₂O₃ transparent ceramics.

Chapter 7 discusses the role of sintering additives. The effects of CaO single doping and CaO-ZrO₂ co-doping on the densification, grain growth and optical quality of Y₂O₃ ceramics are explored.

Chapter 8 gives the conclusion and recommendations for the future work.

Chapter 2 Background

2.1 Crystal structure of sesquioxide ceramics

The space group of sesquioxide crystal is $Ia\bar{3}$. RE_2O_3 takes the cubic bixbyite (C type) crystal structure, where RE implies Y, Lu, Sc and other lanthanide rare earth elements. Figure 2.1 shows the bixbyite structure of a typical sesquioxide, Y_2O_3 . Y atoms take 8a and 24d sites, while all the O atoms are located at normal sites, 48e.¹⁵

Fig. 2.1 Illustration of the bixbyite crystal structure.¹⁵

There is another explanation that the bixbyite structure can be regarded as an evolution from the fluorite (CaF_2) crystal structure. Figure 2.2 shows the evolution process from fluorite to bixbyite crystal structure. The large circles (shown in Fig. 2.2 (a), both white and black) represent oxygen atoms, and small black circles represent metallic ions. One-fourth of the O atoms are removed from the fluorite crystal lattice (large black circles), and metallic ions (small black circles) are moved in the directions of the small arrows. Then the remaining oxygen atoms are rearranged as shown in Fig. 2.2 (b). This

structure is called a C type M_2O_3 structure, and it is normally seen for medium to heavy rare earth sesquioxides. Lu_2O_3 , Sc_2O_3 , and the other lanthanide oxides also take this structure.¹⁵

Fig. 2.2 Crystal structure evolution from (a) MO_2 fluorite structure to (b) C type M_2O_3 structure.¹⁵

The physical, thermal and optical properties of Y_2O_3 are listed in the Table 2.1. Related with the cubic bixbyite structure, Y_2O_3 crystal is optically isotropic, with a broad range of transparency (0.23-8 μm).

Table 2.1 Physical, thermal and optical properties of Y_2O_3 ¹⁶

Physical, thermal and optical properties of Y_2O_3			
Melting point ($^{\circ}C$)	2410	Transparency range (μm)	0.23-8
Structure type	Bixbyite (cubic)	Refractive index (1000nm)	1.8892
Lattice constant ($\text{\AA}$)	10.607	Phonon energy (cm^{-1})	560

Thermal expansion			
coefficient at 300 k (10^{-6}K^{-1})	7.5	Mohs hardness	6.8
Thermal conductivity non-doped at 300 k (W/m · k)	13	Density (g/cm⁻³)	5.04

2.2 Factors that affect transparency of ceramics

Fig. 2.3 A schematic showing the light scattering sources of transparent ceramics.¹⁶

Polycrystalline ceramics are composed of randomly oriented micro-crystallites which are separated by grain boundaries generally with thickness of 2-10 atomic dimensions. Fig. 2.3 shows a typical microstructure of a ceramic. Typically, the scattering sources of ceramics include: (1) the presence of grain boundaries, (2) residual pores within the grains and on the grain boundaries, (3) secondary phases on the grain boundaries, (4) double refraction from birefringent ceramics, (5) impurities within grains and (6) surface roughness.¹⁰ In the case of laser ceramics, the scattering centers will lead to the decreasing of amplification efficiency of solid-state lasers. Therefore, the quantity of

scattering sources in transparent ceramics should be effectively controlled to perform an effective laser gain medium.

The strategy to realize highly transparent ceramics is to remove all possible scattering centers of light, such as removal of pores and second phase (impurity or glass phase) at grain boundaries, and to achieve isotropic lattice structure as well as high surface finish. Generally, impurities and the second phase can be easily removed by the precise control of the initial stoichiometry and strict monitoring during the fabrication process. However, the removal of residual pores to achieve full density ($> 99.9\%$ of the theoretical density) is the most challenging part. On the one hand, residual pores are considered the predominant light scattering sources in a given transparent ceramic because there is a huge difference between air and the host materials in refractive index. On the other hand, the porosity of un-sintered ceramic green bodies formed by both dry pressing and other wet forming techniques is usually over 40%. The huge initial amounts of pores make it even harder to obtain fully dense ceramic structures (porosity $< 0.1\%$).

2.3 Ceramic Powder

2.3.1 The basic units

Fig. 2.4 Interrelations between crystallites, particles and agglomerates.¹⁷

Figure 2.4 shows the relationships between crystallites, particles and agglomerates. Generally, all ceramic powders are composed of primary particles and their agglomerates. Primary particles are formed by crystallites which are single crystals that made out of a few unit cells. An agglomerate is defined as a small assemblage of primary particles, forming a “network of interconnective pores”¹⁸. The size and shape of agglomerates can be either uncontrolled (obtained during synthesis) or controlled by the process of granulation.

The size and porosity of the agglomerates vary depending on the number of primary particles and the way of their packing. The strength of an agglomerate, which determines the way of de-agglomeration, depends on the strength of the adhesive forces.

2.3.2 The competitive forces in agglomeration during synthesis

Various forces contribute to the formation of agglomerates: electrostatic forces, van der Waal forces, liquid bridges, capillary forces, solid bridges and polymer bridges. Agglomerates that formed due to weak attractive forces are called soft agglomerates which can be broken down to primary particles or small agglomerates by light mechanical forces or ultrasonication. Agglomerates formed by solid bridges between particles are called hard agglomerates which do not disintegrate into primary particles and need strong mechanical forces for breaking down to smaller agglomerates. In powders synthesis for ceramics, hard agglomerates are especially undesirable.

In an aqueous solution, oxide particles usually have charged surface thanks to the surface hydroxylation and transformation of the acquired surface hydroxyl groups depending on the solution pH, as shown in Fig. 2.5. The surface charge attracts counterions from the mother liquid. In this case, a layer of progressively changing charge concentration based on the distance from the interface can be formed in the bulk

solution. The layer is divided into two parts: (a) The layer near the particle surface, where counterions are adsorbed, is called Stern layer. (b) The layer next to the Stern layer is called diffuse layer. Both layers taken together are called double layer (Fig. 2.6).

Fig. 2.5 Effect of pH on the hydroxylated oxide particle surfaces.

Fig. 2.6 The electrical double layer in a solution near the particle surface.

When two particles in a solution come close due to random movements, the double layers of each particle overlap. Because of the same charge that the double layers of the two particles exhibit, electrostatic repulsion takes place. This hinders a possible contact of the particles and hence obstructs the formation of agglomerates.

However, there is also another force, van der Waals attraction forces, affecting the agglomeration behaviors. For a pair of particles synthesized in an aqueous solution, the nature of their interaction is decided by the repulsion energy (V_R) and the attraction energy (V_A). Thus, the total energy (V_T) is given by $V_R + V_A$. Fig. 2.7 shows the relationship of the V_R , V_A and V_T regarding to the particle distances. When the ion concentration is low or the distance between two particles is large, the particle interaction is dominated by the electrostatic repulsion. Under this condition, V_T (max) remains much larger than the kinetic energy of the dispersed particles. As a result, only weak agglomeration occurs. If the concentration of ions in the solution becomes higher, the particles will come closer. The van der Waals attractive forces become the domination and the kinetic energy is much larger than V_T (max). In this case, a strong agglomeration occurs.

Fig. 2.7 The effects of the electrostatic repulsion and van der Waals attraction forces on the potential energy between two particles.¹⁷

Liquid bridges connecting two particles are formed when they are drying from an aqueous solution. The residual liquid at the contact region exerts a capillary pressure, leading to an attractive force between the particles.

Solid bridges can be formed in two different ways: (a) when the liquid bridges between two particles are dried, the capillary force will lead to the shrinkage of the neck region and generate agglomeration; (b) when the particles are calcined at elevated temperatures, in which process there is a material transport at the neck region between two particles in contact.

The well understanding of the competitive forces regarding to agglomeration can be helpful to the prevention of agglomeration during powder synthesis or de-agglomeration in the following process. Various measures must be taken into consideration, such as optimum solution concentration, controlled pH, optimum reaction rate, time of particle aging, replacement of adherent water by organics, introduction of dispersants, mechanical de-agglomerations (milling). All of those will be addressed in the following chapters.

2.4 Sintering models

2.4.1 Driving force for sintering

During the ceramic sintering process, there is an accompanied decrease of the free energy of the system. The driving force for sintering refers to the sources that give rise to the lowering of the free energy.

Under the pressure-less sintering condition, the driving force of sintering is the reduction of the total interfacial energy. The total interfacial energy of a compact is γA ,

where γ is the specific surface (interface) energy and A is the total surface (interface) area of the compact. The reduction of the total energy can be expressed as:

$$\Delta(\gamma A) = \Delta\gamma A + \gamma \Delta A \quad (2.1)$$

Figure 2.8 shows the typical phenomena that occur during sintering. Both grain coarsening and densification lead to the total reduction of energy. Grain coarsening is related to the change of interfacial area (ΔA), while densification is related to the change of interfacial energy ($\Delta\gamma$). For solid state sintering, $\Delta\gamma$ is associated with the replacement of solid/vapor interfaces (surface) by solid/solid interfaces. In a sintering process, when the diffusion mechanisms that lead to densification dominate, pores tend to shrink, and finally be removed as sintering proceeds. However, if the diffusion mechanisms that lead to grain coarsening are in domination, both grain size and pore size will grow larger and suppress the driving force for densification. In this case, the complete densification of a compact will become very difficult. In practice, a sintering process is the competition between the two mechanisms.

Fig. 2.8 Basic phenomena occurring during sintering.¹⁹

As for the pressure assisted sintering, like hot pressing and hot isostatic pressing, the external pressure provides the major contribution to the driving force. The work done by the external pressure on the system of 1 mole particles can be expressed by:²⁰

$$W = p_a V_m \quad (2.2)$$

where p_a is the applied pressure, V_m is the molar volume, and W represents the driving force for densification.

2.4.2 Diffusion mechanisms

During sintering of ceramics, matter is transported from high chemical potential regions to low chemical potential regions. Fig. 2.9 shows six diffusion mechanisms relating to sintering: (1) surface diffusion, (2) lattice diffusion from the surface, (3) vapor transport, (4) grain boundary diffusion, (5) lattice diffusion from the grain boundary, and (6) dislocation resulted plastic flow.²¹ All of them contribute to the growth of necks between particles. However, only (4), (5) and (6) lead to densification, while (1), (2) and (3) lead to coarsening and reduce the driving force for sintering and hence, reduce the rate of densifying. In real case, all the diffusion mechanisms coexist during sintering. The relatively strengthening of one single mechanism is accompanied by the weakening of the others. The dominating mechanisms change at different sintering stages.

Fig. 2.9 Different diffusion mechanisms illustrated in a three-grain model: (1) surface diffusion, (2) lattice diffusion from the surface, (3) vapor transport, (4) grain boundary diffusion, (5) lattice diffusion from the grain boundary, and (6) plastic flow.²¹

2.4.3 Initial stage sintering

During the initial stage sintering, rapid interparticle neck growth occurs and the effective contact area rate between particles is generally increased from 0 to ~0.2. For the densifying mechanisms, there is also shrinkage accompanying neck growth. As shown in Fig. 2.10, the two-sphere model for densifying mechanisms accounts for interpenetration of the spheres. Assuming that the neck between two particles (with radius a) has a circular section with radius X and the cross-section with radius r , the main geometrical parameters can be derived as shown in the table of Fig. 2.10.

The initial stage usually lasts until the radius of the neck between the particles has reached 0.40-0.50 of the initial particle radius. In this stage, grain growth does not occur. Grain boundary is confined to the neck area, which is because the migration of the

boundary away from the neck would require a significantly increase in energy and area. After the neck area is slightly increased due to neck growth, the inhibition effect to grain boundary migration decreases and grain growth becomes possible. When grain growth occurs, it can be considered as the termination of the initial stage sintering.

Fig. 2.10 The two-sphere model of the initial-stage sintering for (a) non-densifying mechanisms and (b) densifying mechanisms.

2.4.4 Intermediate stage sintering

During the intermediate stage sintering, the pore phase is continuous. There are open pore channels sitting along the grain edges, as shown in Fig. 2.11. Densification occurs by the shrinking of the pores to reduce their cross-section and the material flux of grain boundary diffusion and lattice diffusion. As a result, the pores pinch off and finally become isolated pores at the three-grain junctions, which is the beginning of the final stage sintering. The intermediate stage usually covers the major part of the sintering, corresponding to the relative density change from ~65% to ~90%.

Fig. 2.11 Coble geometrical models for the intermediate stage sintering based on a hexagonal neck and a cut through the neck (A-B) with the material flux paths for grain boundary diffusion and lattice diffusion.

2.4.5 Final stage sintering

The final stage sintering begins when the pores pinch off and become isolated pores at the grain junctions. As the sintering proceeding, the pores shrink continuously thanks to the grain boundary diffusion and lattice diffusion mechanisms, and finally may disappear. The relative density in this stage achieves ~90% or above. When all the pores have been eliminated, the sintering would be accomplished, and ceramics are fully densified.

As the densification of ceramics in the final stage generally accompanies with grain growth, pore evolution and pore-boundary interactions, the microstructure in the final stage can develop in various ways.

2.5 Microstructure evolution

2.5.1 Grain growth

Grain growth occurs in both dense and porous polycrystalline solids at sufficiently high temperatures. During the initial stage and intermediate stage sintering, grain boundary migration rate is relatively low and grain growth is not likely to occur because the large open pores on grain boundaries can act as a drag force against the boundary movement. Nevertheless, during the final-stage sintering, when all the pores pinch off, this pinning effect disappears and fast grain growth will occur due to grain boundary diffusion.

Grain growth can be divided into two types: normal grain growth and abnormal grain growth. For normal grain growth, the grain growth models can be expressed as:

$$G^m = G_0^m + Kt \quad (2.3)$$

where G is the grain size at time t , G_0 is the grain size at $t=0$, and K is a temperature-dependent rate constant obeying the Arrhenius equation.

The grain boundary mobility (M_b) is related to the diffusion coefficient of atoms across the grain boundary (D_b), which is given by:²¹

$$M_b = \frac{D_b}{kT} \left(\frac{\Omega}{\delta_{gb}} \right) \quad (2.4)$$

where Ω is the atom volume, k is the Boltzmann constant, T is the absolute temperature, δ_{gb} is the grain boundary thickness.

Force on a pore-free grain boundary is given by:

$$F_b = 2\gamma a^2 / G \quad (2.5)$$

Where γ is the specific surface energy of grain boundary, a is the atomic size, G is the grain size.

Abnormal grain growth refers to a structure that shows very large grains in a matrix of finer grains. It can be caused by inhomogeneous particle size of the starting material, inhomogeneities in chemical composition and particle packing. During the ceramic fabrication, abnormal grain growth must be well-controlled or avoided. This is because abnormal grain growth during sintering limits the attainment of high density and it is commonly detrimental to the properties of the material.²²

2.5.2 Pore evolution

In the early stage of sintering, grain growth is very limited in porous green bodies. Grain coarsening dominates and result in the rounding of the particles shapes and the growth of the necks, leading to the microstructural changes to decrease the energy of the system.⁵ Actually, the sintering of compacts can be interpreted as a network of contacting grains interpenetrated by a network of porosity. Therefore, an understanding of pore evolution is necessary for a broader understanding of the microstructure evolution.

