Fabrication and characterization of rare-earth doped sesquioxide laser ceramics

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**
SINGAPORE

**FABRICATION AND CHARACTERIZATION OF
RARE-EARTH DOPED SESQUIOXIDE LASER
CERAMICS**

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

2017

STATEMENT OF ORIGINALITY

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

2017/01/13
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ABBREVIATIONS

YAG	Yttrium aluminum garnet
Nd	Neodymium
Tm	Thulium
Ho	Holmium
CW	Continuous wave
EDX	Energy-dispersive X-ray spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
FESEM	Field Emission Scanning Electron Microscope
BET	Brunauer-Emmett-Teller
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
HP	Hot press
HIP	Hot isostatic press
CIP	Cold isostatic press

ABSTRACT

Sesquioxide transparent ceramics such as Y_2O_3 , Lu_2O_3 , and Sc_2O_3 , have received a great attention as potential high powder solid-state laser hosts. To meet the laser applications requirements, porosity of the ceramics must be lower than 0.01%. Densification of ceramics is closely related to quality of powders, sintering additives and sintering techniques. In the present research, comprehensive studies concerning the above factors are conducted in the view of ceramics science.

Rare-earth ions doped Y_2O_3 powders have been synthesized by using solid-state reaction and chemical co-precipitation process, respectively. It was found that slurry concentration during ball milling affects the morphology and agglomeration degree of the powders, and thus influences the densification and grain growth of Y_2O_3 ceramics. However, it was difficult to completely eliminate the hard agglomeration by ball milling. In comparison, the powders synthesized by chemical co-precipitation process had more uniform particle size. Densification was strongly affected by both the agglomeration degree and the purity of powders. At the optimized calcination temperature of precursor (1300 °C), Y_2O_3 nanopowders with high purity and low degree of aggregation were obtained. ZrO_2 , as the sintering additive, was effective in inhibiting the agglomeration of powders during the calcination. Meanwhile, it prevented the pore-boundary separation by solute drag mechanism during the sintering process. Reduction of the amount of sintering additives enhanced the thermal conductivity of Y_2O_3 ceramics. Grain boundary diffusion rate of Y_2O_3 could be well controlled by co-doping with ZrO_2 and Al_2O_3 . Addition of a very small amount of Al_2O_3 (81.8 wt ppm) enhanced densification and grain growth rate due to the activated sintering mechanism. Sintering method was equally important in terms of achieving full densification. Differentiate densification

was prevented by using low heating rate or a three-step sintering process. Through optimizing the sintering maps (densification and grain growth) of Y_2O_3 and Lu_2O_3 ceramics respectively, nearly full densification of the ceramics without sintering additives was achieved. Hot isostatic press (HIP) sintering provided a strong driving force for the densification of ceramics, thus sintering temperature could be greatly reduced and pore-boundary separation was prevented. Room temperature CW laser oscillations were demonstrated both on the 5 at.% Yb: Y_2O_3 and the 8 at.% Yb: Lu_2O_3 transparent ceramics fabricated in the project

1

INTRODUCTION

1.1 Motivation

In the past decades, solid-state lasers have been widely used in metal processing, medical applications¹, optical transmission and environmental detection systems². Apart from that, they have been demonstrated as a promising device for future nuclear-fusion applications.¹ Since the first successful continuous-wave (c.w.) laser oscillation was generated by using an Nd:YAG single crystal at room temperature in 1964,³ designs of solid-state lasers using various single crystals have continually progressed.¹

Since Ikesue et al.^{4,5} successfully fabricated transparent neodymium-doped yttrium aluminum garnet (Nd:YAG) ceramics and first achieved their laser oscillation in 1995, YAG ceramics have become one of the important laser host materials. Nowadays, it is not unrealistic to fabricate highly transparent YAG-based ceramics that have optical transmittance comparable to YAG single crystals. Moreover, ceramics have advantages such as high yield, short fabrication period and ease of making large sizes.^{6,7} In addition, specially designed structure such as composite structure is much easier to realize in ceramics. This technique could be well utilized to improve the thermal conduction of ceramics during laser operation.^{1,8} In fact, the highest power of solid state lasers (>100 KW) achieved to date was originated from the Nd:YAG ceramics provided by the

Konoshima corporation⁹, implying the great potential of the garnet ceramics for high power lasers.

Recent studies indicated that sesquioxide transparent materials, such as Y_2O_3 , Lu_2O_3 , and Sc_2O_3 , possess lower thermal expansion, higher thermal conductivity and lower phonon energy than YAG, and thus are considered as another excellent host material for solid-state lasers.¹⁰⁻¹² 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, which is higher than that of the undoped YAG (10.7 W/mK).¹³ For high-power solid-state lasers, efficient heat removal is critical, because the rise in temperature increases the population of the terminal laser level, which decreases the lasing efficiency. Moreover, the temperature gradient in laser rods, associated with nonradiative relaxation of the active ions, induces thermal lensing effects,¹⁴ which is detrimental to the laser operation. In this respect, thermal conductivity of the ceramics should be as high as possible for effective heat removal. Thanks to the relatively high thermal properties of sesquioxides that they become more promising laser gain medias for the high power solid-state laser applications.

However, growth of sesquioxide single crystals is 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 sophisticated and expensive facilities.^{1, 15} 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. Relatively low mechanical strength is another problem for the single crystals. In this respect, sesquioxide transparent ceramics become very important in terms of replacing single crystals to become the main solid-state laser host materials. Transparent ceramics have various advantages over single crystals, such as cost-effectiveness, large-scale production, feasibility of shape controlling and better mechanical properties.

Therefore, sesquioxide transparent ceramics would be very promising alternative host materials for high power laser applications. The primary problem existing in ceramics is that it is very difficult to remove all the scatterings and achieve fully transparency (comparable to single crystals), which is the main constraint on solid-state laser applications.

1.2 Objectives and scope

It is important to fully understand the main factors leading to scatterings in sesquioxide transparent ceramics. The purpose of this research is to develop processes to remove all the scattering centers such as impurities, secondary phases, and residual pores, and achieve full transparency in sesquioxide transparent ceramics. This research is organized to address the following objects:

1. Fabrication of well dispersed sesquioxide nano-powders with homogeneous particle size and good sinterability.
2. Explore the role of sintering additives on the densification of sesquioxide ceramics.
3. Investigate the microstructure evolution during sintering, thus the most favorable sintering method can be developed to sinter ceramics.

1.3 Dissertation Overview

The thesis addresses the process of fabricating sesquioxide transparent ceramics for solid-state laser applications.

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

Chapter 2 reviews the classic sintering theory concerning the densification of ceramics. In addition, various methods regarding the fabrication of sesquioxide transparent ceramics are reviewed.

Chapter 3 discusses how does different ball milling conditions influence the quality of powders, and the subsequent densification of Y_2O_3 transparent ceramics.

Chapter 4 addresses the problems of obtaining high quality Y_2O_3 raw powders using chemical co-precipitation process. In addition, how the sintering additive (ZrO_2) influences the agglomeration of powders is discussed.

Chapter 5 addresses the importance of sintering controls on the full densification of Y_2O_3 ceramics. The first room temperature laser oscillation of $Ho:Y_2O_3$ transparent ceramics is demonstrated.

Chapter 6 discusses the role of Al_2O_3 on the densification and grain growth of Y_2O_3 transparent ceramics. Reducing the doping amount of ZrO_2 is realized by co-doping with a small amount of Al_2O_3 or assisting the densification by HIP sintering.

Chapter 1 Introduction

Chapter 7 discusses the disadvantages of sintering additives. The possibility of fabricating sesquioxide transparent ceramics without sintering additives is explored.

Chapter 8 gives the conclusions and the suggestion for future work.

2

BACKGROUND

2.1 Crystal structure of sesquioxide ceramics

RE_2O_3 (RE implies Y, Sc, Lu and other lanthanide rare earth elements) takes the cubic bixbyite (C type) crystal structure. Its space group is $\text{Ia}\bar{3}$. Take Y_2O_3 as an example. Figure 2.1 shows the bixbyite structure with two yttrium cations (Y^{3+}). Y atoms take 8a and 24d sites, while all the O atoms are located at normal sites, 48e. Another explanation is that the bixbyite structure can be regarded as evolved from the fluorite (CaF_2) crystal structure, that is, one-fourth of the O atoms are removed from the fluorite crystal lattice.¹⁶

Fig. 2.1 Illustration of the bixbyite crystal structure.¹⁶

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. Some of the oxygen atoms are removed from this structure and metallic ions 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.¹⁶ Table 2.1 exhibits the physical, thermal and optical properties of Y_2O_3 . It can be seen that it has a broad range of transparency (0.23-8 μm). Thanks to its cubic crystal structure that Y_2O_3 ceramic is optically isotropic. The phonon energy of Y_2O_3 is 560 cm^{-1} , which is lower than that of YAG (700 cm^{-1}).¹⁶ The lower photon energy can decrease the energy loss due to nonradiative transition, improve the probability of radiative transition, and thus ensures higher luminescence quantum efficiency.^{17, 18}

Fig. 2.2 Crystal structure evolution from (a) MO₂ fluorite structure to (b) C type M₂O₃ structure.¹⁶

Table 2.1 Physical, thermal and optical properties of Y₂O₃.¹⁶

Physical, thermal and optical properties of Y ₂ O ₃			
Melting point (°C)	2410	Transparency range (μm)	0.23-8
Structure type	Bixbyite (cubic)	Refractive index @1000nm	1.8892
Lattice constant (Å)	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

Fig. 2.3 A schematic showing the light scattering sources of transparent ceramics.¹

Polycrystalline ceramics are composed of many randomly oriented crystals (grains), with grain sizes ranging from several hundred nanometers to over one hundred micrometers. The thickness of a clean grain boundary is generally in the order of 2-10 atomic dimensions. Fig. 2.3 shows a typical microstructure of a ceramic. There are certain possible scattering sources such as (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. Compared with single crystals, ceramics are more likely to be scattered by their grain boundaries and residual pores. In the case of solid-state lasers, “unclean” grain boundaries or residual pores, even if a very small amount, will lead to light scattering and the decreasing of amplification efficiency. In order to perform an effective laser gain medium, the quantity of scattering sources in transparent ceramics should be controlled to be less than several tens percent mm^{-1} .¹

Therefore, in order to obtain transparent ceramics without scatterings, it is important to obtain ceramics with clear grain boundaries. In other words, there should not be grain boundary pores, secondary phases and impurities in grain boundaries, as they will act as scattering centers that can strongly degrade the transparency. Generally, it is relatively easier to remove the secondary phases and impurities within grain boundaries, provided that the initial stoichiometry is precisely controlled and the whole process is strictly monitored. In this case, the most demanding point is how to effectively remove the residual pores. After all, before sintering, green bodies shaped by dry pressing or other

wet forming techniques tend to have porosity of above 40%. How to remove all these pores and obtain fully dense ceramics (porosity<0.1%) should be a big challenge. Residual pores are considered the predominant light scattering sources in a given transparent ceramic, because of the huge difference in refractive index between air and the host materials.