Fig. 2.12 shows the equilibrium shape of a pore which is determined by the number and the shape of the grains attached to it. At equilibrium, the chemical potential of the atoms in the pore surface must be the same, which means that the curvature of each pore surfaces is the same. The force can be expressed as:

$$\cos\left(\frac{\Psi}{2}\right) = \frac{\gamma_{gb}}{2\gamma_{sv}} \quad (2.6)$$

where ψ is the dihedral angle, γ_{gb} is the specific grain boundary energy, and γ_{sv} is the specific surface energy.

Assuming that for a pore with a dihedral angle $\psi=120^\circ$ surrounded by N grains, the pore has straight sides if $N=6$, convex sides if $N<6$, and concave sides if $N>6$. The pore with convex surface tends to shrink because the surface of the pore migrates towards its

center of the curvature (Fig.2.12(a)). In contrast, the pore with concave surface tends to grow. The thermodynamic analysis has been given by Kingery²³ that for a given dihedral angle (ψ), pores with a coordination number (N) greater than a critical value (N_C) will grow, whereas pores with $N < N_C$ will shrink. The relationship between ψ and N_C is given by:

$$\Psi = \frac{180^\circ N_C - 360^\circ}{N_C} \quad (2.7)$$

Fig. 2.12 Pore shape and stabilities determined by the pore coordination number (N) and the dihedral angle (ψ): (a) $N=3$, concave surfaces; (b) $N=8$, convex surfaces.²²

During actual sintering, the pore coordination number is always changing. For example, during the final stage sintering, with the proceeding of grain growth, the number of grains surrounding a pore will tend to decrease, which means that the pore with a high

initial N value will not grow consistently during sintering. It will begin to shrink sooner or later, depending on the evolution of grain size. However, owing to the decreasing driving force for densification with the increasing of the grain size, the complete elimination of this kind of pore will be still difficult. Therefore, it can be concluded that the large pores in a powder compact will have large values of N and will therefore be difficult to shrink, leading to residual porosity in the sintered material. The importance of reducing the degree of powder agglomeration and controlling particle packing for high density green body is therefore clear.

2.5.3 Pore-boundary interactions

The primary barrier to the full densification of a ceramic compact is from the separation of pores from grain boundaries.²⁴ It is known that pores on the grain boundaries can easily be filled primarily by the grain boundary diffusion mechanism. However, once a pore is trapped inside a grain, in other words, pore-boundary separation occurs, forming an intragranular pore, it is not likely to be removed. In this case, the interaction between pores and grain boundaries must be investigated.

Small size isolated pores on the grain boundary can be dragged along by the moving grain boundary and the shape of pores can be distorted by the force of the grain boundary. Fig. 2.13 shows a typical interaction between a grain boundary and an attached pore with different transport paths.

Fig. 2.13 Possible transport paths for a pore moving with a grain boundary²⁰

For each of the mechanisms indicated in Fig. 2.13, the pore mobility (M_p) is given by:²²

$$M_p = \frac{AD\Omega}{kTr^n} \quad (2.8)$$

where A is a constant, Ω is the atomic volume, k is the Boltzmann constant, T is the absolute temperature, r is the pore radius, D is the appropriate diffusion coefficient, and n is an exponent that depends on the diffusion mechanism: $D=D_s$ and $n=4$ for surface diffusion; $D=D_l$ and $n=3$ for lattice diffusion; $D=D_g$ and $n=3$ for vapor transport.

Maximum force on a spherical pore exerted by an attached boundary F_p :

$$F_p = \pi r \gamma \quad (2.9)$$

where r is the pore size, and γ is the specific surface energy of grain boundary.

The pore velocity (v_p) is defined as:

$$v_p = F_p M_p \quad (2.10)$$

Therefore, taking the effects of pore-boundary interactions on the kinetics of grain growth into consideration, pore-boundary separation will occur when $v_p < v_b$, which can be written as:

$$F_p M_p < F M_b \quad (2.11)$$

where F refers to the effective driving force on the boundary. Considering that N is the average number of pores surrounding a grain, Eqs. 2.11 can also be written as:

$$F_p M_p < (F_b - N F_p) M_b \quad (2.12)$$

Where M_b and F_b have been given in Eqs. 2.4 and 2.5, respectively.

Basing on the pore-boundary separation condition above, Brook has developed a model as shown in Fig. 2.14.²⁵ There are three regions in the diagram. For smaller, more mobile pores, they remain attached to the grain boundary without exert drag force on the boundary, so the boundary migration is controlled by the boundary mobility. In another region, larger, less mobile pores that still attached to the boundary, the boundary motion is controlled by the pore mobility owing to the pore drag effect. In the third region, pore-boundary separation occurs, where the boundary controls the migration when large pores are separated.

Fig. 2.14 Dependence of pore-boundary interaction on microstructural parameters.²⁵

Therefore, one effective way to prevent the pore-boundary separation is to restrain the pore size, remaining the high moving velocity of pores. This can be achieved by using well dispersed raw powders with low degree of agglomerations, forming homogeneous green bodies and increasing the initial packing density.

Another way is to use sintering additives to suppress the grain boundary mobility. As is shown in Fig. 2.14 (dash line), the introduction of dopants has the effect of extending the region of pore attachment. The possible explanation is that the dopants can form solid solution with the host material and then segregate at grain boundary. For the diffusion rate of segregated solute is generally slower than that of the host ions, the boundary migration is limited. Therefore, larger, less mobile pores can migrate with boundary rather than separate. In addition, aliovalent solute whose ionic radius is larger than the host ions might be more favorable in terms of inhibiting grain growth, as the grain boundary diffusion rate could be lowered as well.

2.6 Theoretical transmittance

The following two equations exhibit the calculation of theoretical light transmittance of a defect-free single crystal:²⁶

$$T=(1-R)^2e^{-\alpha t} \quad (2.13)$$

$$R=\frac{(n-n_a)^2}{(n+n_a)^2} \quad (2.14)$$

where α is the loss factor, t is the sample thickness, n is the refractive index of the single crystal, and n_a is the refractive index of air (approximately 1.000). If there is no scattering loss in the sample, then α is 0. Taken $n_a=1$, the theoretical transmittance can be expressed as:

$$T=100\left[1-\left(\frac{n-1}{n+1}\right)^2\right]^2 \quad (2.15)$$

For instance, at the wavelength of 500 nm, the refractive index of Y_2O_3 is 1.947. Therefore, the theoretical transmittance of Y_2O_3 at 500 nm wavelength is 80.4% based on the above equations.

2.7 Fabrication of sesquioxide ceramics

2.7.1 Powder preparation

It is known that in order to achieve highly transparent sesquioxide ceramics, powders with high purity, narrow particle size distribution, and low degree of agglomeration must be obtained. Generally, many methods have been developed for sesquioxide powder synthesis, such as ball milling^{27–29}, sol-gel processing³⁰, combustion synthesis^{31,32}, homogeneous precipitation^{33–36}, and chemical co-precipitation^{37–39}. Currently, chemical co-precipitation has been considered as a desired powder

synthesizing method. It has various advantages like simple synthesis process, short fabrication period, mass production, high powder purity, controllable rare earth ions doping concentration. Therefore, many studies on the chemical precipitation under different conditions have been conducted to decrease the powder agglomeration and promote the powder sinterability.

Saito et al. synthesized fine needle-shaped yttrium carbonate precursor by using long aging time (2 days) after precipitation.⁴⁰ After calcining the precursor at 1100 °C, weakly agglomerated Y₂O₃ powders with high sinterability were fabricated. He et al. synthesized round Y₂O₃ particles with isotropic surfaces by pre-treating the starting material with sulfuric acid.⁴¹ It was found that treating with sulfuric acid could inhibit mass transfer processes of powders related to densification. Li et al. studied the effect of different precipitants, ammonia (NH₄OH) and ammonium hydrogen carbonate (NH₄HCO₃), on powders' morphology and densification of YAG ceramics.⁴² It was found that the ammonium hydrogen carbonate derived precursor exhibited much weaker soft agglomeration. Jung et al. studied the effects of calcination atmosphere on Y₂O₃ particles.⁴³ They found that vacuum calcination is a crucial step to realize a dense spherical Y₂O₃ particle. After calcined at 1100 °C under vacuum, the pores inside the synthesized particles were notably reduced and the sinterability of Y₂O₃ was obviously promoted.

In addition, dispersants have been utilized to reduce agglomerates in chemical coprecipitation processes. Ikegami et al. found that adding ammonium sulfate was able to decrease the agglomerates of yttrium powders.⁴⁴ Specifically, compared with un-doped powders, sulfate-ion-doped yttria particles shown round edge after calcination and monodispersed particles were produced after calcined at > 1000 °C. Takayasu et al studied the morphology change of sulfate-doped Y₂O₃ powders and further demonstrated that doping with sulfate ions was able to prevent agglomeration by inhibiting grain boundary diffusion and lattice diffusion.⁴⁵ By using similar methods,

other sesquioxide powders (Lu_2O_3 and Sc_2O_3) with low degree of agglomeration were fabricated widely by different groups.^{46–48}

2.7.2 Forming technique

The commonly used forming techniques of sesquioxide ceramics includes dry pressing generally followed by cold isostatic pressing (CIP)^{49–51}, and slip casting^{37,52–55}.

The advantage of dry forming pressing followed by CIP is that it is easy to operate and time saving. Firstly, powders are loaded into a stain steel mold and pressed under pressure of 1 to 20 MPa to form initial pellets. Then the pellets are put into a CIP machine and further pressed under 50-200 MPa. The whole process can be easily completed within one hour. The relative density of the pellets shaped by this method can reach 55%. The packing homogeneity is relatively good on small samples.

The initial density and microstructural uniformity of ceramic green bodies can be improved by using wet forming technique like slip casting. It was found that compared with the CIP method, the green bodies shaped by slip casting have much narrower pore size distribution, which can greatly increase the sinterability of ceramics.^{55,56} In addition, it is more flexible in forming the ceramic shapes as wanted. Some composite structures like layered structures and core-shell structures can be achieved by slip casting, which will fulfill the requirement of different laser applications.

2.7.3 Sintering technique

2.7.3.1 Vacuum sintering

Vacuum sintering is a sintering process that allows ceramics to be densified under vacuum condition. It could achieve better results than those run at atmospheric pressure. By using vacuum sintering, translucent or transparent sesquioxide ceramics typically Y_2O_3 ^{12,57,58}, Sc_2O_3 ^{39,46}, and Lu_2O_3 ⁵⁹⁻⁶¹ have been successfully fabricated. However, owing to the relatively high densification temperature of sesquioxide ceramics, the driving force provided by vacuum sintering is inadequate. Some sintering strategies like rapid rate sintering⁵⁰ and two-step sintering⁶² have been utilized, though, it is still very hard to completely remove the pores inside ceramics. In this case, pressure-assisted sintering is widely used. Under high pressure condition, the driving force for densification is the dislocation resulted plastic deformation.⁶³ It allows ceramics to be fully densified at relatively low sintering temperature, thus grain growth could be well controlled during the final stage sintering.

2.7.3.2 Hot pressure (HP) sintering

HP is a high-pressure low-strain-rate powder metallurgy process for forming of a powder compact at a temperature high enough to induce sintering and creep processes. It is achieved by the simultaneous application of pressure and heat. Densification at high pressure works through particle rearrangement and plastic flow at the particle necks. HP has become an important technique for transparent ceramic fabrication.

In 1969, Dutta et al. successfully fabricated transparent Y_2O_3 ceramics by using hot pressing at low temperature ranging from 1300-1500 °C under high pressure ranging from 5000-7000 psi.⁶⁴ The obtained specimen showed sub-micron grain size and the infra-red transmission was over 80%. In 2010, Podowitz et al. fabricated transparent Eu: Y_2O_3 scintillator ceramics using hot pressing method.⁶⁵ The Eu: Y_2O_3 ceramics were sintered under 40 MPa at maximum temperature of 1580 °C. The in-line transmittance reached 70 % at 600 nm. In 2011, lasing grade Yb: Y_2O_3 ceramics was achieved by hot

pressing submicron co-precipitation powders at 1550 °C.¹⁴ The ceramic could lase in both cw and pulsed mode with 45% slope efficiency.

2.7.3.3 Hot isostatic pressing (HIP)

HIP subjects to a component to both elevated temperature and isostatic gas pressure in a high-pressure containment vessel. When the chamber heats up, the pressure inside the vessel will increase. Different from the HP whose pressure is applied along a single axis, the pressure in HIP system is applied to the material from all directions.

HIP technique has been widely used in the fabrication of transparent sesquioxide ceramics. Generally, hot isostatic pressing is used as the last step, combining with vacuum sintering and HP sintering. After pre-sintering, ceramics reach a relatively high density. Then the residual pores can be completely removed by a subsequent HIP step during the final-stage densification. The applied pressure of HIP is ranging from 50-300 MPa. Thanks to the high pressure, the ceramics can be densified at relatively low temperature, inhibiting the grain growth and intragranular pore formation.

In the last decades, highly transparent rare-earth doped sesquioxide ceramics have been realized, using vacuum sintering or hot pressure sintering plus HIP strategy. In 1996, Nd-doped $\text{HfO}_2\text{-Y}_2\text{O}_3$ ceramics with excellent transmittance were successfully fabricated by vacuum sintering at 1650 °C followed by HIP-ing at 1700 °C under 196 MPa of Ar.⁶⁶ The transmittance of the obtained ceramics in visible and infrared range was almost equivalent to that of a Nd:Y₂O₃ single crystal. In 2011, sub-micron grained transparent Er-doped Y₂O₃ and Sc₂O₃ ceramics were reported by Ballato et al.⁶⁷ The ceramics were fabricated by two-step sintering followed by HIP-ing at 1300 °C under 206 MPa for 3 h. The grain size was restrained to 0.3 μm and the superior mechanical property was also demonstrated. In addition, transparent Yb:Lu₂O₃ and Ho:Lu₂O₃

ceramics fabricated by HP plus HIP were reported by Sanghera and Kim.^{68,69} 2.5 W laser output of Yb:Lu₂O₃ and 0.2 W of Ho:Lu₂O₃ were realized, respectively. The highest laser efficiency of 10% Yb:Lu₂O₃ even reached 74%.⁷⁰ Recently, Ho-doped Y₂O₃ ceramics were fabricated by vacuum sintering at 1500 °C and HIP-ing at 1450 °C.⁷¹ The output power at 2 μm reached 1.3 W with a slope efficiency of 31.2%. It has been demonstrated that HIP is an efficient way to eliminate scattering sources inside ceramics and hence realize better optical properties.

Chapter 3 Fabrication of sesquioxide powders by chemical co-precipitation method with dispersants

3.1 Introduction

It is known that to fabricate fully densified sesquioxide ceramics, the degree of agglomeration in the raw powders should be as low as possible. This is because green bodies made from strongly aggregated powders tend to have non-uniform pore size distribution, which causes differential densification.^{72–74} In addition, the large pores induced by the agglomeration would be very difficult to eliminate, even using HIP.⁷⁵ Therefore, full densification of a compact is largely determined by the quality of the raw powder, especially the degree of agglomeration. Chemical co-precipitation process had been widely used to synthesize sesquioxide powders. High quality nano-sized sesquioxide powders have been reported by using this method.^{44,47,76} Also, it could be found that the degree of agglomeration of a powder is closely related to the morphology and dispersity of the precursors.

Dispersants have been utilized to reduce agglomerates in chemical co-precipitation processes. Ikegami et al. found that adding ammonium sulfate was able to decrease the agglomerates of yttrium powders.⁴⁴ Specifically, compared with un-doped powders, sulfate-ion-doped yttria particles shown round edge after calcination and monodispersed particles were produced after calcined at $> 1000\text{ }^{\circ}\text{C}$. Takayasu et al studied the morphology change of sulfate-doped Y_2O_3 powders and further demonstrated that doping with sulfate ions was able to prevent agglomeration by inhibiting grain boundary diffusion and lattice diffusion.⁴⁵ Lu et al fabricated highly transparent Ln_2O_3 ceramics by layered rare-earth hydroxide nanosheets precursor and demonstrated that the best sinterable oxide powders were prepared at the $\text{SO}_4^{2-}/\text{Ln}^{3+}$ molar ratio of 0.03.⁷⁶ Moreover, many organic dispersants have been reported in recent

years: Uckikoshi adopted PEI into Y_2O_3 suspensions.⁷⁷ Jin et al compared Dolapix CE64, Dispex A40 and Darvan C-N.⁵³ He et al. studied the dispersion behavior of aqueous Y_2O_3 suspensions using TAC dispersant and high density ceramics were achieved.⁷⁸

In this chapter, Yb-doped lutecia powders ($\text{Yb}:\text{Lu}_2\text{O}_3$) were synthesized by chemical co-precipitation method, using ammonium sulfate $((\text{NH}_4)_2\text{SO}_4)$ and polyacrylic acid (PAA) as dispersants, respectively. The effects of dispersants on the powder morphology, dispersity and sinterability were discussed. The optical properties of the as-sintered ceramics were also evaluated.

3.2 Fabrication process

Commercial powder of ytterbium oxide (Yb_2O_3 , purity>99.99%) was dissolved into nitric acid. Commercial lutecia powder (Lu_2O_3 , purity>99.999%, Jiahua Advanced Material Resources Co., Ltd, Jiangyin, China) was dissolved into hydrochloric acid forming LuCl_3 solution. The solutions were stoichiometrically mixed according to the chemical formula of $(\text{Yb}_{0.08}\text{Lu}_{0.92})_2\text{O}_3$ and diluted by distilled water to make a mother solution with Re^{3+} concentration of 0.2 mol/L. Dispersants were added into the mother solution as shown in table 3.1. Precipitant was a mixed $\text{NH}_4\text{OH}+\text{NH}_4\text{HCO}_3$ solution with a molar ratio of 1:0.9. The general process of ceramic fabrication by chemical co-precipitation is shown in Fig.3.1. Precipitant was dripped into the mother solution until the pH reached the range of 8 to 9. After being aged for 12 h, the slurry was filtered, washed three times with pure water and three times with ethanol, respectively, to remove undesired ions in the solution. Then, the precursor was dried and calcined in a muffle furnace (Nabertherm LHT 04/17) at 1200 °C for 3 h. After sieving, the obtained powder was dry pressed into pellets and cold isostatic pressed (CIP) at 200 MPa. The green bodies were vacuum sintered ($p \leq 10^{-3}$ Pa) at various temperatures and hot

isostatic pressed under 198 MPa. After annealing in air at 1000°C for 10 h (Nabertherm LHT 04/17; Lilienthal, Germany), the Y_2O_3 ceramics were mirror polished on both surface by using a Hyprez precision lapping machine (Model: EJW400-IN-D; Engis, Kanagawa-ken, Japan).

Table 3.1 Detailed information of the Yb:Lu₂O₃ powders.

Number	Dispersant	Dispersant concentration
N	NA	NA
S	(NH ₄) ₂ SO ₄	30 at.%
P	PAA	2 wt%

Fig. 3.1 Flow chart of the chemical co-precipitation process.

3.3 Characterization

Morphologies of the Lu_2O_3 commercial powder, $\text{Yb:Lu}_2\text{O}_3$ precursor and calcined powder were observed by a field-emission scanning electron microscope (FESEM, JSM-7600F, JEOL, Tokyo, Japan). Fourier Transform Infra-Red (FTIR) spectra were recorded by a FTIR Spectrometer (Frontier, PerkinElmer, USA) using KBr pellets. Microstructural analysis of the bulk ceramics was measured by a scanning electron microscope (SEM, JSM-6360A, JEOL, Tokyo, Japan). Relative density was calculated using the Archimedes method. In-line optical transmission was measured by an Ultraviolet-visible spectrometer (Carry 5000, Agilent, Santa Clara, CA, USA).

Room temperature continuous-wave laser performance of the as-sintered 8 at.% $\text{Yb:Lu}_2\text{O}_3$ ceramics was evaluated. The sample with the highest in-line transmission was selected and processed into $4 \times 4 \times 2$ mm polished but uncoated slabs. The ceramic slabs were wrapped with indium foil and put in a two-mirror cavity with total cavity length of 12 mm. The pump source was a fiber-coupled laser diode whose central wavelength is 940 nm. The input plano-plano mirror (IM) was dichroic coated with high reflectivity ($R > 99.7\%$) for 1000-1100 nm and high transmission for pump wavelength. The output mirror was a plano-plano output coupler (OC). The laser output power was measured with a laser power/energy meter (NOVAII, OPHIR).

3.4 Results and discussion

3.4.1 Powder characterization

Figure 3.2(a) shows the morphology of the Lu_2O_3 raw powder. There are obvious hard agglomerates whose size is in the range of 1-5 μm . The primary particle could not be distinguished from the image. Fig. 3.2(b) shows the $\text{Yb:Lu}_2\text{O}_3$ powder synthesized by

co-precipitation method without using any dispersants and calcined at 1200 °C for 3 h. The dispersity of the powder was dramatically improved after the co-precipitation process. Primary particles are easily distinguished, whose sizes are around 100 nm. It is demonstrated that co-precipitation method could greatly change the particle morphologies and reduce the degree of powder agglomeration. However, large agglomerates with the size of around 1 μm still can be found.

Fig. 3.2 FESEM image of (a) commercial Lu₂O₃ powder and (b) Yb:Lu₂O₃ synthesized by co-precipitation method.

Fig. 3.3 (a) and (b) show the FESEM images of Yb:Lu₂O₃ precursors synthesized using (NH₄)₂SO₄ and PAA as dispersants, respectively. Large agglomerates could not be observed in both precursors. The precursor synthesized with PAA exhibits better dispersity and lower degree of soft agglomeration. This is because during the precipitation process, the chemical function group of COO⁻ anchored with the precursor monomers and the long carbon chain of PAA provided homogeneous separation between metal precursors.⁷⁹

After calcining at 1200 °C for 3 h, the morphologies of the Yb:Lu₂O₃ powders show obvious differences. The primary particle units are easy to be distinguished in the (NH₄)₂SO₄ doped powder (S powder), with primary particle size of 120 nm (Fig. 3.3 (c)). The particles are aggregated only by electrostatic forces without solid bridges in between. This is in coincidence with the previously reported results that the sulfate ions in Y₂O₃ powders could inhibiting grain boundary diffusion and lattice diffusion and hence prevent the formation of necks between particles.^{44,45} As for the PAA doped powder (P powder), the primary particle size is around 85 nm. However, it exhibits a coral-like structure whose particles possess round edge and stick together. The initial decomposition temperature of PAA is around 300 °C. As the temperature rising, PAA started to decompose. Meanwhile, the physical separation effect of the long carbon chain between precursors became weaken. Therefore, the diffusion in the particle contacting area led to the formation of agglomerates.

Fig. 3.3 Morphology of precursors and calcined Yb:Lu₂O₃ powders synthesized using (a)(c) 30 at.% (NH₄)₂SO₄, and (b)(d) 2 wt% PAA.

Fig. 3.4 shows the particle size distribution of the powders using different dispersants. There are two peaks in the S powder. Based on the FESEM images, it can be speculated that the first peak at 0.17 μm indicates the distribution of primary particle units dispersed by ultrasonic. The second peak at 4.7 μm indicates the size distribution of the particles compacted by electrostatic force. As for P powder, apart from the first two peaks similar to those in the S powder, there is an extra peak corresponding to the hard agglomerates. As a result, the P powder shows wilder particle size distribution and higher degree of agglomeration.

Fig. 3.4 Particle size distribution of Yb:Lu₂O₃ powders synthesized using (NH₄)₂SO₄ (S Powder) and PAA (P Powder).

3.4.2 Vacuum sintering behavior

Figure 3.5 shows the relative densities of the Yb:Lu₂O₃ samples derived from S powder and P powder after vacuum sintering at different temperatures. Firstly, the higher relative density (90%) of S powder at earlier sintering stage (1400 °C) suggests the higher initial density of the green body. It is known that powders with narrow particle size distribution are easier to form homogeneous green bodies and increase the initial packing density.⁸⁰ In addition, the densification temperature of S powder is lower than that of P powder. For instance, the samples derived from S powder rapidly densified in the temperature range of 1460-1540 °C and the final density is 98.9%. However, the rapid densifying temperature range of P powder is 1500-1650 °C and the highest density is merely 97.8%.

Fig. 3.5 Sintering map of the Yb:Lu₂O₃ samples derived from different powders.

Fig. 3.6 presents the microstructural evolution of the Yb:Lu₂O₃ samples derived from different powders. As the densification temperature of S powder is relatively low, there is only slight grain growth when the temperature was increased from 1460 °C (0.61 μm) to 1540 °C (1.63 μm). At 1540 °C, only isolated pores locating on the grain boundaries

and the density has reached 98.7%. It indicates the beginning of the final stage sintering. As the sintering temperature was further increased, pore-boundary separation occurred. At 1600 °C, pores were trapped by grains forming intragranular pores and the grain size reached 9.92 μm.

The microstructure evolution of the P samples is more complicated. 1) The higher degree of agglomeration contributes to the higher porosity of the green bodies. According to Kingery's model²³, for a pore with a dihedral angle ψ surrounded by N grains, the pore will grow if N is greater than a critical value (N_C), whereas pore will shrink when $N < N_C$. N_C can be calculated according to:

$$\Psi = \frac{180^\circ N_C - 360^\circ}{N_C} \quad (3.1)$$

In a high porosity green body, there are more grains surrounding each pore. In other words, N is greater than N_C . Hence pores tend to grow during sintering. As shown in Fig. 3.6 (b) and (d), the pore size at 1540 °C is greatly larger than that at 1500 °C. 2) When the temperature rose from 1500 °C to 1540 °C, the grain grows rapidly (0.66 μm to 3.41 μm) with a slight density increase. It indicates that in the initial stage and intermediate stage sintering, the process dominated by both coarsening and densifying mechanisms rather than by densifying only. 3) In order to increase the driving force for densification, the sintering temperature was continuously improved. However, it resulted in the overlarge grain size which reached 12.92 μm at 1650 °C (Fig. 3.6 (f)) and finally 15.25 μm at 1700 °C (Fig. 3.6 (h)).

Fig. 3.6 SEM images of the samples derived from (a)(c)(e)(g) S powder and (b)(d)(f)(h) P powder and vacuum sintered at different temperatures.

Fig. 3.7 shows grain size of the as-sintered ceramics sintered at different vacuum sintering temperature for 5 h. It reveals that the critical temperatures where fast grain growth occurs are different. For S powder, obvious grain growth started at 1540 °C, while the critical temperature of P powder is only 1500 °C.

Fig. 3.7 Grain size of the Yb:Lu₂O₃ ceramics as a function of sintering temperature.

Previous studies have shown that full densification of ceramics by sintering followed by HIP would only be possible when the open pores were completely eliminated.⁸¹ In addition, during pressure assisted sintering, the densification rate can be expressed as¹⁹:

$$\frac{dp}{dt} = \frac{101D_b\delta_b V_m P_{\text{appl.}}}{RTG^3} (1-\rho)^{\frac{1}{3}} \quad (3.2)$$

$$\frac{dp}{dt} = \frac{61D_l V_m P_{\text{appl.}}}{RTG^2} (1-\rho)^{\frac{2}{3}} \quad (3.3)$$

It can be seen that in order to enhance the densification rate by hot isostatic pressing, a reduction in grain size is necessary.

Fig. 3.8 presents the SEM image of the P-sample after vacuum sintering at 1520 °C for 30 h. Compared with Fig. 3.6 (b), it is obvious that continuous pores have been pinched off. The relative density is improved from 88% to 93.3%, while the grain size is

restricted within 0.82 μm . It reveals that porosity and grain growth control can be realized by lowering the sintering temperature as well as lengthening soaking time.

Fig. 3.8 SEM image of the Yb:Lu₂O₃ ceramic fabricated derived from P powder and vacuum sintered at 1520 °C for 30 h.

3.4.3 HIP treatment

Figure 3.9 presents the in-line transmission and microstructure of S sample after vacuum sintering at 1500 °C for 10 h followed by HIP-ing at 1480 °C. The obtained ceramic exhibits a dense structure, with average grain size 0.96 μm . The transmittance reached 79.3% at 600 nm. It indicates that nearly all the pores have been eliminated by HIP treatment, demonstrating the excellent homogeneity and sinterability of the S powder. The absorption between 900-1100 nm is corresponding to the transition of Yb³⁺ from the ground state $^2F_{7/2}$ to the excited state $^2F_{5/2}$.

Fig. 3.9 In-line transmission with inset SEM image of the 8 at.% Yb:Lu₂O₃ ceramic derived from S powder after vacuum sintering at 1500 °C for 10 h plus HIP at 1480 °C.

Fig. 3.10 (a) presents the in-line transmissions of Yb:Lu₂O₃ ceramics that derived from P powder and sintered under different conditions. The highest transmittance comes from the P sample that was vacuum sintered at 1520 °C for 30 h and HIP-ed at 1480 °C, which is 78.5% at 600 nm. When the HIP-ing temperature was increased to 1510 °C, the transmittance was slightly decreased to 73.4%. In addition, under the same HIP-ing conditions, when the vacuum sintering temperature was increased to 1550 °C and 1570 °C, the transmittance was also decreased to 67.7% and 65.2%, respectively. It indicates that both vacuum sintering temperature and HIP-ing temperature have a great influence on the transparency of the ceramics.

Moreover, the highest transmittance of P samples is still lower than that of S samples in the visible wavelength range (400-760 nm). This is caused by the nano-sized residual pores inside the P sample, as circled in Fig. 3.10 (b). Fig. 3.10 (c) shows the photograph of the P sample after vacuum sintering at 1520 °C for 30 h and HIP at 1480 °C. A certain degree of haze could be observed.