2.3 Theoretical transmittance

The following two equations exhibit the calculation of theoretical light transmittance of a defect-free single crystal:^{19, 20}

$$T=(1-R)^2\exp(-\alpha t) \quad 2.1$$

$$R = \frac{(n - n_a)^2}{(n + n_a)^2} \quad 2.2$$

Where α is the absorption coefficient, 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 value can be calculated based on the formula:

$$T=100[1-((n-1)/(n+1))^2]^2 \quad 2.3$$

For instance, at the wavelength of 500 nm, the refractive index of Y_2O_3 is 1.947.²⁸ Therefore, the theoretical transmittance of Y_2O_3 at 500 nm wavelength is 80.4% based on the above equation.

2.4 Sintering

2.4.1 Driving force for sintering

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 $\Delta(\gamma A) = \Delta\gamma A + \gamma\Delta A$.

Here, grain coarsening leads to the change of interfacial area and densification leads 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. Figure 2.4 shows the typical phenomena associated with sintering. It can be seen that both grain

coarsening and densification lead to the total reduction of energy. If the diffusion processes that lead to densification dominate, pores will shrink and finally be removed with sintering proceeds. However, if the diffusion processes that lead to grain coarsening dominate, both grain size and pore size will grow larger. Moreover, the increasing of grain size will further suppress the driving force for densification. In this case, the complete densification of a compact will become very difficult. Therefore, a sintering process is actually the competition between the two mechanisms.

Fig. 2.4 Basic phenomena occurring during sintering.²¹

2.4.2 Diffusion mechanisms: for densification and for grain growth

There are six different diffusion mechanisms associated with sintering, as is shown in Fig. 2.5. They are (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. Among them, only the diffusion from grain boundaries lead to densification (pore shrinkage), while the other mechanisms only result in grain coarsening. The distance between particles will not be reduced when

atoms diffuse to the neck from the particle surface. Though the neck size is increased, it is just a kind of atoms redistribution which only leads to grain coarsening. Therefore, the diffusion mechanisms (4), (5), and (6) lead to densification, but the mechanisms (1-3) only lead to neck growth without densification. During sintering, all the diffusion mechanisms coexist in a given ceramic compact. Generally, with sintering proceeds, the relative contributions of different diffusion mechanisms also change. In addition, the relatively strengthening of one single mechanism is accompanied by the weakening of the others. Green bodies will go through three typical sintering stages before fully densified: initial stage sintering, intermediate stage sintering, and final stage sintering.

Fig. 2.5 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.²²

2.4.3 Initial stage sintering

During the initial stage sintering, the effective contact area rate between particles is generally increased from zero to around 0.2. This is called “neck growth”, during which there is generally several percent of interparticle shrinkage. Typically, during the initial stage sintering, relative density of a given ceramic compact would increase from ~0.5 to ~0.6, but also depending on different initial powders and forming techniques. In this stage, there is not grain growth, as the solid-vapor surfaces diverge at an acute angle from the particle-particle contact area.²³ 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.²³

2.4.4 Intermediate stage sintering

During the intermediate stage sintering, the pore phase is continuous. There are open pore channels that are coincident with three-grain edges. With the proceeds of intermediate stage sintering, there are generally both obvious grain coarsening and obvious ceramic densification. During this stage, because of the much surface area of grains, the grain coarsening is primarily associated with surface diffusion and vapor transport. When all the pores are pinched off and become isolated grain junction pores, the final stage sintering begins. Generally, when the final stage sintering begins, relative density of a ceramic compact has increased to about 90%-94%. Figure 2.6 exhibits the typical geometrical models for the intermediate stage and the final stage sintering.²¹

Fig. 2.6 Coble's geometrical models for (a) intermediate stage and (b) final stage sintering.²¹

2.4.5 Final stage sintering

Final stage begins when the pore phase is pinched off. At the beginning of final stage sintering, all the closed pores tend to locate at grain junctions. Relative density achieves 93% or above, as is revealed in Fig. 2.7. With the further proceeds of final stage sintering, the pores located at grain boundaries can further shrink thanks to the grain boundary diffusion and lattice diffusion mechanisms. When all pores on grain boundaries have been eliminated, the sintering process would be completed and ceramics are fully densified.

However, in the case of final-stage sintering, pore-boundary separation is very easy to occur before completion of densification, generating intragranular pores. Compared with grain boundary pores, intragranular pores are very difficult to remove, as only lattice diffusion mechanism contributes to their elimination. Moreover, the activation energy for lattice diffusion is much higher than that for grain boundary diffusion, resulting in that the diffusion rate of lattice diffusion is orders lower than that of grain boundary diffusion. During the initial stage and intermediate stage sintering, grain boundary migration rate is relatively low and thus pore-boundary separation is difficult to occur, because the many pores 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. Once the moving velocity of grain boundary is higher than that of pores, pore-boundary separation will inevitably occur.

Fig. 2.7 A schematic showing the densification curve of a powder compact and the three sintering stages.²¹

2.4.5.1 Pore-boundary interactions

The primary barrier to the full densification of a ceramic compact is from the separation of pores from grain boundaries.²⁴ Pores attached to grain boundaries can be filled primarily by the grain boundary diffusion process. However, once a pore is detached, and locates within the grain, it can only shrink by the much slower mechanism of lattice diffusion. Consequently, observations indicate that once trapped inside a grain, the pore does not exhibit significant shrinkage.

In order to completely remove pores and sinter ceramics to high density, the microstructure that pores are attached to grain boundaries must always be maintained during the final stage sintering. Fig. 2.8 shows a typical interaction between a grain boundary and an attached pore in the final stage of sintering. It can be seen that with the migrating of the grain boundary, a dragging force is applied on the pore attached to it. Therefore, the pore is dragged along and moves toward the same direction with the moving grain boundary. In addition, the pore shape is distorted due to the dragging force of the grain boundary. Specifically, the trailing surface of the pore becomes more

strongly curved, while its leading surface becomes less strongly curved. The difference in curvature leads to the flux of atoms from the leading surface to the trailing surface, thus the pore moves along with the grain boundary.

In order to better understand the reason why pore-boundary separation would occur during sintering, the intrinsic driving forces associated with boundary movement and pore movement should be explored respectively.

Fig. 2.8 Possible transport paths for a pore moving with a grain boundary.²⁵

2.4.5.2 Pore mobility

For each of the mechanisms indicated in Fig. 2.8, analysis of the atomic flux from the leading surface of the pore to the trailing surface yields pore mobility, M_p , of the form^{25, 26}:

$$M_p = \frac{AD\Omega}{kTr^n} \quad 2.4$$

$$D = D_0 \exp\left(\frac{-Q}{kT}\right) \quad 2.5$$

Where A is a constant, Ω is the atomic volume, k is the Boltzmann constant, T is the absolute temperature, r is the radius of the pore, 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. Q is the activation energy corresponding to the different diffusion mechanisms.

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

$$F_p = \pi r \gamma \quad 2.6$$

Where γ is the specific surface energy of grain boundary.

Therefore, combining Eqs. 2.4 with 2.6, the maximum moving velocity of the pore, V_p , can be expressed as:

$$V_p = F_p \cdot M_p = \frac{AD_0\Omega\pi\gamma}{kTr^{n-1}} \exp\left(\frac{-Q}{kT}\right) \quad 2.7$$

According to Eq. 2.7, small pores tend to have very high mobility and thus are able to remain attached to the boundary.

2.4.5.3 Grain boundary mobility

During the final stage sintering, the grain boundary mobility is primarily related to the sintering temperature, the segregated boundary solute phases, and the grain boundary diffusion coefficient. The value of grain boundary mobility (M_b) is given by²⁵:

$$M_b = \begin{cases} \frac{D_b\Omega}{kT\delta_{gb}} (\text{undoped}) \\ \frac{D'_b\Omega}{4kT\delta_{gb}\sigma C} (\text{doped}) \end{cases} \quad 2.8$$

Equation 2.8 represents the grain boundary mobility of the pure ceramic without foreign ions' doping (intrinsic mobility) and the grain boundary mobility of the ceramic with doping, respectively. D_b and D'_b represent respective diffusion coefficient of atoms across the boundary, Ω is the atomic volume, k is the Boltzmann constant, T is the absolute temperature, δ_{gb} is the grain boundary thickness, σ is a partition coefficient for the solute distribution between the boundary and the lattice, and C is the concentration of the solute atoms in the lattice.

Chapter 2 Background

Force on a pore-free boundary, owing to its curvature, is given by:

$$F_b = 2\gamma a^2/G \quad 2.9$$

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

Combining Eqs. 2.6, 2.8 and 2.9, grain boundary moving velocity (V_b) is given by:

$$V_b = (F_b - NF_p)M_b = \begin{cases} \left(\frac{2a^2}{G} - N\pi r\right) \frac{D_b \Omega \gamma}{kT\delta_{gb}} (pure) \\ \left(\frac{2a^2}{G} - N\pi r\right) \frac{D'_b \Omega \gamma}{4kT\delta_{gb}\sigma C} (doped) \end{cases} \quad 2.10$$

Where N is the average number of pores surround a grain.

It can be seen that there are several different ways that could be utilized to control the moving velocity of grain boundaries. For example, as D_b is increased exponentially with the increasing sintering temperature, grain boundary moving velocity will be improved if sintering temperature is increased. On the other hand, if there is solute phase segregated at grain boundaries during sintering, grain boundary mobility tends to be suppressed. However, it should be noted that the doping of solute phase will not always suppress the grain boundary mobility. For example, if the size of doped ions is much smaller than the host atoms, or activated sintering or liquid phase sintering is triggered by the doping, the grain boundary diffusion coefficient will be improved drastically. In this case, the enhancement of boundary mobility caused by grain boundary diffusion might be greater than the solute drag effect of the solute phases, and the boundary mobility will be increased.

2.4.5.4 Pore-boundary separation conditions

In order to prevent the pore-boundary separation, it should be ensured that the maximum moving velocity of a pore is higher than the moving velocity of a boundary. In other words, the following law must be obeyed: $V_b \leq V_p$.

Combining the Eqs. 2.7 and 2.10, the conditions for pore separation and pore attachment can be obtained, which is shown in Fig. 2.9. Figure 2.9 shows the grain size versus pore size map revealing at which conditions the pore-boundary separation will occur. With the pores attached to the boundary, the mobility of the boundary/pore can either be controlled by boundary control or by pore drag (pore control). This is completely determined by the ratio of grain size to pore size. Generally, if pore size is

small and grain size is large, it is boundary control, at which situation the pore-boundary separation will not occur. However, in the sintering of ceramics where the densification is accompanied by coarsening, both the average grain size and the average pore size increase. A trajectory for densification accompanied by coarsening of the microstructure is also shown in Fig. 2.9. If the separation region is not intereseected, then the attainment of complete densification is possible. With sintering proceeds, pore-boundary separation might occur when the pores grow larger. With another situation, if pore size is large and grain size is small, it is pore control. At this situation, pores could be well attached to grain boundaries as well. That is the reason why pore-boudnary separation is generally not detected during the initial stage or the intermediate stage sintering. It can be referred that during the final stage sintering, the ratios of grain size to pore size are most likely located at the boundary control region.