Fig. 3.10 (a) In-line transmissions of 8 at.% Yb:Lu₂O₃ ceramics that derived from P powder under different sintering conditions, (b) SEM image and (c) photograph of the P sample after vacuum sintering at 1520 °C for 30 h and HIP at 1480 °C.

3.4.4 Room temperature laser oscillation

Fig. 3.11 shows the CW laser output power of P sample versus the absorbed pump power measured using three different output couplers (OC=5%, 10%, 15%). The output power increased linearly with the increase of the absorbed pump power, and no output power saturation was observed. With the T=5% output coupler, a maximum output power of 3.0 W was achieved with 20 W absorbed pump power, corresponding to a slope efficiency of 21.2%.

Fig. 3.11 CW laser output power as a function of the absorbed power for the P- 8 at.% Yb:Lu₂O₃ ceramic lasing at 1079 nm.

Fig. 3.12 shows the CW laser output power of S sample versus the absorbed pump power measured using three different OC (2.4%, 5%, 12%). It is worth noticing that although the transmittance of the S sample was higher (Fig. 3.10 (a)), the optimized laser efficiency of the S sample was merely 7.2% with output power of 0.42 W, which was much lower than those of P sample.

Fig. 3.12 CW laser output power as a function of the absorbed power for the S- 8 at.% Yb:Lu₂O₃ ceramic lasing at 1079 nm.

3.4.5 Impurity induced photodarkening

After pumped by the 940 nm laser diode, a cross-like darkened part on the ceramic slab can be observed, as shown in Fig. 3.13 (a). The darkened part right fit the laser beam irradiation trace during the CW laser operation. Fig. 3.13 (b) shows the in-line transmission of the ceramic before and after pumping. In the testing wavelength range (200-800 nm), there is a transmission degradation at 400-700 nm. This phenomenon is very similar to the previous reported pump laser induced photodarkening in ZrO₂-doped Yb:Y₂O₃ ceramics⁸². In that paper, 1 at.% ZrO₂ was doped into Yb:Y₂O₃ ceramics as sintering additive. After irradiated by a 940 nm LD, photodarkening phenomenon can be observed with broadband absorption at 400-700 nm. The explanation is that as electrons of the Yb³⁺ were resonantly pumped to the excited state, some of them were trapped at the Zr⁴⁺ sites forming the Zr³⁺ color centers. The electrical or irradiation induced color centers have also been reported in some aliovalent ions doped transparent materials like Si⁴⁺-doped YAG⁸³, Y³⁺-doped ZrO₂^{84,85}, and B³⁺-doped SiO₂⁸⁶.

Fig. 3.13 (a) The photograph of the S- 8 at.% Yb:Lu₂O₃ ceramic slab pumped by a 940 nm laser beam, and (b) in-line transmission of the S- 8 at.% Yb:Lu₂O₃ ceramic slab before and after pumping.

However, considering that no aliovalent ions have been induced as sintering additive, the possible reason is that the SO₄²⁻ ions have not been completely removed by calcination. Fig. 3.14 shows the FTIR spectra of the Yb:Lu₂O₃ precursor and powders after calcination. The absorption bands in the S precursor, which are in the range ~1015-1160 cm⁻¹, are diagnostic of SO₄²⁻. After 1200 °C calcination, a very weak absorption in the range ~1015-1160 cm⁻¹ in S powder still can be detected. In comparison, the FTIR spectra of P powder do not exhibit any absorption in that range. It suggests the existence of the residual SO₄²⁻ in S powder.

After sintered in oxygen-free atmosphere, the S^{6+} in SO_4^{2-} might be reduced to S^{4+} and dissolved into the $Yb:Lu_2O_3$ lattice. Owing to the charge imbalance, the substitution of Y^{3+} by S^{4+} would produce positively charged regions, which would trap free electrons during laser operation hence form color centers. In this case, the laser efficiency was greatly compromised by the photodarkening effect.

Fig. 3.14 Fourier transform infrared spectra of the $Yb:Lu_2O_3$ precursor and powder after calcination.

3.5 Conclusions

In this chapter, well dispersed 8 at.% $Yb:Lu_2O_3$ powders have been synthesized by using chemical co-precipitation method. $(NH_4)_2SO_4$ and PAA were induced, respectively, working as dispersants. Highly transparent 8 at.% $Yb:Lu_2O_3$ ceramics have been successfully fabricated using two different kinds of powders.

The $(NH_4)_2SO_4$ doped $Yb:Lu_2O_3$ powder showed lower degree of agglomeration and better sinterability. It has been demonstrated that green bodies derived from S powder had higher initial density and were densified at lower sintering temperature. After

vacuum sintering at 1500 °C for 10 h and HIP-ing at 1480 °C for 4 h, the S sample showed higher in-line transmittance which reached 79.3% at 600 nm. However, the residual sulfur contamination carries the potential risk of degrading the laser performance of ceramics. The photodarkening effect caused by the residual sulfur would result in low lasing efficiency.

Using PAA as dispersant, very loose precursors were obtained. After calcination, certain agglomerates were detected in the powders, which contributed to the residual pores in the as-sintered ceramics. However, by optimizing the sintering strategy, transparent Yb:Lu₂O₃ ceramics have been fabricated which transmittance 78.5% at 600 nm. A maximum output power of 3.0 W was achieved corresponding to a slope efficiency of 21.2%. The photodarkening was not observed in P sample.

Chapter 4 Preparation of sesquioxide nano-powders with low degree of aggregation by a spray precipitation method

4.1 Introduction

In Chapter 3, effects of dispersants on sesquioxide powder synthesis and ceramic fabrication have been discussed. Indeed, powder's morphology, dispersity and sinterability could be improved by the utilization of dispersants. However, there is also possibility that impurities could be introduced owing to the dispersant's incomplete elimination. In this case, the doping concentration and eliminating condition of dispersants need to be well controlled. Moreover, alternate method to reduce the degree of powder agglomeration is worth studying.

In order to improve the precursor quality, a spray technology has been proposed recently.^{87,88} In those studies, particle morphology has been improved. However, powders synthesized by the spraying method and the normal method were not well compared under the same experimental condition. Specifically, the detailed information on how spraying method affected agglomeration of powders and the subsequent sintering process have not been studied.

In this work, the spray precipitation method was employed. The way how the spray precipitation technique affected the morphology and aggregation degree of the Y_2O_3 precursors, the calcined powders, and the subsequent densification was systematically studied. In order to better clarify the principle, dispersants and sintering additives were not used in the present study.

4.2 Fabrication process

Y_2O_3 nanopowder was synthesized by using the forward-strike precipitation method. Firstly, commercial Y_2O_3 powder (purity > 99.99%) was dissolved into hot hydrochloric acid and then diluted with distilled water to make YCl_3 mother solution, with Y^{3+} concentration of 0.2 mol/L. Precipitant was a mixed solution of $\text{NH}_4\text{OH} + \text{NH}_4\text{HCO}_3$ with a molar ratio of 1:0.9. Fig. 4.1 shows a schematic diagram of the experimental setup, where the mother solution was divided into two bunches. In the first group, the yttrium precursor was precipitated by dripping the precipitant into the mother solution (D precursor), as shown in Fig. 4.1 (a). Inner diameter of the pipe shown in Fig. 4.1 (a) is 3 mm, with a droplet size of about 4.5 mm (Fig. 4.1 (c)). In the other group, precipitant was spraying atomized into the mother solution (S precursor), as shown Fig. 4.1 (b). It is worth mentioning that the size of the sprayed droplet is merely 180 μm , as shown in Fig. 4.1 (d).

Fig. 4.1 Schematic diagrams of (a) dripping method and (b) spraying method and drip sizes of the (c) dripping method and (d) spraying method.

In both cases, the precipitant was introduced into the mother solution at a rate of 6 ml/min, until the pH value reached 8.5. After aging for 12 h, the slurry was filtered, washed for three times each with pure water and ethanol, respectively, to remove the undesired ions in the solution. Then, the precursors were dried and calcined at 1200 °C for 3 h. After passing through a 160-mesh sieve, the obtained powders were dry pressed into pellets of 15 mm in diameter and cold isostatic pressed (CIP) at 200 MPa. The green bodies were then vacuum sintered ($p \leq 10^{-3}$ Pa) at temperatures from 1450 to 1800 °C to examine the sintering behaviors. Selected samples were further hot isostatic pressed (HIP-ed) at 1480 °C for 3 h at 196 MPa in argon gas for further densification. After annealing in air at 1000 °C for 10 h (Nabertherm LHT 04/17, Lilienthal, Germany), the Y₂O₃ ceramics were mirror polished on both surfaces, with thickness of about 2.5 mm, by using a Hyprez precision lapping machine (Model: EJW400-IN-D; Engis, Kanagawa-ken, Japan).

4.3 Characterization

Morphologies of the powders were observed by using a Leo 1550 field-emission scanning electron microscope (FESEM; Leo 1550, Cambridge, Cambridgeshire, UK). Particle size distribution was measured by using a LA-960 particle size analyzer. Brunauer–Emmett–Teller (BET) surface area of the powders was measured by using a Micromeritics Tristar II-3020 nitrogen absorption apparatus (Norcross, GA). Crystalite size was characterized by using a Shimadzu X-ray diffractometer (XRD, Shimadzu, Kyoto, Japan). Bulk densities of the ceramics were measured using the Archimedes method. In-line transmittance was recorded by using a UV–VIS–NIR spectrometer (Carry 5000, Agilent, Santa Clara, CA). Microstructures of the bulk ceramics were observed by using a scanning electron microscopy (SEM, JSM-6360A, JEOL, Tokyo, Japan). Average grain size was measured by using the Nano Measure software, with at least 200 grains countered for each sample.

4.4 Results and Discussion

4.4.1 Powder Properties

Figure 4.2 shows FESEM images of the Y_2O_3 precursors and the calcined powders fabricated by using different methods. Although, in certain areas the precursor synthesized by using the dripping method (D-precursor) showed high local dispersity, large hard agglomerates with a size much larger than $10\text{ }\mu\text{m}$ were frequently observed, as shown in Fig. 4.2 (a). In contrast, such large hard agglomerates were not observed in the sprayed precursor (S-precursor), as illustrated in Fig. 4.2 (b). High-magnification FESEM image (Fig. 4.2 (b) inset) confirms the absence of hard agglomeration in S-precursor. Figure 4.2 (c) shows FESEM image of the D-powders after calcining at $1200\text{ }^\circ\text{C}$ for 3 h. The primary particle size of the D-powders was about 90 nm , with a BET surface area of $10.89\text{ m}^2/\text{g}$. However, it is obvious that a certain number of large agglomerates were present in the D-powder, as highlighted with red circles. The primary particle size of the S-powder was 80 nm (Fig. 4.2 (d)), however it exhibited much lower degree of agglomeration. No agglomerates of $>2\text{ }\mu\text{m}$ were observed in the S-powder. BET surface area of the S-powder was also much higher ($14.61\text{ m}^2/\text{g}$) than that of the D-powder.

Fig. 4.2 FESEM images of the precursors and calcined powders synthesized with drip precipitation and spray precipitation methods: (a) D-precursor, (b) S-precursor, (c) D-powder and (d) S-powder.

Fig. 4.3 shows particle size distributions of the two powders after calcination. Both of the powders have two peaks. The first peak indicates the size distribution of the particles compacted by electrostatic force, which is twice or triple of the primary particle size. The other peak shows the degree of agglomeration including both soft and hard agglomerations. It can be found that the D-powder has a wide range of agglomeration size from 740 nm to 5.2 μm (Fig. 4.3 (a)). In sharp contrast, the S-powder showed much less agglomeration, with much smaller sizes and narrower size distribution (740 nm to 1.6 μm), as revealed in Fig. 4.3 (b). This observation is consistent with the FESEM images of the powders.

Fig. 4.3 Particle size distributions of the Y_2O_3 powders prepared by (a) drip and (b) spray precipitation methods.

To better compare the degree of agglomeration in those two powders, the particle sizes of the Y_2O_3 powders characterized by different methods were listed in Table 4.1. The BET particle size (D_{BET}) was calculated according to the formula $D_{\text{BET}}=6/(\rho \cdot S_{\text{BET}})$, where ρ is the theoretical density of Y_2O_3 crystal (5.03 g/cm^3) and S_{BET} is the BET surface area. Interestingly, the crystallite size of the D-powder (54 nm) was smaller than that of the S-powder (94 nm), however showed a higher value in D_{BET} , which indicates the existence of hard agglomeration. The S-powder showed similar values among the D_{BET} , D_{FESEM} , and D_{XRD} , suggesting low agglomeration degree of the powders.

Table 4.1 Particle sizes of the Y_2O_3 powders characterized by different methods

Synthesize method	BET surface area (m ² /g)	D _{BET} (nm)	Primary	Average	Agglomeration size from PSD (μm)	Crystallite size from XRD (nm)
			particle size from FESEM (nm)	particle size from PSD (nm)		
D-powder	10.89	110	90	300	0.7-5.2	54
S-powder	14.61	82	80	240	0.7-1.6	94

As analyzed above, both of the powders have soft agglomeration and hard agglomeration. Generally, in soft agglomerations, particles are held together by weak van der Waals force and the influence of which on the sintering behavior could be greatly reduced after the powders being packed into dense green bodies. However as for hard agglomerations, the particles are bonded together by strong bonds and are not likely to be broken into small particles or soft agglomerations once formed. Theoretically, hard agglomerations could lead to heterogeneous green bodies which could lead to morphology defects in the sintered bodies. Thus the agglomeration type and degree of the D-powder and S-powder are further investigated by the following sintering experiments.

4.4.2 Vacuum sintering behavior

Figure 4.4 shows relative density versus vacuum sintering temperature of the Y₂O₃ ceramics derived from the two powders. At a given sintering temperature, relative density of the S-Y₂O₃ ceramic was much higher than that of the D-Y₂O₃ ceramic. For example, after sintering at 1450 °C, relative density of the D-Y₂O₃ ceramic was only 86%, while that of the S-Y₂O₃ ceramic was about 90%. In both groups, the relative

density increased with increasing sintering temperature. When the temperature was higher than 1650 °C, the densification rate slowed down, ceramics approaching maximum relative density. The maximum relative density that the S-Y₂O₃ ceramic could reach was about 99.8% whereas that of the D-Y₂O₃ ceramic was merely 97.8%. Therefore, it is concluded that the residual pores in the D-Y₂O₃ ceramic are more difficult to be removed during the sintering.

Fig. 4.4 Relative densities of the Y₂O₃ samples derived from different powders.

Fig. 4.5 shows SEM images of the Y₂O₃ ceramics sintered at 1450 and 1550 °C, where the samples were already at the final-stage of sintering. At a given sintering temperature, the average grain size of the S-Y₂O₃ ceramic and the D-Y₂O₃ ceramic was nearly identical. However, the pore size and pore density that they exhibited were quite different. For example, at 1450 °C, although both the D-Y₂O₃ ceramic and the S-Y₂O₃ ceramic had an average grain size of 0.48 μm (Fig. 4.5 (a) and (b)), it is obvious that average pore size of the former (0.24 μm) was much larger than that of the latter (0.11 μm). After sintering at 1550 °C, the average grain size of the S-Y₂O₃ ceramic was slightly increased to about 0.71 μm, along with significant decrease in pore size and pore density (Fig. 4.5 (d)). In sharp contrast, a certain number of large pores were still present in the D-Y₂O₃ ceramic (Fig. 4.5 (c)), which could be linked to the large hard

agglomeration of the initial powder. According to Ciftcioglu et al., the presence of large hard agglomerates would lead to compacts with non-uniform pore size distribution, while the coarser pores might be remained in the sintered body.⁷⁴ As the sintering proceeds, the removal of these residual large pores would become more and more difficult. This is because at the final-stage of sintering, densification rate can be related to the grain size through the following equation⁸⁹:

$$\frac{d\rho}{dt} = \frac{733D_b\delta_b\gamma_s V_m}{RTG^4} \quad (\text{Caused by grain boundary diffusion}), \quad (4.1)$$

and

$$\frac{d\rho}{dt} = \frac{441D_l\gamma_s V_m}{RTG^3} (1 - \rho)^{\frac{1}{3}} \quad (\text{Caused by lattice diffusion}), \quad (4.2)$$

where D_b is the boundary diffusion coefficient, D_l is the lattice diffusion coefficient, δ_b is the diffusion thickness of the grain-boundary diffusion, γ_s is the specific surface energy of the solid, V_m is the molar volume, T is the absolute temperature, and G is the grain size. It is revealed that the removal of the remaining larger pores in Fig. 4.5 (c) becomes nearly impossible, as the densification rate is decreased significantly as the grain size is increased. This can be further verified by sintering trajectories of the ceramics, as shown in Fig. 4.6. The S-Y₂O₃ ceramic had smaller average grain size than the D-Y₂O₃ ceramic at the same relative density. It is also demonstrated that the maximum relative density of the D-Y₂O₃ ceramic was only 97.8%, while the S-Y₂O₃ ceramic could be steadily densified to above 99.8%.

Fig. 4.5 SEM images of the Y_2O_3 ceramics derived from the D-powder (a, c) and S-powder (b, d) sintered at 1450°C (a, b) and 1550°C (c, d) for 5 h.

Fig. 4.6 Sintering trajectories for the S- Y_2O_3 and D- Y_2O_3 ceramics sintered at temperatures between 1450°C and 1800°C for 5-20 h.

4.4.3 Post HIP Treatment

In order to achieve higher transparency, the vacuum sintered samples were further densified by using hot isostatic pressing (HIP). It is well known that there are two criteria for HIP treatment.⁸¹ Firstly, the pre-sintered ceramics should have no open pores, thus argon gas can be prevented from entering the ceramics during HIP treatment. Secondly, in order to maximize the driving force for densification, average grain size of the pre-sintered samples should be as small as possible. According to Fig. 4.5 (c) and (d), both the D- and S-Y₂O₃ ceramics vacuum sintered at 1550 °C for 5 h had relatively small average grain size (~0.7 μm). More importantly, open pores were not observed in both samples, making them suitable for HIP treatment. Fig. 4.7 shows SEM images of the two samples after HIPing at 1480 °C for 3 h. After HIP treatment, a certain number of lenticular voids were observed at grain boundaries of the D-Y₂O₃ ceramic (Fig. 4.7(a)). Some of the voids were in large size with the longer axes 4 μm, which were confirmed by the inset optical transmission images. Similar lenticular voids have been reported in zirconia ceramics.⁷² According to Rhodes et al., closely packed agglomerates might undergo preferential intra-agglomerate sintering and pull away from neighboring agglomerates, so that large lenticular voids were left, which were difficult to close. After sintering, the dense zones were surrounded by the large lenticular voids. In contrast, the HIPed S-Y₂O₃ ceramic showed a pore-free microstructure (Fig. 4.7(b)), confirming the high sinterability of the S-powder.

The in-line optical transmittance and photograph of the two ceramics are shown in Fig. 4.7 (c). It is clear that the transmittance of the S-Y₂O₃ ceramic was much higher than that of the D-Y₂O₃ ceramic. The S-Y₂O₃ ceramic showed an in-line transmittance of 81.6% at 1200 nm, which was remained to be 76.1% at 600 nm.

Fig. 4.7 SEM images of the (a) D- and (b) S-Y₂O₃ ceramics after HIP treatment at 1480 °C, with the inset in (a) showing an optical transmission micrograph of the D-Y₂O₃ ceramic. (c) In-line optical transmittance and photograph of two samples.

4.5 Conclusions

It has been demonstrated that spray precipitation is a very effective approach to reduce the degree of agglomeration of Y_2O_3 precursor and powder. Therefore, the S-powder exhibited much higher densification rate and thus higher final sintered density. Without using sintering additives, Y_2O_3 transparent ceramics could be fabricated by using the S-powder. After vacuum sintering at 1550 °C for 5 h, followed by HIPing at 1480 °C for 3 h, the S- Y_2O_3 ceramics possessed an in-line optical transmittance of 81.6% at 1200 nm. It is believed that this simple spray precipitation method is also applicable to synthesize other ceramic powders.

Chapter 5 Fabrication and microstructural characterizations of lasing grade Nd:Y₂O₃ ceramics

5.1 Introduction

As is introduced in Chapter 1, sesquioxide transparent ceramics (typically Y₂O₃, Lu₂O₃ and Sc₂O₃) have been considered as a promising material for the application of high-power solid-state lasers. Moreover, the neodymium-doped yttria materials have comparable stimulated emission cross-sections at 1075 nm and 1079 nm, which could be potentially exploited for the coherent terahertz generation and remote sensing.^{90–93} Therefore it is very attractive if Nd:Y₂O₃ transparent ceramics with lasing grade optical quality could be fabricated.

In order to fabricate transparent ceramics that fulfill the requirements for high power laser applications, it is critical to realize defect-free microstructures to minimize the scattering loss. To achieve this goal, researchers have made great efforts to synthesize powders with low degree of agglomerations, high sinterability by using the chemical co-precipitation^{37,49,94}, ball milling⁹⁵, and sol-gel combustion⁹⁶ processes. Meanwhile, translucent and transparent Nd-doped sesquioxide ceramics have been fabricated by using various sintering strategies: vacuum sintering^{51,95,97}, H₂ atmosphere sintering⁴⁹, hot pressing (HP)⁹⁸, hot isostatic pressing (HIP)⁹⁹, and spark plasma sintering (SPS)¹⁰⁰. However, restrained by the relatively high scattering losses, reports on laser oscillations realized by Nd:Y₂O₃ ceramics are very limited. In 2001, by using the Nd:Y₂O₃ ceramics provided by Konoshima Chemical Co. Ltd., Lu et al. achieved highly efficient laser oscillation with Nd:Y₂O₃ ceramics for the first time. In their experiments, a maximum laser output power of 160 mW was obtained with a slope efficiency of 32%.¹⁰¹ In 2017, by using the high quality Nd:Y₂O₃ ceramics from World-Lab Co. Ltd., S. Sattayaporn et al. demonstrated laser emission with a maximum output power of 3.5 W at 1.074 μm,

with a slope efficiency of 31.1%.¹⁰² However, in these papers as the optical characterization and laser operation were the main concerns, the detailed information on the fabrication and material property characterization of the lasing grade Nd:Y₂O₃ ceramics have not been addressed.

In this chapter, well dispersed Nd:Y₂O₃ nano-powders were synthesized by a spray precipitation method. The sintering behavior, microstructure, and optical properties of the obtained Nd:Y₂O₃ ceramics were characterized and analyzed. Lasing grade Nd:Y₂O₃ ceramics were fabricated using vacuum sintering followed by hot isostatic pressing, the in-line transmission of which reached 81.6% at 1000 nm and remained 81.1% at 650 nm.

5.2 Ceramic fabrication

The starting material was commercial Y₂O₃ powder (99.999%, Jiahua Advanced Material Resources Co., Ltd, China) dissolved into hot hydrochloric acid (37%, EMSURE) at about 80 °C. Nd(NO₃)₃ and YCl₃ solutions were mixed with the composition of (Nd_{0.006}Y_{0.994})₂O₃ and were diluted with deionized water as the mother solution, with Y³⁺ concentration of 0.2 mol/L. Then, precipitants, the mixed solution of NH₄HCO₃ + NH₄OH (molar ratio 1:0.9) was sprayed into the mother solution at a rate of 6 ml/min, until the pH reached 8.5. The mixing method and experimental setup were the same as shown in Chapter 4. The precipitates were aged for 24 h, then filtered and washed with deionized water and ethanol, respectively, to remove undesired ions. After drying at 60 °C for 2 days, the precursor was calcined at 1200 °C for 5 h to obtain the Nd:Y₂O₃ powders. Then, the as calcined powders were sieved and dry pressed into pellets. The compacts were sintered under vacuum at a temperature range of 1480-1650 °C for 7 hours with 5 °C/h heating rate and cooling rate. The hot isostatic press (HIP) was conducted at 1510-1570 °C for 4 hours at 198 MPa in argon gas. After HIP-ing,

the samples showed dark blue color, which turned blue after annealing in air at 1000 °C. Then the ceramics were polished, and the final sample had a thickness of 5 mm.

5.3 Characterization

The particle morphology was characterized by using a field-emission scanning electron microscope (FESEM, Leo 1550, Cambridge, Cambridgeshire, UK). Microstructural analysis of the bulk ceramics after sintering was measured by a scanning electron microscope (SEM, JSM-6360A, JEOL, Tokyo, Japan) and an optical transmission microscope (Olympus BX53-P, Tokyo, Japan). Relative density was evaluated by the Archimedes method. The grain boundary structures were observed by using a high-resolution transmission electron microscope (TEM, JEOL-2100F, JEOL, Tokyo, Japan). In-line optical transmission was measured by an ultraviolet-visible spectrometer (Carry 5000, Agilent, Santa Clara, CA, USA). The distribution of chemical elements in the sintered ceramics was analyzed by FESEM/EDX (JSM-7600F, JEOL, Tokyo, Japan).

5.4 Results and discussion

5.4.1 Material properties

Figure 5.1 shows the FESEM image of the Nd:Y₂O₃ powders prepared by the spray precipitation method. The particles were uniform and well dispersed with a primary particle size of about 100 nm. Large hard agglomerations were not detected.

Fig. 5.1 FESEM image of the Nd:Y₂O₃ powders prepared by the spray precipitation method and calcined at 1200 °C for 5 h.

Figure 5.2 shows the sintering map (relative densities and grain sizes) of the Nd:Y₂O₃ ceramics vacuum sintered at different temperatures. The figures clearly demonstrated that as the sintering temperature increased to 1550 °C, the relative density of the ceramics rapidly increased to above 96% with only slight grain growth. In this sintering stage, pore channels were enclosing, and finally became isolated pores. In contrast, as the sintering temperature further increased and was higher than 1550 °C, the grain growth is accelerated due to the degradation of pore pinning effect, leading to the slowing down of the densification process.

Fig. 5.2 Sintering map of the Nd:Y₂O₃ ceramics.

Figure 5.3 (a) shows a fracture surface of the Nd:Y₂O₃ ceramics after vacuum sintering at 1550 °C for 7 h. The average grain size of the vacuum sintered samples was 1-2 μm, with only closed pores. Fig. 5.3 (b) shows a polished surface of the Nd:Y₂O₃ ceramics after HIPing at 1540 °C. It can be seen that the ceramic is fully densified after the HIP treatment, with an average grain size of about 1.9 μm. The uniform grain size indicates excellent homogeneity and sinterability of the synthesized powders. Neither intergranular nor intragranular pores were detected. Fig. 5.3 (c) shows a photo taken by a transmission-mode optical microscope that images the inside of the Nd:Y₂O₃ ceramic body. It exhibits excellent optical homogeneity without observation of residual pores.

Fig. 5.3 SEM images of the Nd:Y₂O₃ ceramics after (a) vacuum sintering at 1550 °C for 7 h and (b) HIPing at 1540 °C for 4 h, (c) Internal transmission optical micrograph of the HIPed ceramic.

Figure 5.4 shows a typical high resolution TEM image of a grain boundary in the Nd:Y₂O₃ ceramic. The corresponding diffraction pattern and the lattice planes of the right grain were labeled on the image. The TEM results confirm the absence of residual

pores and secondary phases at the grain boundary. Based on the Nd_2O_3 - Y_2O_3 phase diagram, in the present sintering temperature range (1300-1600 °C), the solubility of Nd_2O_3 in the cubic Y_2O_3 phase is over 30 at.%, much higher than the present doping concentration.¹⁰³ It well explains the absence of the secondary phases. The thickness of the grain boundary shown is far below 1 nm. It is believed that such thin grain boundaries would not cause optical losses at the lasing wavelengths ($>1\ \mu\text{m}$) of the $\text{Nd}:\text{Y}_2\text{O}_3$ transparent ceramics.¹⁰⁴

Fig. 5.4 Transmission electron microscope (TEM) image of a typical grain boundary area the corresponding diffraction pattern of the $\text{Nd}:\text{Y}_2\text{O}_3$ ceramics.

According to Ramirez et al., Nd^{3+} tends to segregate at the grain boundaries of $\text{Nd}:\text{YAG}$ ceramics, which may result in the change of refractive index spatially and decrease the total fluorescence quantum efficiency of the Nd^{3+} ions.¹⁰⁵ In order to check the distribution of the Nd^{3+} ions in the obtained $\text{Nd}:\text{Y}_2\text{O}_3$ ceramics, FESEM/EDX was used to analyze the chemical elements (Nd, Y and O). Fig. 5.5 shows the FESEM image of a polished surface of the $\text{Nd}:\text{Y}_2\text{O}_3$ ceramic and the EDX mapping of Nd, Y and O. It revealed that the local segregation of Nd^{3+} ions at grain boundaries was not detected. More precisely, all the elements are homogeneously distributed in the ceramic. No detectable segregation at the grain boundaries could be identified. This is plausible

because of the small grain size of the Nd:Y₂O₃ ceramics, which was 1.9 μm . As is reported, if average grain size was less than 2 μm , the microscopic variation of Nd³⁺ concentration could be minimized.¹⁰⁵

Fig. 5.5 (a) FESEM image and corresponding EDX mappings with (b) Nd-L α , (c) Y-K α , and (d) O-K α for the HIP-ed Nd:Y₂O₃ ceramic.

5.4.2 Optical properties

Figure 5.6 (I) illustrates the in-line transmission of 5 mm thickness Nd:Y₂O₃ transparent ceramic samples hot isostatic pressed at 1510-1570 $^{\circ}\text{C}$. It can be seen that after being HIP-ed at 1540 $^{\circ}\text{C}$ for 4 h, the Nd:Y₂O₃ ceramics showed the best optical quality. It is worth noting that we got nearly coincident in-line transmission curves from different areas of a given sample, implying the samples had good homogeneity and good measurement consistency. The absorption peaks and the corresponding excitation levels of the Nd³⁺ transitions from the ground state ⁴I_{9/2} were labeled on the graph (Fig.