Fig. 2.9 Grain size versus pore size map showing the conditions for pore attachment and pore separation.²⁶

Therefore, one effective way to prevent the pore-boundary separation is to restraint the pore size, thus the maximum moving velocity of pores is relatively high. It is

revealed from Fig. 2.9 that pore size must be maintained below a critical value to ensure attachment. This can be achieved by using well dispersed raw powders with homogeneous particle size. The finer raw powders are used, the more likely to obtain green body with small and homogeneous pore size. Hard agglomeration of powders should be avoided, as large pores can be generated after packing due to the agglomeration of powders, which are very difficult to eliminate during sintering.²⁷ Figure 2.10 illustrates two typical sintering phenomena using different initial powders. Large initial pores are very likely to survive from sintering, because, in the end, they tend to either be trapped by grains or remain located in grain boundaries due to differentiate densification²⁸. In addition, increasing the initial packing density will also help to decrease the initial pore size, thus making the pores much easier to remove.

Fig. 2.10 Schematic diagrams of microstructure evolution using (a) fine initial powders and (b) agglomerated powders.

Another effective approach to inhibit the separation is suppressing grain boundary mobility. This can be achieved by using sintering additives (dopants) that can form solid solution with the host material and then segregate at grain boundaries. The doping concentration is generally below its solid solubility limit in the host material. In this mechanism, there is strong interaction between the grain boundary and the segregated

solute, thus the solute tends to be dragged along with the moving boundary. The diffusion rate of solute is generally slower than that of the host ions. So it becomes the rate controlling species. This effect of inhibiting grain growth is called 'solute drag' effect. The grain boundary mobility limited by solute drag is lower than the intrinsic mobility, allowing larger pores to migrate with the boundary before separation. The separation region is therefore shifted to larger grain and pore sizes, as is revealed in Fig. 2.9. It is known that the grain boundary mobility is proportional to the diffusivity of the segregated solute, and inversely proportional to its segregated concentration (σC). Therefore, the effectiveness of the dopant in suppressing grain growth is dependent on its ability to segregate at the grain boundaries. 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.

2.5 Pore evolution

It is known that during sintering of ceramics, the internal surface area of the system tends to be decreased. It can be realized by filling pores with new grain boundary areas. In addition, the grains have a tendency to grow to reduce the energy associated with the grain boundaries, thereby leading to an increase in the diffusion distance. Therefore, the energy of the system is decreased. The equilibrium shape of a pore is determined by the number and shape of the grains attached to it. At equilibrium, the chemical potential of the atoms in the pore surface is the same everywhere, which is to say that the curvature of the pore surface is the same everywhere. Figure 2.11 shows the forces analysis originated from a grain boundary and an attached pore. At equilibrium, the forces are balanced²⁵:

$$\cos\left(\frac{\Psi}{2}\right) = \frac{\gamma_{gb}}{2\gamma_{sv}} \quad 2.11$$

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

Figure 2.11 (a) shows a pore surrounded by three grains. The coordination number is 3 ($N=3$). It can be noticed that the surface curvature of the pore is concave, resulting that the surface of the pore migrates towards its center of curvature, thus it will shrink. Figure 2.11 (b) shows a pore surrounded by 8 grains ($N=8$). In this situation, the surface

curvature of the pore is convex, which is determined by the balance of forces at the pore/grain boundary junctions. Unfortunately, this pore will grow due to its convex curvature. According to the thermodynamic analysis of Kingery²⁸, for a given dihedral angle, pores with a coordination number (N) greater than a critical value (N_C) will grow, whereas pores with $N < N_C$ will shrink. N_C value can be calculated from measuring the dihedral angle Ψ based on the following equation²⁹:

$$\psi = \frac{180^\circ N_c - 360^\circ}{N_c} \quad 2.12$$

Once the equilibrium dihedral angle is given, the maximum permitted pore coordination number (N) that leads to the shrinkage of pores can be calculated. Figure 2.12 shows the SEM image of the Nd:YAG ceramic with different coordination number.²⁹ Three types of pores are included in this microstructure: (1) large pore with high coordination number ($N=11$) and convex pore surface, (2) medium sized pore with critical coordination number ($N=5$) and plane surface and (3) small pore with low coordination number ($N=3$) and concave pore surface. Through measuring the dihedral angle Ψ (108°) from Fig. 2.12 and substituting it into the Eq. 2.12, N_C could be calculated ($N_C=5$). This value is good consistent with the SEM observation.

However, pore coordination number is always changing during sintering. 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, the complete elimination of this pore will become very difficult, as the driving force for densification is decreased significantly with the increase in grain size, which will be discussed in the next section.

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. This once again indicates that using initial powders without agglomeration is very important. In addition, it is equally critical to ensure the uniformity of ceramic green bodies.

Fig. 2.11 Pore-boundary interactions with different coordination number (N) and dihedral angle: (a) the pore with $N=3$ and concave surfaces and (b) the pore with $N=8$ and convex surfaces.²⁵

Fig. 2.12 Nd:YAG ceramics showing pores with different coordination number during the final stage sintering.²⁹

2.6 Densification rate during the final-stage sintering

During the final-stage sintering, porosity has been very low, thus surface diffusion mechanism does not dominate during this stage. Grain boundary diffusion or lattice diffusion mechanism tends to dominate the final-stage densification of ceramics.

2.6.1 Pressureless sintering

If the densification is dominated by grain boundary diffusion, the densification rate is expressed as³⁰:

$$\frac{d\rho}{dt} = \frac{733D_b\delta_b\gamma_s V_m}{RTG^4} \quad 2.13$$

Where D_b is the boundary diffusion coefficient, δ_b is the diffusion thickness of 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.

In the case of lattice diffusion, the densification rate is expressed as³⁰:

$$\frac{d\rho}{dt} = \frac{441D_l\gamma_s V_m}{RTG^3} (1 - \rho)^{\frac{1}{3}} \quad 2.14$$

Where D_l is the lattice diffusion coefficient.

In a real system, both the grain boundary diffusion and the lattice diffusion mechanisms contribute to the final-stage densification.³⁰ The driving force for the pressure-less sintering is the capillary pressure. However, the relative contributions of grain boundary diffusion and lattice diffusion to the densification vary with grain size. Specifically, the smaller grain size, the higher relative ratio of grain boundary area to grain volume, and thus the more domination of grain boundary diffusion is obtained. Considering that the diffusion rate of grain boundary diffusion is much higher than that of lattice diffusion, it is important to control the grain size before densification complete.

2.6.2 Pressure assisted sintering

During sintering, when external pressure is applied on ceramics, densification equations are slightly different to those without external pressure. Specifically, in the case of grain boundary diffusion, the densification rate is expressed as²¹:

$$\frac{d\rho}{dt} = \frac{101D_b\delta_bV_mP_{appl.}}{RTG^3} (1 - \rho)^{\frac{1}{3}} \quad 2.15$$

where $P_{appl.}$ is the effective pressure at grain boundaries. In the case of lattice diffusion, the densification rate is expressed as²¹:

$$\frac{d\rho}{dt} = \frac{61D_lV_mP_{appl.}}{RTG^2} (1 - \rho)^{\frac{2}{3}} \quad 2.16$$

It can be seen that if an external applied pressure (e.g. 200 MPa) is applied during the sintering, the driving force for densification would be much higher. In addition, according to Eqs. 2.15 and 2.16, a reduction in grain size could lead to great enhancement in the densification rate.

2.7 Fabrication of sesquioxide ceramics

2.7.1 Powder synthesis

In order to sinter ceramics to high density, raw powders with uniform particle size and low degree of aggregation must be provided. Recently, some methods have been used to synthesize sesquioxide fine powders, including ball milling process^{31–34}, sol-gel process³⁵, chemical co-precipitation process^{2, 12, 36–39}, and combustion method^{40–42}.

Currently, chemical co-precipitation process is considered to be the best for the powder synthesizing. On one hand, the fabrication process is relatively simple, with relatively short production period, thus mass production can be realized. Meanwhile, the powders synthesized by this method have relatively good reproducibility. More importantly, nano-sized powders with initial particle size of 30-400 nm, low agglomeration, and good homogeneity can be achieved.

During the last decades, researchers developed many ways to decrease the agglomeration of powders using chemical co-precipitation process. Saito et al. synthesized fine needle-shaped yttrium carbonate precursor by using long aging time (2 days) after precipitation.³⁷ After calcining the precursor at 1100 °C, weakly agglomerated Y₂O₃ powders with high sinterability were fabricated. Li et al. studied the effect of different precipitants, ammonia water (NH₄OH) and ammonium hydrogen carbonate (NH₄HCO₃), on powders morphology and densification of YAG ceramics.⁴³ It was found that the use of ammonia water as the precipitant produced gel-like precipitate which exhibited severe agglomeration after drying. In comparison, the ammonium hydrogen carbonate derived precursor exhibited much weaker soft agglomeration. It had much smaller shrinkage after drying and easier to be crushed. After calcination at 1100 °C, the NH₄HCO₃ derived yttria powders exhibited good dispersity and sinterability. Ikegami et al found that the adding of ammonium sulfate ((NH₄)₂SO₄) into the yttrium precursor solution was able to decrease the agglomeration of yttrium precursor.⁴⁴ Specifically, loosely agglomerated flake like yttrium precursor could be produced after the sulfate ion's doping. After calcination, the sulfate ion doped yttria particles exhibited round edges and narrow particle size distribution. The reason is that sulfate ion had suppressed the grain boundary diffusion and/or lattice diffusion of particles during powder calcination, thus densification of particles was suppressed and hard agglomeration of particles was prevented.⁴⁵ By using similar methods, other sesquioxide powders (Lu₂O₃ and Sc₂O₃) with low agglomeration were fabricated widely by different groups.^{36, 46–50}

2.7.2 Forming technique

The commonly used techniques for the shaping of sesquioxide green bodies are cold isostatic pressing (CIP)^{12, 38, 51, 52} and slip casting^{34, 53, 54}.

The main advantage of the CIP technique is that the forming process is very easy

and time saving. Firstly, the powders are dry pressed by a stain steel mold to produce the initial pellets, with a general pressure 1 to 20 MPa. Then the pellets are put in a CIP machine at pressure of 50-200 MPa. The whole process can generally be completed within one hour. So it is very suitable for mass production. In addition, the packing homogeneity is relatively good on small samples.

Slip casting is a technique that is also suitable for mass production of ceramics. The most significant advantage for this technique is that it is able to shape ceramic powders with different shape as wanted. Meanwhile, if the slurry with high solid concentration and suitable viscosity could be produced, the ceramic green bodies tend to have high initial relative density and very good homogeneity. In addition, it was found that compared with the CIP method, the green body shaped by slip casting has much narrower pore size distribution, which can greatly increase the sinterability of ceramics.⁵³ Therefore, slip-casting is a good way to improve the particle packing density and decrease the pore coordination number. Another advantage of slip casting is that it is relatively easy to realize composite structure such as layered structure and core-shell structure, which will improve the heat transfer during lasing.

2.7.3 Sintering aids

Sintering is the competition of densification and grain growth. With the increasing of sintering temperature, both the relative density and grain size of ceramics are increased. However, rapid grain growth during the final-stage sintering will drastically decrease the driving force for densification, and is very likely to induce pore-boundary separation. In terms of achieving high transparency of ceramics, the basis for the selection of sintering additives should be suppressing fast grain growth, completing full densification before pore-boundary separation occurs.