5.6 (II)).⁶⁶ The measured transmission was 81.6% at 1000 nm and remained 81.1% at 650 nm, which equals to the theoretical value of Y₂O₃ single crystals calculated by: $T=[1-((n-1)/(n+1))^2]^2$, where n is the refractive index.²⁶ The high transmission of the sample at the NIR and visible wavelength range indicates that both the scattering losses due to the Mie scattering and Rayleigh scattering were extremely low. The inset in Fig. 5.6 (II) shows the appearance of the ceramic under indoor light (Fig. 5.6 II(a)) and illuminating by a He-Ne laser (Fig. 5.6 II(b)), respectively. It is to note that when the ceramic was irradiated by the laser beam from one side, neither visible scatters nor light path could be observed inside the ceramic, implying that the sample has very low degree of scattering losses.

Fig. 5.6 In-line transmission of the Nd:Y₂O₃ transparent ceramics (I) HIP-ed at different temperatures, and (II) under the optimized sintering and HIP-ing condition, with labels representing the excitation levels from the ground state of ⁴I_{9/2}. The inset showing the photograph taken under (a) indoor light, (b) illuminating by a He-Ne laser from one side.

The fluorescence spectrum ($\lambda_{\text{ex}}=808$ nm) of the Nd:Y₂O₃ ceramic is shown in Fig. 5.7. The strong fluorescence emission group at ~ 1100 nm is related to the ⁴F_{3/2}-⁴I_{11/2} transitions. The two emission peaks at 1075 nm and 1079 nm have comparable spectral intensity. It could be easy to achieve simultaneous oscillation leading to dual wavelength laser emission. Another group of fluorescence emission locating at ~ 1358 nm corresponds to the ⁴F_{3/2}-⁴I_{13/2} transitions.

Fig. 5.7 Fluorescence spectrum of the Nd:Y₂O₃ ceramic.

5.4.3 Room temperature laser oscillation

The test sample was an uncoated 0.6 at.% Nd:Y₂O₃ transparent ceramic slab with a dimension of 3×3×5 mm³. Fig. 5.8 shows the laser setup, which consists of a fiber-coupled laser diode pump source (central wavelength 803-808 nm) and a two-mirror cavity with a total cavity length of 15 mm. The input mirror (IM) was coated with high transmission ($T > 96\%$) at 808 nm and high reflection at the lasing wavelength (1.08 μm). The output mirror (OC) was coated with a transmission of $T = 10\%$ at the oscillating wavelength. The slab temperature was controlled at 20 °C by water-cooling.

Fig. 5.8 Schematic diagram of the diode end-pumped Nd:Y₂O₃ ceramic laser setup.

(LD: laser diode, IM: input mirror, OC: output mirror)

Fig. 5.9 shows the output power vs the absorbed pump power of the laser for the ${}^4F_{3/2}$ - ${}^4I_{11/2}$ transition. The inset shows the laser emission spectrum under the maximum output power. The laser simultaneously oscillates at two wavelengths, centered at 1074.6 nm and 1078.8 nm, respectively. The output power grows linearly with the absorbed pump power. Under 9.0 W absorbed pump power the maximum output power obtained was 3.6 W, and the corresponding slope efficiency was 45.2 %. The high laser efficiency confirms the excellent optical property of our ceramics. Considering that no pump saturation was observed under the highest available pump power in the experiment, it is anticipated that even higher output power would be achieved under a higher absorbed pump power.

Fig. 5.9 CW laser output power and spectrum of the laser operation with ${}^4F_{3/2}$ - ${}^4I_{11/2}$ transition.

The CW laser operation with ${}^4F_{3/2}$ - ${}^4I_{13/2}$ transition was also evaluated as shown in Fig. 5.10. In this experiment, the center wavelength of the laser was 1357.6 nm, and a maximum output power of 2.2 W was obtained with a slope efficiency of 27.4%.

Fig. 5.10 CW laser output power and spectrum of the laser operation with ${}^4F_{3/2}$ - ${}^4I_{13/2}$ transition.

It is worth mentioning that using an uncoated 0.6 at.% Nd:Y₂O₃ ceramic slab provided by us, Zhu et al has achieved the highest slope efficiency for the Nd:Y₂O₃ ceramic lasers.¹⁰⁶ For the ${}^4F_{3/2}$ - ${}^4I_{11/2}$ transitions, a maximum output power of 3.01 W with slope efficiency of 49.6% was obtained at an absorbed pump power of 7.0 W. For the ${}^4F_{3/2}$ - ${}^4I_{13/2}$ transitions, single wavelength oscillation at 1357.7 nm was obtained. A maximum output power of 1.68 W with slope efficiency of about 29.3% was achieved at an absorbed pump power of 6.7 W.

5.5 Conclusion

In conclusion, lasing grade 0.6 at.% Nd:Y₂O₃ transparent ceramics have been successfully fabricated by using powders in-house synthesized with a spray precipitation method and the vacuum sintering plus HIP technique. The obtained ceramics showed pore-free microstructures, without detectable secondary phases on the grain boundaries as well. The in-line transmission reached 81.6% at 1000 nm and

remained 81.1% at 650 nm, which equals the theoretical value of Y_2O_3 single crystals. CW lasing performances of the ceramics under $^4\text{F}_{3/2}$ - $^4\text{I}_{11/2}$ and $^4\text{F}_{3/2}$ - $^4\text{I}_{13/2}$ energy transitions were evaluated. A maximum output power of 3.6 W with a slope efficiency of 45.2% simultaneously oscillating at 1074.6 nm and 1078.8 nm, and 2.2 W at 1357.6 nm with corresponding efficiency 27.4% were obtained, respectively. The results demonstrated that excellent quality Nd: Y_2O_3 laser ceramics could be fabricated by the vacuum sintering plus hot isostatic pressing process, and the Nd: Y_2O_3 laser ceramics can be promise for the high power and high efficient laser applications

Chapter 6 Submicron-grained Yb:Lu₂O₃ transparent ceramics with lasing quality

6.1 Introduction

High thermal conductivity is a critical parameter for the gain media of the high-power lasers. Although the thermal conductivity of pure YAG is quite high, which is about 11.0W/mK, the value quickly decreases as YAG is doped with high concentration laser activated ions. In contrast, sesquioxide materials have lower phonon energy and higher thermal conductivity than YAG.^{12,38,107} Especially for the Lu₂O₃, when doping some rare-earth laser ions e.g. Yb³⁺, due to that Yb³⁺ and Lu³⁺ have close atomic mass and ionic radius, even under high Yb³⁺ doping concentrations there is only a slight decrease on its thermal conductivity, as shown in Fig. 6.1¹⁰.

Fig. 6.1 Thermal conductivity versus dopant concentration for crystals.^{108–111}

Fabrication of laser quality rare-earth ions doped Lu₂O₃ ceramics has been demonstrated by several research groups. In 2011, Sanghera et al. reported the

fabrication of high quality 10 at.% Yb:Lu₂O₃ ceramics by using hot pressing plus HIPing method. With their ceramic samples they first demonstrated CW lasing with a slope efficiency of 10%, which was then improved to 74%.^{68,70} In 2014, An et al. reported the fabrication of highly transparent Nd:Lu₂O₃ ceramics by using spark plasma sintering (SPS) process. They achieved CW laser oscillation with an output power of 0.21 W and a slope efficiency of 14% with their ceramic samples.¹⁰⁰ Based on the open literatures, so far Konoshima Chemical Co. has produced the best quality rare-earth ions doped sesquioxide laser ceramics. Together with their collaborators they have reported a series of results on the high efficiency laser oscillations with their Er:Lu₂O₃¹¹², Er:Y₂O₃¹¹³, Yb:Y₂O₃¹¹⁴, Tm:Lu₂O₃¹¹⁵, Yb:Lu₂O₃¹¹⁶, and Yb:Sc₂O₃¹¹⁷ laser ceramics. However, no detailed information on their powder synthesis and sintering technologies were disclosed.

Generally, in order to obtain highly transparent ceramics, relatively high temperature sintering is needed to achieve the maximum densification. Thus the transparent ceramics obtained have normally large grain sizes. Indeed all the lasing quality Lu₂O₃ ceramics so far reported have grain sizes larger than 5 μm .^{49,68,100,118,119} It is well known that grain size affects the mechanical strength of a ceramic following the Hall-Petch equation. Smaller grain size implies higher mechanical strength and higher thermal shock resistance.¹¹⁷ For the high-energy lasers, thermal shock resistance would be another important factor of the gain media to consider. In addition, according to Zhou et al., reducing grain size into sub-micron scale could also improve the luminescence efficiency of the rare-earth ions doped Lu₂O₃ ceramics.¹²⁰ Therefore, it would be attractive if lasing grade Lu₂O₃ ceramics with submicron grain sizes could be fabricated.

In this chapter, using a spray co-precipitation method we have successfully synthesized well dispersed, nano-size 3.3 at.% Yb:Lu₂O₃ powders with high sinterability. High optical quality submicron grained (0.6 μm) 3.3 at.% Yb:Lu₂O₃ transparent ceramics were fabricated by low temperature densification even without using any sintering aids.

The Yb:Lu₂O₃ transparent ceramic exhibited an optical transmittance of 80.0% at 600 nm. Preliminary laser experiments have also shown high efficiency CW laser oscillation of the ceramic samples.

6.2 Ceramic fabrication

LuCl₃ and Yb(NO₃)₃ solutions were mixed according to the formula (Yb_{0.033}Lu_{0.967})₂O₃ as a mother solution. Then the mixed NH₄HCO₃+NH₄OH solution was sprayed into the mother solution at a rate of 6 ml/min until the pH reached 8.5. After aging for 12 h, the precipitate was washed three times with deionized water and ethanol, respectively. Then, the slurry was dried and thoroughly crushed by using a mortar and pestle. The obtained powders were calcined at 1200 °C for 5 h and then ball milled for 10 h. After sieving, the 3.3 at.% Yb:Lu₂O₃ powders were then dry pressed into pellets with a diameter of 15 mm and cold isostatic pressed (CIP) under 200 MPa. The green bodies were vacuum sintered at a temperature range of 1450-1550 °C. After that, they were hot isostatic pressed (HIP-ed) at 1480 °C under 196 MPa in argon gas. Finally, the ceramics were air annealed at 1200 °C for 10 h in a muffle furnace and were mirror polished on both surfaces.

6.3 Characterization

Powder morphology was observed by using a Leo 1550 field-emission scanning electron microscope (FESEM; Leo 1550, Cambridge, Cambridgeshire, UK). Phase structure of the calcined powders was identified from the X-ray diffraction (XRD) patterns (CuK α radiation, XRD, D8 Advance, Bruker, Germany). Microstructures of the bulk ceramics were observed by using a scanning electron microscopy (SEM, JSM-6360A, JEOL, Tokyo, Japan). The in-line transmittance was recorded by using a UV–VIS–NIR spectrometer (Lambda 950, Perkin Elmer, Waltham, MA). The average grain

size and grain size distribution of the samples were measured by using the Nano Measure software, with at least 200 grains countered for each sample. The mechanical strength was characterized by using a microhardness tester (FM-300e, FUTURE-TECH, Japan) and a criterion electromechanical material testing system (MTS C42, MTS System Corporation, Eden Prairie, MN).

6.4 Results and Discussion

6.4.1 Powder characteristics

Fig. 6.2 FESEM image of the Yb:Lu₂O₃ powders calcined at 1200 °C for 5 h.

Figure 6.2 shows the FESEM image of the Yb:Lu₂O₃ powders after the calcination. The powder was in the form of soft-agglomerates, with primary particle size in the range of 70-130 nm.

Figure. 6.3 shows the XRD patterns of the precursors and the calcined Yb:Lu₂O₃ powders. The precursors were amorphous, while the calcined powders were well crystallized and exhibited diffraction peaks corresponding to Lu₂O₃ with the cubic structure (Entry#96-153-7845).

Fig. 6.3 XRD patterns of the precursors and Yb:Lu₂O₃ powders calcined at 1200 °C.

6.4.2 Sintering characteristics

Figure 6.4 shows the microstructure of Yb:Lu₂O₃ ceramics after vacuum sintering at 1450 °C, 1500 °C and 1550 °C for 10 h, respectively. As the sintering temperature increased, the relative density of the Yb:Lu₂O₃ ceramics was improved from 91.9% to 98.8%, and the grain grew from 0.42 μm to 0.81 μm. It can be seen that pores in the 1450 °C vacuum sintered samples are open, while when the temperature was over 1500 °C, only closed pores could be observed at grain boundaries.

Fig. 6.4 SEM images of the Yb:Lu₂O₃ ceramics after vacuum sintering at (a) 1450 °C (b) 1500 °C and (c) 1550 °C for 10 h.

After hot isostatic pressed at 1480 °C for 4 h, the 1450 °C vacuum sintered samples were opaque and were broken into pieces after air annealing. In comparison, the 1500-1550 °C vacuum sintered samples showed good transparency, whose in-line transmittance and photograph are shown in Fig. 6.5 (thickness 3 mm). The

transmittance of the 1500 °C pre-sintered ceramic was obviously superior than that of the 1550 °C pre-sintered ceramic. It suggests that 1500 °C was a favorable vacuum sintering temperature in the current sintering strategy and the Yb³⁺:Lu₂O₃ ceramics exhibited an excellent optical transmittance through the entire wavelength range. For example, the transmittance reached 80.0% at 600 nm, very close to the theoretical value (80.8% at 600 nm) calculated based on the refractive index of Lu₂O₃ single crystals.¹²¹ The absorption between 900-1100 nm is corresponding to the transition of Yb³⁺ from the ground state ²F_{7/2} to the excited state ²F_{5/2}.

Fig. 6.5 In-line transmission of the Yb:Lu₂O₃ ceramic after vacuum sintering at 1500-1550 °C for 10 h and HIP-ing at 1480 °C/4 h with the inset showing the photograph (left 1500 °C, right 1550 °C).

6.4.3 Mechanical properties and thermal conductivity

Figure 6.6 (a) shows the SEM image of the Yb:Lu₂O₃ ceramics after vacuum sintering at 1500 °C for 10 h and hot isostatic pressing at 1480 °C for 4 h. The relative density of the as-sintered ceramic reached 100%. It can be seen that all the pores were eliminated and the ceramics exhibited a dense microstructure with a sub-micron average grain size

of about 0.6 μm . As is shown in Fig. 6.6 (b), the grain size distribution of the sintered ceramics was very narrow (0.3-1.6 μm), without the observation of abnormal grain growth, implying that the sinterability of the powders was very good. The Vickers hardness of the fabricated Yb:Lu₂O₃ ceramics was 892.8 HV and the compressive strength was 152 MPa, indicating the great mechanical strength of the submicron-grained ceramics.

Fig. 6.6 (a) The SEM image and (b) grain size distribution of the Yb:Lu₂O₃ ceramics after vacuum sintering at 1500 $^{\circ}\text{C}$ for 10 h and hot isostatic pressing at 1480 $^{\circ}\text{C}$ for 4 h.

Fig. 6.7 shows the thermal conductivity of the Yb:Lu₂O₃ ceramics versus temperature, which is calculated by:

$$\lambda_c = \alpha \rho C \quad (6.1)$$

where α is the thermal diffusivity measured by laser-flash method, ρ is the density of the Yb:Lu₂O₃ ceramic (9.41 g/cm³), and C is the specific heat capacity of Lu₂O₃ (255.8 J/(kg·K)). The room temperature (25 °C) thermal conductivity is 11.8 W/mK. This value is much higher than that of 3 at% Yb:YAG (7.6 W/mK) and 3 at% Yb:Y₂O₃ (7.4 W/mK).¹⁶

Fig. 6.7 Thermal conductivity of the Yb:Lu₂O₃ ceramics.

6.4.4 Room temperature laser oscillation

Room temperature laser performance of the 3.3 at% Yb:Lu₂O₃ transparent ceramics was also evaluated. The pump source used is a fiber-coupled laser diode with maximum power of about 25 W at the wavelength of 940 nm. Collimated by a convex lens with focus length of 35 mm, the pump beam was then focused into the Yb:Lu₂O₃ ceramic with a spot radius of about 140 μ m by a spherical convex lens with a focus length of 100 mm. The dimension of the polished but uncoated ceramic slab was 4 mm $\times$ 4 mm

$\times 3$ mm. The slab was wrapped with indium foil and mounted in a copper block, whose temperature was controlled by water-cooling at 18 °C. A simple two-mirror cavity with total cavity length of about 12 mm was employed in the experiment. The input plano-plano mirror was dichroic coated with high reflectivity ($R > 99.7\%$) for 1000-1100 nm and high transmission for pump wavelength. The output mirror was a plano-plano output coupler. Three output couplers (O.C.) with transmission of $T = 2.4\%$, 5% and 12% were utilized in the experiment. The laser output power was measured with a laser power/energy meter (NOVA II, OPHIR).

Figure 6.8 (a) shows the CW laser output power versus the absorbed pump power measured using three different output couplers. The output power increased linearly with the increase of the absorbed pump power, and no output power saturation was observed. With the $T = 12\%$ output coupler, a maximum output power of 2.5 W was achieved with 14 W absorbed pump power, corresponding to a slope efficiency of 24.2%. Fig. 6.8 (b) shows the typical optical spectrum of the laser emission under the maximum output power of 2.5 W. It can be seen that the center wavelength of the laser was about 1079.8 nm measured with a high-resolution optical spectrum analyzer (AQ6375, Yokogawa Electric, Tokyo).

Fig. 6.8 (a) CW laser output power as a function of the absorbed pump power and (b) output spectrum of the Yb:Lu₂O₃ ceramic laser at 1079.8 nm.

It is worth mentioning that the slope efficiency of the laser could be further increased if the surfaces of the ceramic could be coated and a pump laser diode at 976 nm could be used. In the current experiment the Fresnel reflections on the surfaces of the ceramic have contributed significant losses to the laser. For the Yb-doped lasers due to smaller quantum deficit a higher lasing efficiency is anticipated if pumped at 976 nm than at

940 nm. Nevertheless, the preliminary laser experiment has already clearly showed a promising laser performance of the ceramics.

6.5 Conclusion

In conclusion, by using a spray co-precipitation method 3.3 at.% Yb:Lu₂O₃ nanopowders have been successfully synthesized, which showed good sinterability at relatively low temperature under a vacuum sintering plus HIP-ing sintering strategy. Highly transparent submicron-grained (0.6 μm) 3.3 at.% Yb:Lu₂O₃ ceramics have been successfully fabricated. The great mechanical strength and high thermal conductivity of the submicron-grained ceramic have been verified. The room temperature (25 °C) thermal conductivity is 11.8 W/mK. The in-line transmittance of the 3 mm thickness ceramic samples could reach 80.0% at 600 nm. Pumped by a fiber coupled laser diode at 940 nm, an uncoated Yb:Lu₂O₃ ceramic slab has produced 2.5 W output power under an absorbed pump power of 14 W with a slope efficiency of 24.2%.

Chapter 7 Doping effects of aliovalent sintering additives

7.1 Investigation of small amount Ca-doped Y₂O₃ transparent ceramics

7.1.1 Introduction

Owing to the high melting temperature of Y₂O₃ (2430 °C), it is hard to fabricate fully densified Y₂O₃ ceramics at a relatively low sintering temperature.⁶³ Moreover, it is widely known that intragranular pores are easily generated during high temperature sintering. In this case, in order to promote the densification, sintering additives with different valent were utilized.

In previous studies, tetravalent sintering aids, for example, Th⁴⁺, Hf⁴⁺, and Ti⁴⁺ were reported.^{122–124} For example, the introduction of Zr⁴⁺ in transparent Y₂O₃ ceramics as sintering aids was widely studied and highly transparent Zr-doped Y₂O₃ ceramics have been fabricated.^{38,125,126} Trivalent cations like La³⁺ was also proven to be an effective sintering additive for Y₂O₃ by a number of studies.^{95,98,127,128} Only a few studies on the divalent sintering aids (Ca²⁺, Mg²⁺) were conducted. In 1990, Katayama et al firstly reported the sintering and electrical properties of 1 mol% CaO doped Y₂O₃ sintered in air and proved that CaO was effective for improving the sinterability.^{129,130} In 2010, Kodo et al investigated the grain boundary mobility of divalent cations doped Y₂O₃ by pressure-less sintering in air, with the doping concentration of 1 mol%.¹³¹

However, in the previous studies, proper doping concentration of CaO in Y₂O₃ has not been investigated. Successful fabrication of highly transparent CaO-doped Y₂O₃

ceramics has not been reported. Also, there is a lack of studies on the optical, mechanical and thermal properties for a fully densified CaO-doped Y_2O_3 ceramic.

In this part, we induced small amounts of CaO (< 0.15 wt.%) into Y_2O_3 as sintering additive. Highly transparent CaO-doped Y_2O_3 ceramics was successfully fabricated by vacuum sintering followed by hot isostatic pressing (HIP). The sintering behavior of Y_2O_3 samples with different doping concentration was investigated. The optical, mechanical and thermal properties of as-sintered ceramics were analyzed.

7.1.2 Experimental Procedure

The starting material was commercial Y_2O_3 powder (99.999%, Jiahua Advanced Material Resources Co., Ltd, China) dissolved into hydrochloric acid. Using the similar spray precipitation method introduced in chapter 4, Y_2O_3 powder with high purity and low degree of agglomeration was synthesized. Calcium oxide (99.999%, Sigma-Aldrich, USA) was used as dopant source. CaO were mixed with Y_2O_3 powder with the ratio of 0.01 wt.%, 0.02 wt.%, 0.05 wt.% and 0.15 wt.%, respectively, and the mixed powders were ball milled for 15 h using ethanol as ball-milling media. After drying and sieving, the obtained powders were calcined at 1200 °C for 5 h and dry pressed into 20 mm in diameter compacts. The compacts were then cold isostatic pressed (CIP-ed) under 200 MPa. The sintering behavior investigations were conducted after the green bodies were vacuum sintered at a temperature range of 1450-1650 °C. After that, Y_2O_3 ceramics were hot isostatic pressed (HIP-ed) at 1510 °C under 196 MPa, annealed and polished into 3 mm in thickness.

7.1.3 Results and discussion

7.1.3.1 Doping effect

As reported in an earlier paper, the introduction of calcium oxide into yttria under high oxygen pressures can be expressed as equation (7.1):¹²⁹

Considering the vacuum sintering condition in this experiment, where the oxygen pressure is negative, the oxygen vacancies are easy to be generated according to equation (7.2):

Thus, the real reaction under the present experiment condition can be expressed as equation (7.3):

Owing to the similar ionic radius of Ca^{2+} (1.12 Å) and Y^{3+} (1.02 Å), Ca^{2+} could perfectly substitute the site of Y^{3+} , creating one negative charge. It can be seen that by inducing Ca^{2+} into Y_2O_3 under vacuum sintering condition, additional oxygen vacancies could be created. The increase concentration of CaO drives the equilibrium (7.3) to the right side, which contributes to the increase concentration of oxygen vacancies. Chen et al has demonstrated in ref.¹²⁸ that the grain boundary mobility in Y_2O_3 is dominated by cation diffusivity which can be enhanced by the presence of oxygen vacancies. Thus, the grain boundary mobility could be promoted by the introduction of CaO.

7.1.3.2 Densification and microstructure evolution

Figure 7.1 shows the relative density of Y_2O_3 samples with different CaO doping concentration vacuum sintered at 1450-1650 °C. At the same sintering temperature, the relative density increased as the CaO content increased. The maximum density that

could be reached also increased with higher CaO doping concentration. For example, 0.15 wt.% CaO-doped Y_2O_3 reached its maximum relative density (99.5%) at 1600 °C, while the highest density of 0.01 wt.% CaO-doped Y_2O_3 was merely 92.8%. It can be seen that the densification rate has been obviously slowed down at 1550 °C, which indicates the domination of grain growth rather than volume shrinkage at this stage. So there could be only a slight density increase for 0.01 wt.% CaO-doped samples when the sintering temperature was further improved.

Fig. 7.1 Relative density versus vacuum sintering temperature of Y_2O_3 samples with different CaO contents.

Fig. 7.2 shows the variation of average grain sizes as a function of sintering temperatures of the CaO-doped Y_2O_3 ceramics. At a given sintering temperature, the samples with higher doping concentration show higher grain growth rate and exhibit larger grain sizes. As we reported in a previous paper, using the same powder preparation method, the average grain size of the undoped Y_2O_3 samples was about 0.71 μm after being vacuum sintered at 1550 °C. In contrast, the sample doped with 0.01 wt.% CaO reached a larger average grain size (1.1 μm) at the same sintering temperature (1550 °C). It indicates that adding CaO has obviously accelerate the grain

boundary migration rate. What's more, the influence on the grain boundary mobility tends to be greater with the higher doping concentration. This phenomenon could be explained by the following defect analyzation.

Fig. 7.2 Average grain size versus vacuum sintering temperature of Y_2O_3 samples with different CaO contents.

Fig. 7.3 show the microstructure evolution of the 0.02 wt.% and 0.15 wt.% CaO-doped samples during the final-stage sintering. At 1450 °C, both the 0.02 wt.% and 0.15 wt.% samples (Fig. 7.3 (a) and (b)) have the same degree of porosity and grain size ($\sim 0.8 \mu m$). As the temperature was increased, the 0.15 wt.% CaO-doped samples showed an obviously faster densification and grain growth rate, which is coincident with the densification curve shown in Fig. 7.1. At 1550 °C, the average grain size of the 0.15 wt.% CaO-doped sample has increased to $4 \mu m$, with a certain number of intragranular pores. In contrast, intragranular pores were not detected in the 0.02 wt.% CaO-doped samples, even at 1650 °C. It means grain coarsening, rather than densification, has played the leading role in the CaO heavily doped samples. That is why there was a slight density decrease in Fig. 7.1 as the temperature was further increased from 1600

°C to 1650 °C. Therefore, further densification was difficult in the 0.15 wt.% CaO-doped samples.

Fig. 7.3. SEM images of 0.02 wt.% CaO-doped (a), (c), (e) and 0.15 wt.% CaO-doped samples (b), (d), (f), vacuum sintered at 1450 °C, 1550 °C and 1650 °C, respectively.

Fig. 7.4 show the polished surfaces of the ceramics after vacuum sintering at 1550 °C followed by HIP-ing at 1510 °C. After HIP-ing, the 0.02 wt.% CaO-doped ceramic exhibited a fully densified structure, without the detection of residual pores and secondary phases. However, owing to the overlarge grain of the 0.15 wt.% CaO-doped

sample after pre-sintering, the driving force during HIP was not adequate to expel all the pores. Thus, there were still a certain number of isolated pores inside the as-sintered ceramics.

Fig. 7.4 SEM images of the ceramics after vacuum sintering 1550 °C and HIP-ing at 1510 °C with CaO concentration of (a) 0.02 wt.% and (b) 0.15 wt.%.

7.1.3.3 Optical quality

Figure 7.5 shows the in-line transmission of the CaO-doped Y_2O_3 ceramics after the HIPing, with a thickness of 3 mm. The 0.01 wt.% CaO-doped Y_2O_3 ceramic was completely opaque. The 0.02 wt.% CaO-doped Y_2O_3 showed a highest in-line transmission over a wavelength range of 0.2-2 μm, reaching 84.87% at 1200 nm and remaining 81.41% at 600 nm. The transmission degraded when the doping concentration was increased. It reveals that the optical property of the final sintered sample was very sensitive to the CaO doping concentration. Under the present sintering condition, 0.02 wt.% could be a favorable doping concentration. It demonstrates that residual pores could be effectively eliminated by inducing a small amount of CaO to accelerate the densification during sintering process. As far as we know, transparent Y_2O_3 ceramics especially highly transparent Y_2O_3 with CaO as sintering additives have never been reported before.

Fig. 7.5 In-line transmission of the Y_2O_3 ceramics with different CaO contents vacuum sintered at 1550 °C and HIP-ed at 1510 °C.

7.1.3.4 Hardness and thermal conductivity

The Vickers hardness were tested using a digital hardness tester (FM-700e, FUTURE-TECH, Japan). Vickers hardness can be calculated from the following equation⁶⁷:

$$H_V = k \left(\frac{P}{d^2} \right) \quad (7.4)$$

where P is the load applying to the indenter (here is 29.4 N), d is the diagonal length of the indentation, k is the shape factor of the indenter (1.854 for a pyramid-shaped).

The Vickers hardness of the Y_2O_3 ceramics vacuum sintered at 1550 °C followed by HIP-ing at 1510 °C was shown as Table 7.1. Generally, the Vickers hardness decreased with the increasing CaO content related to the increasing grain size. For example, the Vickers hardness of the undoped Y_2O_3 ceramics, initially 738.72, decreased to 689.06 as the doping concentration reached 0.15 wt.%. However, 0.01 wt.% CaO-doped samples showed a lower hardness than the 0.02 wt.% CaO-doped sample. This is

because the porosity in the ceramics is detrimental to the material's mechanical property.

Table 7.1 Mechanical property of Y₂O₃ ceramics with different CaO content

CaO content (wt.%)	Average grain size (μm)	Vickers hardness (HV)
0	1.04	738.72
0.01	1.66	722.21
0.02	1.86	723.84
0.05	2.17	706.14
0.15	3.62	689.06

The thermal conductivity of transparent Y₂O₃ ceramics with different contents of CaO is shown as Fig. 7.6. It was calculated according to the formula:

$$\lambda_c = \alpha \rho C \quad (7.5)$$

where α is the thermal diffusivity measured by laser-flash method, ρ is the theoretical density of Y₂O₃ (5.01 g/cm³), and C is the specific heat capacity of Y₂O₃ calculated by:¹³²

$$C(\text{J/g}\cdot\text{K}) = 0.441 + 1.284 \times 10^{-4} \times T \quad (7.6)$$

In comparison with the undoped Y₂O₃ sample, there is a slight decrease of the thermal conductivity with the increasing CaO doping concentration. This is reasonable because the mismatch of the atomic mass and ionic radius between the substitutions and host crystalline materials could lead to phonon scattering and thermal conductivity reduction owing to the mismatch of the atomic mass and ionic radius.¹³³ However, because of the small amount of CaO doping, the degradation range of the thermal conductivity was very small. For example, the thermal conductivity of 0.15 wt.% CaO-doped sample still reached 14.6 W/mK at room temperature.