In order to prevent pore-boundary separation, many researchers explored ways to suppress fast grain growth during the final-stage sintering. It can be realized either by using the 'solute drag' mechanism or by controlling the grain boundary diffusion coefficient.

The earliest sintering additive used for transparent sesquioxide ceramic is ThO_2 .⁵⁵ Jorgensen and Anderson found that when 10 mol.% ThO_2 was doped into Y_2O_3 ceramics, the grain growth was significantly inhibited during the final-stage sintering thanks to the solute segregation mechanism from ThO_2 . Similarly, through doping 8.1 to 12.1 mol%

La_2O_3 , the grain growth of Y_2O_3 could also be greatly retarded due to the formation of the transient second phase during sintering.⁵⁶ Fig. 2.13 shows the binary phase diagram of Y_2O_3 - La_2O_3 . It can be seen that to play an obvious inhibition effect towards grain growth, a sufficient amount of solute ions is generally required. The doping amount of solute ions is generally close to the solution limit, but not reaches.

Fig. 2.13 The Y_2O_3 - La_2O_3 phase diagram in the Y_2O_3 rich portion.⁵⁶

Another strategy to control the final-stage grain growth is to decrease the grain boundary diffusion coefficient. It is known that in fluorite-structured oxides (Y_2O_3 , Lu_2O_3 , Sc_2O_3), cation diffusion is the rate-controlling step for grain boundary migration, as the diffusion rate of oxygen ions is much faster than that of the cation ions.⁵⁷ In another words, the faster the cation diffusion rate, the more rapid grains will grow. Cation diffusion rate is proportional to the concentration of cation interstitial. Therefore, the grain boundary mobility of sesquioxides could be suppressed by decreasing the concentration of cations interstitial, and vice versa. In order to clarify what will influence the concentration of cations interstitial, it is worth clarifying the defect chemistry existed in the sesquioxides.

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Take Y_2O_3 ceramics as an example. There is Schottky defect for cation:

Frenkel defect for cation:

Frenkel defect for anion:

Combine 2.17, 2.18 and 2.19, the cation defect concentration is given by:

$$\begin{aligned} [V_Y'''] &= [V_O'']^{-1.5} K_S^{0.5} \exp\left[-\frac{\Delta G_S / 2}{kT}\right] \\ &= [O_i'']^{1.5} \left(\frac{K_S^{0.5}}{K_F^{1.5}}\right) \exp\left[-\frac{\Delta G_S / 2 - 3\Delta G_F^A / 2}{kT}\right] \end{aligned} \quad 2.20$$

and

$$\begin{aligned} [Y_i'''] &= [V_O'']^{1.5} \left(\frac{K_F}{K_S^{0.5}}\right) \exp\left[-\frac{\Delta G_F - \Delta G_S / 2}{kT}\right] \\ &= [O_i'']^{-1.5} \left(\frac{K_F K_F^{1.5}}{K_S^{0.5}}\right) \exp\left[-\frac{\Delta G_F - \Delta G_S / 2 + 3\Delta G_F^A / 2}{kT}\right] \end{aligned} \quad 2.21$$

According to Eqs. 2.20 and 2.21, it is noted that the cation defect concentration is closely related to the oxygen defect concentration. Specifically, increase the concentration of oxygen interstitial will decrease the cations interstitial concentration, and thus suppress the grain boundary mobility.

When Y_2O_3 ceramics are doped with tetravalent and divalent additives, the defect equations are:

It can be noticed that two donors of MO_2 in Y_2O_3 produce one oxygen interstitial, while two acceptors of MO in Y_2O_3 produce one oxygen vacancy. According to the Eq. 2.21, the cation interstitial concentration is anti-proportional to the concentration of oxygen interstitial, and proportional to the oxygen vacancy concentration. Therefore, the doping of tetravalent additives MO_2 would decrease the grain boundary mobility, while the doping of divalent additives MO would enhance the grain boundary mobility. Because of such effects, tetravalent sintering additives, like, ThO_2 ⁵⁵, ZrO_2 ^{31, 41, 52, 58, 59},

CeO_2 ⁵⁷, HfO_2 ^{51, 60}, have been widely utilized to control the grain growth of sesquioxide transparent ceramics.

2.7.4 Sintering atmosphere

It is known that Y_2O_3 is actually an amphoteric semiconductor.⁶¹ It exhibits p-type conduction at low temperature and high oxygen pressure, and n-type conduction at high temperature and low oxygen pressure.⁶² The n-p boundary is shown in Fig. 2.14. It implies that the defect structure and grain boundary diffusion of Y_2O_3 will both be affected when sintering in different atmosphere.

The most common atmosphere for sintering ceramics is oxygen, vacuum, hydrogen, nitrogen, air, and argon. However, it is quite difficult to make transparent ceramics in nitrogen, air, or argon atmosphere, as the gas tend to be trapped by the pores and will be difficult to remove during sintering. So far, sintering in vacuum is the most popular route for the sintering of sesquioxide transparent ceramics.^{58, 60, 63–66} It is relative simple and cost effective. During vacuum sintering, pores could be removed without much difficulty, due to the absence of insoluble gas. Sintering in dry hydrogen atmosphere is another route for the fabrication of sesquioxide transparent ceramics. In 2009, Zhang et al. reported the sintering of $\text{Yb}:\text{Y}_2\text{O}_3$ transparent ceramics in hydrogen atmosphere.¹⁰ The transmittance of sintered ceramics reached 80% at 1050 nm, which is very close to the theoretical value of Y_2O_3 . The success of this route implies that hydrogen molecules can be well dissolved into the Y_2O_3 crystal, probably because of their very small atomic size. Therefore, the hydrogen gas can be effectively removed during sintering. Sintering in oxygen atmosphere is another good way to fabricate sesquioxide transparent ceramics. According to Chen et al., oxygen interstitial concentration is proportional to the oxygen partial pressure during sintering.⁵⁷ Therefore, based on the Eq. 2.21, the cation interstitial concentration of sesquioxide ceramics would be decreased if they are sintered in oxygen atmosphere. This phenomenon has been verified by Huang et al.⁶⁷ in 2010, who found that sintering in oxygen atmosphere decreased the grain boundary mobility of Y_2O_3 ceramic during the final-stage sintering.

Fig. 2.14 Boundary of n-type and p-type conduction in Y_2O_3 .

2.7.5 Pressure-assisted sintering

Pressure-assisted sintering is able to densify ceramic powders at relatively low sintering temperatures, thus grain growth could be controlled during the final-stage sintering. Compared with pressure-less sintering, the sintering mechanism of pressure-assisted sintering is different. The main driving force for densification under high applied pressure is the dislocation resulted plastic deformation.⁶⁸ Therefore, pores could be eliminated very fast at relatively low sintering temperature. Typical pressure-assisted sintering techniques include hot pressing (HP) and hot-isostatic pressing (HIP).

2.7.5.1 Hot pressing

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.⁶⁸ This is achieved by the simultaneous applying of pressure and temperature. Densification at high pressure works through particle rearrangement and plastic flow at the particle contacts. HP is mainly used to fabricate hard and brittle materials, which has also become an important technique to obtain transparent ceramics.

In 1969, yttria transparent ceramics with sub-micron grain size were fabricated by using hot pressing at relatively low temperature (1300-1500 °C) and high pressure (5000-7000 psi).⁶⁹ After that, hot pressing has been utilized to densify various transparent ceramics such as spinel⁷⁰, YAG⁷¹, PLZT⁷², and CaF₂⁷³ ceramics. In 2013, Kim et al.⁷⁴ fabricated Ho:Lu₂O₃ transparent ceramics by using hot pressing method. The ceramics could be fully densified when hot pressed at 1300-1700 °C, with very homogeneous and pore free microstructure. In 2015, Gan et al.³¹ reported that Y₂O₃ transparent ceramics can be obtained at the pressure of 20 MPa, with the sintering temperature of 1600 °C. The ceramics exhibited good in-line transmittance (74.4% at 400 nm) and small average grain size (1 μm). In addition, thanks to the utilization of tantalum foil shielding that the hot pressed samples were free from carbon contamination from the graphite mold.

2.7.5.2 Hot isostatic pressing

HIP process subjects a component to both elevated temperature and isostatic gas pressure in a high-pressure containment vessel. The pressure is applied with a gas, generally Ar or N₂. So unlike the HP process that the pressure is applied along a single axis, the pressure is applied isostatic during HIP process.

Hot isostatic pressing technique has also been widely used to fabricated various transparent ceramics, such as Al₂O₃,⁷⁵⁻⁷⁷ spinel,^{77, 78} and YAG⁷⁹⁻⁸¹. The applied pressure during HIPing is generally between 50 and 300 MPa. Therefore, to reduce the possible gas permeation, HIP is generally used as the last step to complete the final-stage densification. Thanks to the applied pressure during sintering, the ceramics can be densified at relatively lower sintering temperatures compared with those sintering in vacuum. In this case, exaggerate grain growth is effectively suppressed and residual pores are constrained to grain boundaries during sintering.

In recent years, many scientists have tried to use HIP to densify sesquioxide transparent ceramics.^{48, 49, 63, 82-84} For example, by using the combination of vacuum

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sintering plus HIPing, high quality transparent ceramics were fabricated by Ikesue et al.⁵¹ With HfO_2 as the sintering additive, the $\text{Nd:Y}_2\text{O}_3$ ceramics exhibited very uniform grains with the average grain size of about 30 μm . Ballato and his colleagues⁴⁸ fabricated sub-micron grained Y_2O_3 and Sc_2O_3 transparent ceramics with very high optical quality. The in-line transmittance at the near-infrared wavelength range has been very close to the theoretical value. Meanwhile, average grain size of the ceramics was only 300 nm. Therefore, mechanical properties of these ceramics were also much better compared with those sintered in vacuum. Similarly, Kim and Sanghera also achieved near full densification of $\text{Yb:Lu}_2\text{O}_3$, $\text{Ho:Lu}_2\text{O}_3$ transparent ceramics by HIPing.^{2, 9, 74, 85} The continuous wave (C.W.) lasing on both ceramics was also realized.

3

FABRICATION OF Y_2O_3 TRANSPARENT CERAMICS BY USING SOLID-STATE REACTION PROCESS

3.1 Introduction

In order to fabricate Y_2O_3 transparent ceramics suitable for laser applications, their relative density should be very close to 100%. It is well known that porosity is the most common residual defect in transparent ceramics.^{29, 86} It can lead to severe degradation of optical quality, because of the huge difference in refractive index between air and the host materials. Many efforts have been made during the past 40 years to eliminate pores in Y_2O_3 ceramics. One effective method is to dope Y_2O_3 with sintering aids, such as La_2O_3 ⁸⁷, HfO_2 ⁵¹, ThO_2 ⁸⁸ and ZrO_2 ⁵⁸, to speed up densification and control grain growth. It is also feasible to decrease porosity and improve optical quality by using hot isostatic pressing (HIP). High quality Er: Y_2O_3 and Nd:YAG ceramics for solid-state lasers have been fabricated successfully by using HIP.^{12, 51} No matter what fabrication methods are adopted, there is a consensus among researchers that to completely remove porosity, highly dispersive and fine raw powders should be available, mostly by using either ball milling^{4, 41} or chemical co-precipitation methods^{10, 44, 47, 89–91}. According to Ciftcioglu⁹², even a small amount of agglomeration of powders would produce coarse pores that were

difficult to remove during the sintering. In 1988, Sordelet et al.⁹³ compared the sintering behaviors of well-dispersed monosized Y_2O_3 powder and agglomerated Y_2O_3 raw powder. They concluded that densification rate of the former was higher than that of the latter. Gong et al.⁹⁴ also demonstrated that the agglomeration degree of co-precipitated YAG powders decreased significantly with the assistance of freeze-drying process, as compared with those dried in oven. The subsequent YAG ceramics from the freeze-dried powder showed much less porosity, larger grain size and better transmittance. All these studies indicated that fabrication of transparent ceramics is very sensitive to the quality of raw powders, especially the degree of agglomeration.

Solid-state reaction is the most widely used route to fabricate ceramics, due to its short fabrication time and feasibility of mass production. Commercial Y_2O_3 raw powders generally have large particle size and severe agglomeration, which are hard to be fully sintered. Therefore, an effective ball milling process should be conducted to break the particles and the agglomeration. It has been proved that ball milling parameters, such as size and density of milling balls⁹⁵, ball and powder filling, slurry concentration⁹⁶ and viscosity of liquid medium⁹⁷, greatly affect ball milling efficiency. Under an appropriate ball milling condition, fine powders with relatively low degree of agglomeration and good sinterability can be produced. For example, Zou et al. demonstrated that an effective ball milling process could help reducing the agglomeration of Lu_2O_3 particles. By using such powders, they succeeded in fabricating Lu_2O_3 transparent ceramics with excellent transmittance (70% at 500 nm wavelength).⁴¹ However, up to now, there have been few reports discussing how specific ball milling parameters would affect densification, grain growth and transmittance of transparent ceramics.

3.2 Fabrication process

Commercial Y_2O_3 (purity >99.99%), and Ho_2O_3 (purity >99.99%) powders were mixed, according to the stoichiometric composition $(Ho_{0.005}Y_{0.995})_2O_3$ with 3 wt% ZrO_2 (purity >99%) as sintering additive. The mixture of Y_2O_3 , Ho_2O_3 , and ZrO_2 powders was then ball milled by using a planetary milling machine (PM400; Retsch, Haan, Germany) for 15 h at a speed of 140 rpm (rotation per minute), with agate balls (5 mm in diameter) and ethanol (99.99% purity; Merck, Darmstadt, Germany) as ball milling

media. Powder and ball filling was fixed (the weight ratio of powder:balls was 1:2). The solid content (C_S) of the slurry (slurry concentration) was adjusted between 33.2 and 17.4 vol% ($C_S=33.2, 23.7, 20.7, 19.5, 18.4$, and 17.4 vol%) by controlling the amount of ethanol. The slurry was then dried at 80 °C for 24 h in an oven and sieved through a 140-mesh screen. After calcined at 800 °C for 3 h to remove organic impurities, the powders were uniaxially pressed into 15 mm diameter pellets at 15 MPa. Then the green body pellets were further cold isostatically pressed (CIPed) at 200 MPa. After CIP, the green bodies were sintered using a vacuum furnace in vacuum ($P \leq 10^{-3}$ Pa) for different times at temperatures ranging from 1400 to 1850 °C. Figure 3.1 shows the flow chart of the solid-state reaction process.

Fig. 3.1 Flow chart of the solid-state reaction process.

3.3 Characterization of the Powders and Sintered Samples

Morphologies of the raw powders and ball milled powders were observed by using a Leo 1550 field emission scanning electron microscope (SEM, Leo 1550, Cambridge, Cambridgeshire, UK). Ball milled slurry viscosity was determined using a Haake Viscometer (model: VT550). The Brunauer-Emmett-Teller (BET) surface area of the powders was examined using a Micromeritics Tristar II-3020 nitrogen adsorption

apparatus. Particle size analysis was carried out on a Particle Size Analyzer (Zeta Plus, Brookhaven). After the vacuum-sintering process, the ceramics were annealed in air at 1400 °C for 10 h (Nabertherm LHT 04/17) to eliminate the oxygen vacancies. Then they were fine polished on both surfaces by using a Hyprez precision lapping machine (Model: EJW400-IN-D, Engis, Japan). Relative densities of the sintered ceramics were determined by using the Archimedes method. Room temperature transmittance of the ceramics was recorded with a UV–VIS–NIR spectrometer (Carry 5000 Spectrophotometer, Varian, USA). Before microstructural observations, the ceramics were thermally etched in air for 1 h at temperatures lower than sintering temperatures by 100 °C. A scanning electron microscope (SEM, JSM-6360A, JEOL, Tokyo, Japan) was then used to exam the sample's surface microstructure. Average grain size of the sintered samples was calculated by the following equation⁹⁸:

$$G = 1.56 L, \quad 3.1$$

Where L is the average linear intercept distance (200 grains counted).

3.4 Results and discussion

3.4.1 Morphology of ball milled powders

Figure 3.2(a) and (b) shows FESEM images of the Y_2O_3 raw powder. It can be seen that the commercial Y_2O_3 raw powders have particle size of 1–4 μm , which is consistent with the result measured by using the Particle Size Analyzer (Fig. 3.2(c), average 2.3 μm). Figure 3.2(b) exhibits a high magnification image of the raw powder. It shows that the particles are strongly agglomerated, as it is difficult to distinguish individual particle unit from the large agglomerates. The corresponding BET surface area (S_{BET}) of the Y_2O_3 raw powders is 2.4 m^2/g .

Fig. 3.2 (a) Low magnification and (b) high magnification FESEM images, and (c) particle size distribution of the high purity commercial Y_2O_3 powders.

Figure 3.3(a) and (b) exhibits FESEM images of the Ho_2O_3 and ZrO_2 raw powders. It is clear that the Ho_2O_3 powders are also highly agglomerated (with BET surface area merely $1.6 \text{ m}^2/\text{g}$), while the ZrO_2 particles are quite uniform in size and are only loosely

agglomerated. Specific surface area of the ZrO_2 powders is $7.9 \text{ m}^2/\text{g}$, corresponding to an equivalent particle size of 150 nm.

Fig. 3.3 FESEM images of the (a) Ho_2O_3 and (b) ZrO_2 raw powders.

Figure 3.4 shows FESEM images of the ZrO_2 -doped $Ho:Y_2O_3$ powders after ball milling. It is obvious that the powders of the 33.2vol% slurry (Fig. 3.4(a)) are still highly agglomerated, as the profiles of the particles are not clear, while those of the 23.7 vol% slurry consist of more fine particles with clear profiles and round surface (Fig. 3.4(b)). With the further decreasing of slurry concentration, the powders from the 18.4 vol% show the lowest agglomeration (Fig. 3.4(c)). This can be confirmed by the BET surface area result (Figure 3.5). The S_{BET} of the 33.2 and 23.7 vol% powders are 4.1 and $5.2 \text{ m}^2/\text{g}$, respectively, while that of the 18.4 vol% powders reaches the maximum of $5.9 \text{ m}^2/\text{g}$. It indicates that the ball milling efficiency is related to the concentration of the slurry: decreasing the slurry concentration from 33.2 vol% to 18.4 vol%, the agglomeration of the powders decreases monotonically. Further decrease in slurry

concentration to 17.4 vol%, no further improvement is observed from the FESEM image (Fig. 3.4(d)), and there is slightly decrease in the BET surface area ($5.8 \text{ m}^2/\text{g}$), implying that the agglomeration degree of milled powders is getting worse with further decreasing slurry concentration. Actually, the slurry concentration has once been reduced to 15 vol%, and the corresponding BET surface area of the powders was further dropped to $5.6 \text{ m}^2/\text{g}$. It demonstrates that the 18.4 vol% slurry concentration was the optimal in the experiment. However, it should be noted that even for the powders ball milled with the optimized slurry concentration, a certain number of agglomerates with the particle size range of $0.5\text{--}1.0 \mu\text{m}$ can still be detected, as revealed in Fig. 3.4(c).

Fig. 3.4 FESEM images of the ZrO_2 -doped $Ho:Y_2O_3$ powders after ball milling with (a) $C_S=33.2 \text{ vol}\%$, (b) $C_S=23.7 \text{ vol}\%$ (c) $C_S=18.4 \text{ vol}\%$, and (d) $C_S=17.4 \text{ vol}\%$.

To better explore the reason why the difference in slurry concentration has caused such difference in the powder properties (morphology and BET surface area), variation of viscosity with the slurry concentration was plotted in Figure 3.5. It is easy to understand that the suspension viscosity decreases with decreasing slurry concentration. Generally, a lower slurry viscosity is more favored, as there would be better dispersion of powders and better particle flow during the ball milling process.⁹⁶ However, there is a limitation because, in a very low viscosity system, the ‘fluid drag’ and highly turbulent

state of slurry would prevent powders from getting access to the grinding zones.⁹⁹ In this case, ball milling efficiency would decline accordingly. In the present work, the best slurry viscosity is 23 mPa·s, corresponding to the slurry concentration 18.4 vol%, and the optimal BET surface area 5.9 m²/g.

Fig. 3.5 BET surface area of powders and slurry viscosity as a function of slurry concentration.

3.4.2 Densification and microstructure evolution

Figure 3.6 presents relative density of the Ho:Y₂O₃ ceramics as a function of sintering temperature for different slurry concentrations. In the range of Cs=33.2~18.4 vol%, the relative density of the sintered samples increases steadily with decreasing slurry concentration, at a given sintering temperature. After sintering at 1850 °C for 2 h, the samples with 20.7-17.4 vol% slurry concentration were sintered to over 99% relative density, while those with slurry concentration of 23.7 and 33.2 vol% had much lower bulk density, reaching only 98.1 and 97.3%, respectively. This implies that the agglomerated powders were difficult to be completely densified. The best solid concentration range lied in between 17.4-20.7 vol%, in terms of densification.

Fig. 3.6 Relative density versus sintering temperature for the ZrO_2 -doped $\text{Ho:Y}_2\text{O}_3$ with various slurry concentrations.

Figure 3.7 shows SEM morphology of the $\text{Ho:Y}_2\text{O}_3$ ceramics for different C_s values, sintered at 1800 °C for 2 h. Grain boundary pores can be observed for the 33.2 vol% ceramics, as shown in Fig. 3.7(a). These pores were probably from the large pores between the agglomerates (Fig. 3.4(a)). Pore grain boundary separation occurred during sintering, so that the pores were difficult to be removed and were entrapped in the sample during the sintering.^{91, 94} Residual pores embraced in the sample will be the major factors that affect transparency. With decreasing slurry concentration, grain growth was gradually improved and pores were removed (Fig. 3.7(b) and (c)).

Fig.3.7 Thermally etched surface SEM images of the ZrO_2 -doped $Ho:Y_2O_3$ ceramics with different slurry concentration sintered at $1800\text{ }^{\circ}C/2\text{ h}$ in vacuum: (a) 33.2 vol%, (b) 23.7 vol% and (c) 18.4 vol%.