Fig. 7.6 Thermal conductivity of the Y_2O_3 ceramics with different contents of CaO versus temperature.

7.1.4 Conclusions

In conclusion, transparent CaO-doped Y_2O_3 ceramics have been successfully fabricated by vacuum sintering plus HIP. The effects of small amount CaO doping with different concentration on the sintering behavior, optical transmission, mechanical strength and thermal properties have been investigated. It has been proven that optimized content of CaO could be effective to improve Y_2O_3 sinterability and exclude residual pores inside the ceramics. The highest in-line transmission (81.41% at 600 nm) was achieved by 0.02 wt.% CaO-doped sample vacuum sintered at 1550 °C and HIP-ed at 1510 °C whose Vickers hardness was 723.84 HV and thermal conductivity at room temperature was 14.8 W/mK.

7.2 Calcium and zirconium co-doped Y_2O_3 transparent ceramics

7.2.1 Introduction

In the previous section, it has been demonstrated that the introduction of CaO could promote grain boundary mobility, and hence, promote the densification rate of Y₂O₃ ceramics. However, there is a problem that the samples presented slight yellowish color after sintering, as shown in Fig. 7.7. Similar phenomenon was also mentioned by Huo et al. in their studies.⁵⁴ The possible reason is that doping with divalent Ca²⁺ could create Ca_Y' and V_O'' as given in equation (7.3). After air annealing, V_O'' sites are compensated by oxygen. However, Ca_Y' sites carrying negative charges still exist inside the ceramics. The charge unbalanced defects work as color centers leading to the color deviation of ceramics. Highly transparent Y₂O₃ ceramics have been fabricated, though, it is well known that color centers could be detrimental to the lasing efficiency.

The tetravalent sintering additive Zr⁴⁺ in transparent Y₂O₃ ceramics has been widely studied.^{38,125,126} The doping of Zr⁴⁺ produces oxygen interstitials and Zr⁴⁺ substitutions at Y³⁺ sites:

However, it was reported that photodarkening effect could be observed when the Zr-doped Y₂O₃ ceramics were irradiated by a laser diode, which was also caused by the charge defects.⁸² In this case, combining equation (7.3) and (7.7), electrical neutrality of the ceramics could be theoretically realized by Ca-Zr co-doping with the same atom ratio.

Fig. 7.7 Pure Y_2O_3 ceramics (left) and Ca-doped Y_2O_3 ceramics (right).

Moreover, flashlamps, which are the earliest pumping source for solid-state lasers, are still widely used in high-power laser applications.⁸³ However, it is known that high intensity ultra-violet (UV) radiation can be produced from a flashlamp during the irradiation. It is widely known that once the solarization phenomenon emerges in a laser host material, transparency of the gain medium will decline and the laser efficiency would degrade significantly.^{83,134–136} For example, the solarization phenomena of a Nd:GGG single crystal led to 45% drop in transmittance of the crystal at the wavelength of 500 nm.¹³⁷ In order to prevent the solarization phenomena, one method is to utilize UV cut filter. For example, Yagi et al. discovered that by using a Sm:glass flow tube as the UV cut filter, the Nd:YAG ceramics pumped with high power flashlamp was durable without solarization phenomena.⁸³ Nevertheless, this method increases the complexity of the system and is not cost-effective. Therefore, if ceramic laser gain media were able to resist the irradiation of UV light without solarization phenomena and pump light without laser induced photodarkening, it would be easier to achieve high power lasers by either flashlamp pump or LD pump.

In this part, different concentrations of CaO and ZrO_2 were introduced into Y_2O_3 ceramics as sintering additives. The charges were balanced by Ca-Zr co-doping with molar ratio of 1:1. Y_2O_3 ceramics with high transparency were fabricated without the

observation of yellowish color deviation. In addition, illuminated by a UV laser, the as-sintered Y_2O_3 ceramics did not show any UV darkness effects.

7.2.2 Experimental procedure

The powder preparation and sintering method were the same as the description in 7.1.2. Calcium oxide and zirconium oxide were added into Y_2O_3 powders as a ratio of 0.05 at.%, 0.1 at.%, 0.2 at.%, 0.3 at.%, and numbered as CZ1, CZ2, CZ3, CZ4, respectively (shown in Table 7.2).

Table 7.2 Ca-Zr doping contents in Y_2O_3 ceramics

Number	CaO (at.%)	ZrO2 (at.%)
CZ1	0.05	0.05
CZ2	0.1	0.1
CZ3	0.2	0.2
CZ4	0.3	0.3

7.2.3 Results and discussion

7.2.3.1 Densification and microstructural characterization

Figure 7.8 shows the densification and grain growth behaviors of Ca-Zr co-doped Y_2O_3 ceramics with different doping concentrations. After vacuum sintering at 1550-1700 °C for 7 h, the relative density of the ceramics rose gradually with increasing doping content. For example, at 1550 °C, relative density of CZ1 was merely 90.2%, while that of CZ4 reached 93.1%. It demonstrated that Ca-Zr co-doping could enhance the densification of Y_2O_3 ceramics during the initial and intermediate stage sintering. As

the sintering temperature increasing, the relative density of all the samples increased. CZ4 achieved full densification at 1650 °C, while the relative density of CZ1 was still going up at 1700 °C. It indicates that the higher level of Ca-Zr co-doping the samples have, the lower the full densification temperature it would be.

There is no significant grain size difference of samples with different contents of sintering additives when the sintering temperature is lower than 1650 °C. However, at 1700 °C, the sample with higher Ca-Zr doping concentration showed smaller grain size. The grain growth behavior here is quite different from that of the Ca-single-doped Y_2O_3 ceramics shown in Fig. 7.2. Generally, acceptor dopants (Ca^{2+}) enhance the grain boundary mobility while donor dopants (Zr^{4+}) suppress the grain boundary mobility.¹²⁸ The present results indicate that Zr^{4+} was in domination at the final-stage sintering, suppressing the grain growth of Y_2O_3 ceramics.

Fig. 7.8 Densification and grain growth behavior of Ca-Zr co-doped Y_2O_3 ceramics with different doping concentrations.

Fig. 7.9 presents the microstructure of the Y_2O_3 ceramics after vacuum sintering at 1575 °C for 30 h plus HIP-ing at 1510 °C for 4 h. The samples have similar grain size which is around 2 μm. It indicates that the contents of sintering additives do not have obvious

effects on the grain growth at relatively low sintering temperatures. The CZ2 sample shows a fully densified structure, without detecting of any intergranular or intragranular pores. Nano-sized residual pores on grain boundaries can be found, more or less, in CZ1, CZ3, and CZ4. It suggests that 0.1 at.% could be the favorable doping concentration under the present sintering strategy.

Fig. 7.9 SEM images of Ca-Zr co-doped Y_2O_3 ceramics vacuum sintered at 1575 °C for 30 h and HIP-ing at 1510 °C for 4 h.

7.2.3.2 Optical properties

After vacuum sintering at 1575 °C for 30 h and HIP-ing at 1510 °C for 4 h, the in-line transmittance of each samples is shown in Fig. 7.10. Samples with relatively low doping concentration (CZ1 and CZ2) exhibit higher transmittance. The CZ2 sample, whose Ca-Zr doping concentration is 0.1 at.%, exhibits the highest transmittance, reaching 82.08% at 600 nm. When increasing the amount of Ca-Zr, there is transparency

degradation. For example, the transmittance of 0.2 at.% co-doped sample is 77.93% at 600 nm and it reduced to merely 58.14% when the doping concentration is increased to 0.3 at.%.

Fig. 7.10 In-line transmittance of HIP-ed Ca-Zr co-doped Y_2O_3 ceramics.

Fig. 7.11 shows the photograph of the Ca-Zr co-doped Y_2O_3 ceramics after vacuum sintering and HIP-ing. It is clear that the CZ2 sample has the best transparency. As the doping amount was further increased, more haze and scatters could be observed. Moreover, compared with the Ca-single-doped Y_2O_3 ceramics in Fig. 7.7, Ca-Zr co-doped Y_2O_3 ceramics show the same color as pure Y_2O_3 ceramics, without color deviation. It is demonstrated that: 1) the yellowish color was resulted from the charge imbalances caused by Ca^{2+} doping; 2) the introduction of Zr^{4+} could effectively balance the charges in the ceramics thus prevent the color deviation.

Fig. 7.11 Photograph of the Ca-Zr co-doped Y_2O_3 ceramics, from left to right: CZ1 (0.05 at.%), CZ2 (0.1 at.%), CZ3 (0.2 at.%), and CZ4 (0.3 at.%).

In order to verify the charge balancing effect of Ca-Zr co-doping, charge balanced and unbalanced Y_2O_3 ceramics were irradiated with a UV laser, with the lasing wavelength of 244 nm and the beam size of 2 mm. The samples are placed on the propagation path of the UV laser, with the surface perpendicular to the laser beam. During the irradiation, the samples are moved slowly in the direction perpendicular to the laser beam, aiming to increase the area of color centers and make them more obvious if they are produced. The irradiation on each sample is lasted for 10 minutes.

As shown in Fig. 7.12, brown color centers were produced by UV laser in the charge unbalanced yttria ceramics. However, yttria ceramics prepared in accordance with charge balanced doping concentration do not present any UV darkness effects.

Fig. 7.12 Photographs of the (a) charge unbalanced and (b) charge balanced Y_2O_3 ceramics after UV laser irradiation.

7.2.4 Conclusions

In conclusion, by co-doping 0.05-0.3 at.% CaO and ZrO_2 as sintering additives, Y_2O_3 ceramics with high transparency have been fabricated. The highest transmittance was achieved by the 0.1 at.% co-doped Y_2O_3 ceramic, which reached 82.08% at 600 nm. The brownish color deviation caused by charged imbalances has been corrected by the equal molar ratio doping of Ca^{2+} and Zr^{4+} . It has been also demonstrated that the charge balanced ceramics could effectively resist UV darkness effects.

Considering that the Ca-Zr co-doping system has never been reported before, the present preliminary results are promising for the fabrication of photo-darkening-free sesquioxide laser ceramics. However, there are still many works remaining to be done, like the influences on the diffusion mechanism during densification, the mechanical property and thermal conductivity changes, and the lasing efficiency of rare-earth ion doped laser ceramics.

Chapter 8 Conclusions and recommendations

8.1 Conclusions

The fabrication of high optical quality, high efficiency sesquioxide laser ceramics is very challenge as it requires to appropriately control the various processing parameters, like powder aggregation degree, green body initial density, sintering temperature and soak time, sintering additives, and grain growth control. In this research, studies have been conducted on the powder synthesis, the sintering behavior and microstructural evolution of different powders, the influences of sintering additives on the densification and grain growth.

Chemical co-precipitation has been proved to be an effective method to synthesize high quality sesquioxide powders. Agglomerations could be generated during either aqueous chemical reaction or calcination process. It was found that as a dispersant PAA could inhibit the formation of large agglomerates during precipitating process and produce loose precursors. $(\text{NH}_4)_2\text{SO}_4$, on the other hand, was effective in inhibiting the agglomeration of powders during the calcination.

However, the experiment also showed that the introduction of dispersants created the potential risk of impurity contamination that could degrade the lasing efficiency of the produced ceramics. To avoid the problem the spray precipitation technique could be applied. It has been demonstrated that spray precipitation is a very effective approach to reduce the degree of agglomeration of Y_2O_3 precursor and powder. Powders synthesized by spray precipitation method exhibited much higher densification rate and thus higher final sintered density. Without using sintering additives, Y_2O_3 transparent ceramics could be fabricated.

Using the powders synthesized by spray precipitation method and vacuum sintering plus hot isostatic pressing (HIP) strategy, sesquioxide transparent ceramics that fulfill the laser requirements have been successfully fabricated. For instance, the in-line transmittance of 0.6 at.% Nd:Y₂O₃ transparent ceramics reached 81.6% at 1000 nm and remained 81.1% at 650 nm, which equals the theoretical value of Y₂O₃ single crystals. The highest CW laser output power and lasing efficiency of a Nd:Y₂O₃ ceramic laser at ~1.08 μ m and ~1.36 μ m were achieved, respectively. Moreover, submicron-grained (0.6 μ m) 3.3 at.% Yb:Lu₂O₃ ceramics have also been fabricated. The great mechanical strength and high thermal conductivity have been verified. The in-line transmittance of the 3 mm thickness ceramic samples could reach 80.0% at 600 nm. Pumped by a fiber coupled laser diode at 940 nm, an uncoated Yb:Lu₂O₃ ceramic slab has produced 2.5 W output power with a corresponding slope efficiency of 24.2% at 1079.8 nm.

Using CaO as a sintering additive, even with very small amount, the grain boundary mobility of Y₂O₃ ceramics could be greatly enhanced. It has been proven that optimized content of CaO (0.02 wt.%) could be effective to improve Y₂O₃ sinterability and exclude residual pores inside the ceramics. However, the accompanying problem of CaO single doping was that color deviation caused by the charge imbalance could be produced. In this case, CaO and ZrO₂ were co-doped into Y₂O₃ ceramics. The highest transmittance of 82.08% at 600 nm has been achieved. The brownish color deviation has been corrected by the equal molar ratio doping of Ca²⁺ and Zr⁴⁺. It has been also demonstrated that charge balanced ceramics could effectively resist UV darkening effect.

8.2 Recommendation for further research

Although highly transparent Y_2O_3 and Lu_2O_3 ceramics have been fabricated and high efficiency laser output have been obtained, there are still many works remaining to be done in the future:

1. The preliminary results in this research have shown that Ca-Zr co-doping system is promising for the fabrication of high quality sesquioxide laser ceramics. For this sintering additive system has never been reported before, there are many aspects remaining to be further investigated, like the influences on the diffusion mechanism during densification, the mechanical property and the variation of thermal conductivity, and the lasing efficiency of rare-earth ion doped laser ceramics.
2. Compared with the current dry pressing followed by CIP forming technique, wet forming techniques like slip casting and tape casting are good approaches to improve the homogeneity and initial density of ceramic green bodies. The reduction of porosity as well as pore size can promote the densification rate, lower the sintering temperature, and remove large scattering sources formed by inhomogeneous packing. It is worth incorporating the wet forming techniques in the fabrication process.
3. Composite structure laser ceramics is a new tendency. On the one hand, better heat removal can be realized by using a ceramic with controlled doping density profiles of the active ions.¹³⁸ On the one hand, by controlling the distribution of laser-active ions in the ceramic, the desired mode of laser operation can be generated.¹⁶

Author's Publications

JOURNAL PAPERS

1. **Danlei Yin**, Jun Wang, Ying Wang, Peng Liu, Jie Ma, Xiaodong Xu, Deyuan Shen, Zhili Dong, Ling Bing Kong, Dingyuan Tang, Fabrication of Er:Y₂O₃ transparent ceramics for 2.7 μ m mid-infrared solid-state lasers, submitted to *Journal of the European Ceramic Society*, 2019, Submitted.
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