In order to illustrate microstructural evolution of the ZrO_2 -doped $Ho:Y_2O_3$ ceramics, SEM images of the 33.2 and 18.4 vol% specimens sintered at temperatures between 1650 and $1800\text{ }^{\circ}C$ are presented in Figure 3.8. For the 33.2 vol% specimens, a porous

structure with the presence of open pore channels is shown in Figure 3.8(a), which is the typical feature of intermediate-stage sintering.²³ When the sintering temperature is increased to 1750 °C, pore phase is eventually pinched off and the pores become isolated (Fig. 3.8(c)). Meanwhile, bulk density reaches 90% of theoretical value at this stage, suggesting that it is the beginning of the final-stage sintering. However, there are large pores existing along the grain boundaries, which are very difficult to remove. It can be noticed that even when the sintering temperature is increased to 1800 °C, there still remains a certain number of pores in the 33.2 vol% sample (Fig. 3.8(d)). In comparison, at a given sintering temperature, the number of pores in the 18.4 vol% sample is much less than that in the 33.2 vol% one. Moreover, it can also be noticed that the 18.4 vol% samples have much smaller average pore size. For the 18.4 vol% samples, only closed pores can be observed after 1650 °C/2 h vacuum sintering (Fig. 3.8(e)), which means that the final-stage sintering has started at this temperature. It illustrates that the starting temperature of final-stage sintering of the finer 18.4 vol% powders is about 100 °C lower than that of the more agglomerated 33.2 vol% powders. This is critical as the final-stage sintering processes are always accompanied by obvious grain growth, during which residual pores are totally removed. Therefore, it enables samples to be fully sintered and densified at a much lower sintering temperature.

Fig.3.8 SEM images of the ZrO_2 -doped $Ho:Y_2O_3$ ceramics with 33.2 vol% slurry concentration under vacuum for 2 h at temperatures of (a) 1650 °C, (b) 1700 °C, (c) 1750 °C, (d) 1800 °C, and 18.4 vol% slurry concentration: (e) 1650 °C, (f) 1700 °C, (g) 1750 °C and (h) 1800 °C.

Figure 3.9 shows the grain size change as a function of sintering temperature for the

33.2, 23.7, and 18.4 vol% samples. The grain size increases with decreasing slurry concentration, at a given sintering temperature, especially at above 1700 °C. The 33.2 vol% samples exhibited the lowest grain growth rate. The reason is that the agglomerated powders have slow densification rate (slow removing speed of porosity), and thus will postpone the final-stage sintering process at a much higher sintering temperature. For example, when sintered at 1700 °C, only a small amount of closed pores (typical feature of final-stage sintering) were observed in the 18.4 vol% samples (Fig. 3.8(f)), while a certain amount of open pores (typical feature of intermediate-stage sintering) were detected in the 33.2 vol% samples (Fig. 3.8(b)). It is well known that these open pores can act as ‘pinning center’ which will decrease grain-boundary mobility and inhibit grain growth.^{100–102} That’s the reason why the agglomerated 33.2 vol% powders have also shown the sluggish in grain growth at above 1700 °C. A similar outcome has been reported by Gong et al.⁹⁴, who found that freeze-dried Nd:YAG powders had much less degree of agglomeration and better sinterability than oven-dried powders, and thus exhibited larger grain size and less porosity after sintering.

Fig.3.9 Grain size as a function of temperature for ZrO_2 -doped $Ho:Y_2O_3$ ceramics with 33.2, 23.7 and 18.4 vol% slurry concentration.

For the sintering of ceramics, final-stage of sintering contributes to the ultimate densification. Thanks to the grain growth of final-stage that residual pores can be eliminated and ultimate densification can be achieved. Figure 3.10 shows microstructures of the ZrO_2 -doped $Ho:Y_2O_3$ sintered for 0.25 h (Fig. 3.10(a)), 2 h (Fig. 3.10(b)), 10 h (Fig. 3.10(c)), and 30 h (Fig. 3.10(d)) at 1800 °C, which illustrates typical

microstructure evolution of final-stage sintering. The isolated pores shown in Figure 3.10(a) are separated by large defect-free regions, indicating that final-stage densification is in progress. With increasing sintering time, there is obvious grain growth, accompanied by the removal of the residual pores. It can be seen that transparency of the ceramics steadily increases with increasing time at 1800 °C (Fig. 3.11).

Fig. 3.10 SEM images of the ZrO_2 -doped $\text{Ho:Y}_2\text{O}_3$ ceramics with $C_S=18.4$ vol% sintered at 1800 °C for (a) 0.25, (b) 2, (c) 10 and (d) 30 h.

Fig. 3.11 Photographs of the ZrO_2 -doped $\text{Ho:Y}_2\text{O}_3$ ceramics ($C_S=18.4$ vol%, 2.14 mm thick) with increasing time at 1800 °C: (a) 2 h, (b) 10 h and (c) 30 h.

To determine the final-stage kinetic grain growth exponents of the ZrO_2 -doped $\text{Ho:Y}_2\text{O}_3$ ceramics, the grain growth data at 1800 °C are plotted according to the following equation:

$$G^n - G_0^n = kt, \quad 3.2$$

Where G is the average grain size, G_0 is the average grain size at initial sintering time (0.25 h), and t is sintering time. Figure 3.12 illustrates grain growth kinetics for the 33.2, 23.7 and 18.4 vol% samples sintered at 1800 °C for 0.25-30 h, according to Eq. 3.2. Grain size information and n values of 2-4 were used for Eq. 3.2, respectively, and it was found that $n=3$ provided the best fit for all pellets and firing time. According to Kochawattana and Stevenson^{103, 104}, a grain growth exponent of 3 indicated that grain growth was controlled by either liquid phase mass transport or solute drag mechanisms in solid-state systems, provided that the case was boundary controlled migration. As shown in Fig. 3.10, only a small number of isolated grain boundary pores were observed in the 1800 °C/0.25 h sample, which suggests that grain growth was most likely controlled by grain boundary migration rather than pore drag. Meanwhile, no liquid phase was used in our samples. Therefore, it is reasonable to conclude that the cubic grain growth kinetics shown in Figure 3.12 were due to solute drag. It also implies that agglomeration degree of powders does not affect the actual sintering mechanism of the ceramics, though it indeed has a great influence on the microstructural evolution, such as densification and grain growth rate. This result is very similar to that of Rhodes²⁷ and Huisman¹⁰⁵.

Fig. 3.12 $G^3 - G_0^3$ vs sintering time at 1800 °C for the ZrO_2 -doped $Ho:Y_2O_3$ ceramics with different slurry concentrations.

3.4.3 In-line transmittance

Figure 3.13 shows inline optical transmittance of the ZrO_2 -doped $Ho:Y_2O_3$ ceramics with different slurry concentrations sintered at 1800 °C for 30 h. All the absorption peaks are related to holmium ion (Ho^{3+}) absorption in the Y_2O_3 matrix. It can be noticed that with decreasing slurry concentration, transmittance steadily increased and reached the maximum in the sample with slurry concentration of 18.4 vol%. Then it slightly dropped with further decrease in slurry concentration, implying that the optimal slurry concentration was 18.4 vol%. For this sample, the in-line transmittance reached 65% at 500 nm.

Fig. 3.13 In-line optical transmittance spectrum of the ZrO_2 -doped $Ho:Y_2O_3$ ceramics (2.14 mm thick) with different slurry concentrations.

3.5 Conclusions

Transparent ZrO_2 -doped $Ho:Y_2O_3$ ceramics were fabricated by using solid-state reaction method. It was found that morphology and agglomeration degree of powders were influenced by ball milling conditions. With decreasing slurry concentration from 33.2 to 18.4 vol%, densification and normal grain growth were gradually improved. The optimized concentration was 18.4 vol%, where the powders had relatively low degree of agglomeration, the pellets had high densification rate, and the $Ho:Y_2O_3$ ceramics showed the optimal transmittance, which is 65% at 500 nm. However, it can be noticed that agglomeration was not completely eliminated by the current ball milling process. In

addition, the highest in-line transmittance was still much lower than the theoretical value (80.4% at 500 nm).

Chapter 3 Fabrication of Y_2O_3 transparent ceramics by using solid-state reaction process

4

FABRICATION OF Y_2O_3 TRANSPARENT CERAMICS BY USING CHEMICAL CO-PRECIIPITATION PROCESS

4.1 Introduction

Commercial sesquioxide raw powders generally have large particle size and severe agglomeration, which are difficult to be sintered to uniform microstructures with full densification. In Chapter 3, ball-milling process was utilized to break the agglomeration of commercial raw powders. It has the distinctive advantage that relatively fine powders could be got with a very short period (1 day) and with high yield. However, the problem lies in that there was still a certain amount of agglomeration existed in the powders. Meanwhile, it is also difficult to obtain fine powders with round surface and good homogeneity by ball milling. In addition, impurities induced from the ball milling media (balls and jar) are also the potential source of contamination.

In order to further increase the homogeneity and decrease the agglomeration degree of powders, other methods, including alkalide reduction method¹⁰⁶, sol-gel synthesis³⁵, combustion synthesis⁴², and chemical co-precipitation^{12, 36, 37, 39, 44, 45, 48, 85}, have been

developed to replace ball milling process. Among them, the chemical co-precipitation method is much favored, due to its capability of synthesizing powders with high uniformity, low degree of agglomeration, high purity and relatively large scale production⁸⁵. For example, high quality Yb:Y₂O₃ and Yb:Lu₂O₃ transparent ceramics were developed by using co-precipitated powders by the Konoshima company, with promising laser properties.^{107–110} Using co-precipitated nano-powders, Ballato and colleagues^{18, 23} fabricated submicrometer-grained Sc₂O₃ transparent ceramics, with the combination of two-step sintering and hot isostatic pressing (HIP) process. The ceramics exhibited very small grain size (~300 nm) and showed transmittance close to the theoretical value in the near-infrared wavelength range. The reduction of grain size resulted in significant improvement in microhardness and fracture toughness of the transparent ceramics, which made them more applicable to high-energy laser systems.¹² The success in fabricating highly transparent submicrometer-grained ceramics was attributed to the precise control of the sintering process and more importantly, to the success on synthesizing nano powders without aggregation.

On the other hand, to obtain highly transparent sesquioxide ceramics, ultra-high purity of raw powders is necessary. It is known that impurities, such as transition metals and some nonmetal inclusions present in powders, even at ~10 wt. ppm, would influence the sintering behavior and worsen the optical quality.^{85, 111} For example, Yagi and Yanagitani¹¹¹ found that it is difficult to obtain highly transparent Y₂O₃ if the amount of Si exceeds 10 wt. ppm. For this reason, Kim and Sanghera et al. developed an additional purifying process before the subsequent precipitation process, i.e., recrystallization treatment.^{74, 85} After that, the total concentration of the foreign metal impurities (Mg, Al, Si, Ca, Fe, Co, Ni et al.) in the co-precipitated powders was decreased to be below 10 wt. ppm. Using these powders, highly transparent Ho: Lu₂O₃, Yb: Lu₂O₃ and Yb: Y₂O₃ ceramics could be fabricated.^{74, 85, 112} No matter what process is utilized, there is a consensus among researchers, that is, to achieve total transparency of the sesquioxide ceramics, high purity raw powders with little agglomeration should be used.

During the process of synthesizing sesquioxide precursors, SO₄²⁻ has been widely utilized as an inorganic dispersant.^{36, 44, 46} The presence of the SO₄²⁻ could help producing monodispersed particles with more isotropic surfaces⁴⁴, thus decreasing the agglomeration of both the precursors and the oxide powders. However, the complete dissociation of sulfate from the final powders was difficult. Therefore, in order to

minimize the nonmetal impurities, such as SO_4^{2-} , NO_3^- and CO_3^{2-} , high calcination temperatures of above 1000 °C are generally required.^{36, 44} Actually, it has been reported that there was still 100 ppm of sulfur remaining in the sulfate doped yttria powders even after calcining at 1200 °C.⁴⁴ However, a high calcination temperature would inevitably lead to the increase in particle size, which, according to the Herring's Scaling Law¹¹³, will cause the decline in sinterability of the powders. Another disadvantage is that 'necks' between particles could be formed during the high temperature calcination, to form hard agglomerates.¹¹⁴ Therefore, the calcination temperature should be carefully controlled in this respect.

In this chapter, the fabrication of Ho:Y₂O₃ transparent ceramics from powders prepared by using a chemical co-precipitation method was reported. The effects of calcination temperature on morphology and evolution of crystal size of the powders were examined. Densification, grain growth and transmittance of the Ho: Y₂O₃ ceramics made from different powders were discussed in detail.

4.2 Fabrication process

4.2.1 Materials Processing

Commercial yttrium oxide (Y₂O₃, purity >99.99 %), holmium oxide (Ho₂O₃, purity >99.99 %) and Zirconium oxychloride octahydrate (ZrOCl₂·8H₂O, purity >99.5 %) were used as the starting materials. First, Y₂O₃ and Ho₂O₃ were dissolved in the diluted nitric acid, while ZrOCl₂·8H₂O was dissolved in the ultra-pure water. The obtained nitrate solutions were stoichiometrically mixed according to the chemical formula of (Y_{0.965}Ho_{0.005}Zr_{0.03})₂O₃, with Y³⁺ concentration 0.5 mol/L. Then, 5 g (NH₄)₂SO₄ was added into 1 liter of the above solution. After that, a mixed NH₄OH+NH₄HCO₃ precipitant (molar ratio 1:0.9) was dropped into the mother solution at a rate of 6 mL/min under mild agitation (stirring rate 400 rpm) at room temperature. The ultimate pH value of the suspension was kept in the range of 8-9. After being aged for 4 h, the precursor was filtered using a suction filter, washed five times with ultra-pure water and twice with ethanol (99.99 % purity; Merck, Darmstadt, Germany), and then dried at 60 °C for 24 h in air. After being crushed, the precursor was calcined in

a muffle furnace (Nabertherm LHT 04/17) at 1100-1400 °C for 5 h. The resultant oxide powders were uniaxially pressed into 15 mm diameter pellets at 15 MPa. The green pellets were further cold isostatically pressed (CIPed) at 200 MPa. After CIP, the green bodies were sintered in a vacuum furnace equipped with tungsten mesh as the heating element at vacuum of $\leq 10^{-3}$ Pa for various times at temperatures ranging between 1560 and 1850 °C. The flowchart of the chemical co-precipitation process is shown in Fig. 4.1. Then the ceramics were air annealed at 1400 °C for 10 h in a muffle furnace (Nabertherm LHT 04/17) to remove the color centers. After annealing, they were fine polished on both surfaces, with thickness of around 2.50 mm, using a Hyprez precision lapping machine (Model: EJW400-IN-D, Engis, Japan).

Fig. 4.1 Flowchart of the chemical co-precipitation process.

4.2.2 Characterization

Morphologies of the precursors and calcined powders were observed by using a JEOL JEM-2010 transmission electron microscope (TEM, JEOL JEM-2010, Kyoto, Japan). Phase identification was performed by using a Shimadzu X-ray diffractometer (XRD, Shimadzu, Kyoto, Japan) with $CuK\alpha$ radiation. Scanning speed was $1.5^\circ 2\theta$ per minute. Specific areas of the powders were measured by using the BET method (ASAP, 2020) with N_2 absorption using a Monosorb. Before BET analysis, the powders were

degassed at 120 °C for 6 h to eliminate absorbed moisture. Thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the precursors were conducted on a TGA-DSC analyzer (Q600-SDT, TA Instruments). Bulk densities of the sintered samples were measured by using the Archimedes method. Optical transmittance of the ceramics was recorded using a UV–VIS–NIR spectrometer (Carry 5000, Agilent, Santa Clara, CA, USA). Microstructure of the samples was examined by using a scanning electron microscope (SEM, JSM-6360A, JEOL, Tokyo, Japan) and an optical transmission microscopy (Olympus BX53-P, Tokyo, Japan). Average grain size of the sintered samples was determined by using the mean linear intercept method (over 200 grains calculated)⁹⁸:

4.3 Characterization of the co-precipitated powders

Figure 4.2 shows the FTIR spectra of the precursor and the calcined $\text{Ho:Y}_2\text{O}_3$ powders. The broad absorption band lies between 3000 and 3700 cm^{-1} are associated with the hydroxyl stretching vibration, while the weak peak located at 1635 cm^{-1} can be attributed to the presence of absorbed water.^{115, 116} The bands at 1513 and 1407 cm^{-1} are assigned to the splitting of ν_3 stretching vibration of CO_3^{2-} (asymmetric and symmetric stretches, respectively).¹¹⁵ The peaks at 846 and 761 cm^{-1} are also apparent in the precursor, which can be assigned to N-O stretching origin from the NO^{3-} remains. The most prominent bands appeared at 563 cm^{-1} are assigned to the Y-O vibration of cubic Y_2O_3 , implying that all the powders exhibited good crystallization.

Fig. 4.2 Fourier transform infrared spectroscopy (FTIR) spectra of (a) the precursor and the $\text{Ho:Y}_2\text{O}_3$ powders calcined at (b) 1100 °C, (c) 1200 °C, (d) 1300 °C, and (e) 1400 °C for 5 h.

Figure 4.3 presents XRD patterns of the $\text{Ho:Y}_2\text{O}_3$ precursor and calcined powders. It is obvious that the precursor was amorphous before calcining, which was crystallized into cubic Y_2O_3 phase (JCPDS 41-1105) after being calcined at 1100-1400 °C. Impurity phase was not detected in the calcined oxide powders.

Fig. 4.3 XRD patterns of the $\text{Ho:Y}_2\text{O}_3$ precursor and resulted powders after calcined at different temperatures.

Figure 4.4 shows TEM images of the precursor and the $\text{Ho:Y}_2\text{O}_3$ calcined powders. The precursor was flake like, with an average particle size of 30 nm (Fig. 4.4(a)). Average particle size of the powders calcined at 1100 °C (Fig. 4.4(b)) was about 71 nm, which was increased to 100 nm and 130 nm at 1200 and 1300 °C, respectively (Fig. 4.4(c) and (d)). It can be seen that these particles had clear profiles and round surface, suggesting good dispersion and low degree of agglomeration. However, when the calcining temperature was increased to 1400 °C, obvious 'neck growth' was found between particles (Fig. 4.4(e)). The primary particles connected through the bridges were difficult to be identified, indicating the accelerated agglomeration of particles.

Fig. 4.4 TEM images of the precursor (a) and the $\text{Ho:Y}_2\text{O}_3$ powders calcined at different temperatures: (b) 1100 °C, (c) 1200 °C, (d) 1300 °C and (e) 1400 °C.

Figure 4.5 shows variation of BET specific area (S_{BET}) and the corresponding particle diameter (D_{BET}) of the powders as a function of calcination temperatures. The particle size D_{BET} was calculated according to the formula $D_{\text{BET}} = 6/(\rho \cdot S_{\text{BET}})$, where ρ ($=5.03 \text{ g/cm}^3$) is the theoretical density of Y_2O_3 crystal and S_{BET} is the relative surface area determined by the BET measurement. It can be seen that the BET surface area of the $\text{Ho:Y}_2\text{O}_3$ powders decreased with increasing calcination temperature. For a clear comparison, the D_{BET} and D_{TEM} obtained respectively from BET surface area and TEM

observation are listed in Table 4.1.

Table 4.1 Particle sizes of the yttria powders calcined at different temperatures.

Calcination temperature (°C)	BET surface area (m^2g^{-1})	D_{BET} (nm)	D_{TEM} (nm)
1100	9.8	122	71
1200	7.5	160	100
1300	5.4	221	132
1400	4.4	270	-

Fig. 4.5 Specific surface area (S_{BET}) and the corresponding particle diameter (D_{BET}) of the Ho: Y_2O_3 powders as a function of calcination temperatures.

4.4 Sintering characteristics of the co-precipitated ceramics

Figure 4.6 presents relative density of the Ho: Y_2O_3 ceramics as a function of sintering temperature. It is obvious that at a given sintering temperature, the relative density of the sintered ceramics increased steadily with decreasing calcination temperatures. For example, when sintered at 1760 °C, the 1100 °C calcined powders showed the highest relative density of 99.7%. Then it was followed by the 1200 and 1300 °C calcined ones, which reached 99.3% and 99.1%, respectively. The 1400 °C

calcined powders showed the least densification rate, achieving a relative density of only 98.9%. This can be easily explained by using the Herring's Scaling Law¹¹³: powders with smaller average particle size would have faster densification rate.

Fig. 4.6 Relative density versus sintering temperature for the Ho:Y₂O₃ ceramics with various calcination temperatures.

Figure 4.7 presents SEM images of the Ho:Y₂O₃ powders sintered at 1640 and 1680 °C. It can be seen that there are still open pores in the 1640 °C sintered samples (Fig. 4.7 (a-d)), implying that it was in the intermediate stage of sintering. When the sintering temperature was increased to 1680 °C, obvious grain growth was observed (Fig. 4.7 (e-h)). Meanwhile, pores became isolated, meaning that the final-stage sintering has started. By comparing the 1640 and 1680 °C sintered samples, it is interesting to note that there was obvious pore growth from the intermediate stage to the beginning of the final-stage sintering. This is because, during the normal grain growth process in the final-stage sintering, small pores migrated along the grain boundaries, resulting in pore growth.¹¹⁷ This phenomenon has also been illustrated by Kingery¹¹⁷, when sintering UO₂ ceramics.

Fig. 4.7 SEM images of different Ho:Y₂O₃ powders sintered for 2 h at 1640 °C (a-d) and 1680 °C (e-h). Calcination temperatures of the powders were 1100 °C (a, e), 1200 °C (b,f), 1300 °C (c, g) and 1400 °C (d, h).

Another interesting phenomenon is that the ceramics made from different powders

had a very similar microstructural evolution process, though their initial crystal size was different. For example, all the powders sintered at 1640 °C exhibited almost the same average grain size of about 400 nm, which was increased to about 550 nm at 1680 °C. Therefore, the grain size evolution was closely related to the sintering temperature, but independent of the initial crystal size. Specifically, at a given sintering temperature, grain sizes of the samples made from different powders were same. The variation of grain size with sintering temperature was plotted in Fig. 4.8. It depicts the evolution of grain size from the intermediate stage to the final stage. Obvious grain growth started between 1640 and 1680 °C, meaning the initiation of the final-stage sintering process. In addition, samples made from different powders also exhibited the same grain size after longer sintering time at a given sintering temperature. For example, the grain size of the ceramics sintered at 1760 °C showed average grain sizes of 2.5 and 3.2 μm , respectively, after sintering for 13 and 30 h. It confirms that grain growth was related to sintering temperatures and sintering time, but was hardly affected by the initial crystal size.

During the final-stage sintering, grain growth can be described by the well-known kinetic grain growth equation:

$$G^n - G_0^n = K_0 t \exp(-Q/RT) \quad , \quad 4.1$$

Where G is the average grain size at the time t , G_0 is the initial average grain size, t is sintering time, K_0 is a preexponential constant, Q is the activation energy for grain growth, R is the gas constant and T is the absolute sintering temperature. The grain growth exponent (n value) is related to the diffusion mechanisms for the grain growth: $n=2$ for grain boundary diffusion and $n=3$ for lattice diffusion. Since the grain boundary mobility of the ceramics from different initial powders was proved to be the same at a given sintering temperature, it can be concluded, from the Eq. 4.1, that the activation energy for grain growth was identical for the powders with different initial crystal sizes.

Fig. 4.8 Grain size as a function of sintering temperature for the Ho:Y₂O₃ ceramics with different calcination temperatures.

In order to achieve high transparency, ceramics should have a relative density close to 100%. In other words, all the residual grain boundary pores shown in Fig. 4.7 should be removed. Generally, during the final-stage sintering, densification is accompanied by moderate grain growth. With increasing sintering temperature or sintering time, normal grain growth rate increases, along with the removal of the residual grain boundary pores. Figure 4.9 shows SEM images of the samples from different Ho:Y₂O₃ powders sintered at 1760 °C for 13 h. It can be seen that it has been very difficult to detect the residual pores using SEM. In addition, all the ceramics showed almost the same average grain size of about 2.5 μm, which again verified the negligible effect of the initial crystal size.

Fig. 4.9 SEM images of thermally etched surface of the Ho: Y_2O_3 ceramics from the powders with different calcination temperatures: (a) 1100 °C; (b) 1200 °C; (c) 1300 °C and (d) 1400 °C.

Figure 4.10(a) shows optical in-line transmittance of the Ho: Y_2O_3 ceramics sintered at 1760 °C for 13 h. All the absorption bands were caused by the Ho^{3+} ions. The ceramic from the 1300 °C calcined powder exhibited the highest in-line transmittance, reaching 80 % at 1000 nm, which was 98% of the theoretical value. The theoretical transmittance was estimated to be 81.6% at the wavelength of 1000 nm, based on the formula of $T=100[1-((n-1)/(n+1))^2]^2$. However, obvious decline in transparency at the short wavelength range (≤ 800 nm) could still be detected, meaning that there were a certain number of scatterings. Thanks to the optical transmission microscopy, the residual pores in the interior of the ceramic body could be detected (Fig. 4.10(b)), the presence of which should be responsible for the declining of transmittance at the short wavelength range. In addition, ceramics made from different powders exhibited different transmittance, especially at the short wavelength range. For example, when the calcination temperature was 1100 °C, the transmittance was 73.1 % at 510 nm after the sintering. It was increased to 73.6 % and reaching the maximum of 74.2 % when the

calcination temperatures rose to 1200 and 1300 °C. Table 4.2 shows variation of optical transmittance (at 510 nm) of the Ho:Y₂O₃ ceramics sintered at between 1760 and 1850 °C. It is easy to understand that the transmittance is increased with increasing sintering temperature, because the residual grain boundary pores could be eliminated to a greater extent. For instance, much better transmittance of 81.6% (at 1000 nm) and 77.2 % (at 510 nm) could be achieved for the ceramic sintered at 1850 °C (Fig. 4.11), as compared with that of the ones sintered at 1760 °C (Fig. 4.10), due to the enhancement of normal grain growth and the further elimination of pores. It is also revealed that, at a given sintering temperature, the transmittance was increased slightly as the calcination temperature was increased from 1100 to 1300 °C, which is different from the sintering behavior of un-doped Y₂O₃ reported by Li et al.¹¹⁸ They found that high calcination temperatures of above 1100 °C would result in agglomeration of the Y₂O₃ powders and thus severe degradation of transmittance of the ceramics. For example, the maximum transmittance of 80 % (at 613 nm) could be achieved when the precursors were calcined at 1100 °C, but it dropped dramatically to merely 20 % (at 613 nm) when the calcination temperature was increased to 1200 °C, due to the increasing agglomeration of powders. However, in our present work, strong agglomeration was not detected as the calcination temperature was not higher than 1400 °C. This could be related to the inherent oxygen vacancy defects that endowed the pure Y₂O₃ with relatively high grain boundary diffusion coefficient⁵⁷, which is one of the main driving forces of the powders' agglomeration during calcination⁴⁵. In this case, agglomeration was very easy to be generated during the calcination. Thanks to the Zr⁴⁺ presented in the precursor, the cations' diffusion and the grain boundary diffusion rate could be suppressed⁵⁷. This could be the reason why agglomeration of our Zr-doped Y₂O₃ powders was restricted even at a high calcination temperature of 1300 °C. Without the presence of aggregation, a higher calcination temperature should be favored, as the unwanted elements, such as S, C, H and N, could be removed to a greater extent. To better identify the role of Zr⁴⁺, relative densities of Zr-doped and un-doped Y₂O₃ (without Zr⁴⁺) ceramics as a function of sintering temperatures were plotted in Fig. 4.12. Relative density of the pure Y₂O₃ sintered at 1300 °C for 7 h reached 67.1%, which was significantly higher than that of the green body (with relative density 55%), while that of the Zr-doped ceramic was only 57.4% at this sintering temperature. In addition, final-stage sintering of the un-doped Y₂O₃ ceramics was started at the temperatures 1500-1550 °C, which was about 140 °C

lower than that of the Zr-doped samples. It means that densification of the Zr-doped ceramics was retarded. However, at the final-stage sintering, rapid grain growth was observed in the pure Y_2O_3 ceramics, which can be attributed to the high migration rate of grain boundary, leading to pore-boundary separation and the formation of intra-granular pores. Figure 4.13 compares SEM images of the un-doped and Zr-doped Y_2O_3 ceramics (calcined at 1300 °C) sintered at 1850 °C for 13 h. Average grain size of the pure Y_2O_3 was above 100 μm , with a certain number of intra-granular pores, while that of the Zr-doped $\text{Ho:Y}_2\text{O}_3$ was merely 5.6 μm with a pore-free microstructure.

Fig. 4.10 (a) In-line optical transmittance of the $\text{Ho:Y}_2\text{O}_3$ transparent ceramics (2.5 mm thick) from the powders with different calcination temperatures and (b) typical optical transmission micrograph of the ceramic from the 1300 °C calcined powder. All the samples were sintered at 1760 °C for 13 h.

Table 4.2 Optical transmittance (at 510 nm) of the Ho:Y₂O₃ ceramics with different calcination and sintering temperatures. Holding time was 13 h.

Calcination temperatures (°C)	Transmittance at 510 nm (%)			
	Sintered at 1760 °C	Sintered at 1790 °C	Sintered at 1820 °C	Sintered at 1850 °C
1100	73.1	75.4	72.6	74.5
1200	73.6	75.8	73.5	75.8
1300	74.2	76.2	76.4	77.2
1400	68.5	73.5	74.2	75.4

Fig. 4.11 In-line optical transmittance of the Ho:Y₂O₃ transparent ceramic (calcination temperature 1300 °C) sintered at 1850 °C for 13 h, (Inset) typical optical transmission micrograph of the sample.

Fig. 4.12 Relative density versus sintering temperatures for the Zr-doped and un-doped Y_2O_3 ceramics. Sintering time was 7 h for all the samples.

Fig. 4.13 SEM images of the undoped (a) and Zr-doped (b) $\text{Ho:Y}_2\text{O}_3$ ceramics sintered at 1850 °C/13 h.

Glow discharge mass spectrometry (GDMS) analysis was conducted on the ceramics made from the 1200 °C calcined powders. It was found that there still was 56 wt. ppm of sulfur impurity remained in the final product, implying the complete decomposition temperature of the sulfur compounds was, actually, above 1200 °C in air. Figure 4.14 exhibits the TGA-DSC curves of the yttrium precursor. The TG curve indicates an overall weight loss of 41.65%, much of which (about 40% weight loss) took place at below 750 °C. However, there was still obvious weight loss from 1200 to 1400 °C (0.31%), implying the complete thermal decomposition of the precursor was as high as above 1200 °C. In this case, it is referred that the possibility to achieve full densification and total transparency of the low temperature calcined powders (below

1200 °C) was restricted by the contaminations, sulfur in particular. Further increase in calcination temperature to 1400 °C, there was a significant drop in transmittance due to the increased agglomeration of the powder. It was confirmed that 1300 °C in the present work is the optimal calcination temperature.

Fig. 4.14 TGA-DSC curves of the yttrium precursor. The amount of the sample was 12.00 mg.

Figure 4.15 shows sintering trajectory of the $Ho:Y_2O_3$ ceramics, during the final-stage sintering, with different calcination temperatures. It can be noticed that the sintering trajectory varied with initial crystallite size of the powders: smaller initial crystallite size of the powder led to faster densification rate. However, in the present work, this scaling law worked well only when relative density of the ceramics was below 99.7 %. It seems that fully densification from 99.7 % to over 99.99 % is another case: smaller initial crystallite size of the powder did not necessarily achieve higher final density and higher transmittance of the ceramics, as proven in the Fig. 4.10 and Table 4.2. Therefore, in order to achieve full densification and total transparency, preparation of initial powders with no agglomeration and no impurities is important.

Fig. 4.15 Sintering path of the Ho:Y₂O₃ ceramics with different calcination temperatures.

4.5 Conclusions

Ho:Y₂O₃ transparent ceramics were fabricated using chemical co-precipitated powders and vacuum sintering method according to the chemical composition of (Y_{0.965}Zr_{0.03}Ho_{0.005})₂O₃. High purity Y₂O₃ powders with round surface and low degree of agglomeration could be produced using the current co-precipitation process. The yttrium precursors were calcined in air in the temperature range of 1100-1400 °C. The calcination temperature was important to obtain fine powders with high purity and agglomeration-free. Increasing the calcination temperature from 1100 to 1300 °C, there was particle growth without agglomeration. With the calcination temperature was further increased to 1400 °C, obvious agglomeration of powders was observed. According to microstructures of the ceramics, it was found that the grain growth behavior was independent of the initial crystallite size of the powders. The ultimate densification to ~100 % was related not only to the powder initial particle size and agglomeration, but also to the impurity level. 1300 °C was the optimal calcination temperature, which led to Ho:Y₂O₃ ceramics with in-line transmittance of 81.6 % (at 1000 nm) and 77.2% (at 510 nm) and an average grain size of 5.6 μm.

5

SINTERING CONTROLS ON Y_2O_3 TRANSPARENT CERAMICS

5.1 Vacuum sintering

5.1.1 Introduction

In chapters 3 and 4, the effect of initial powders on the densification of Y_2O_3 ceramics was studied. It was found that optical quality of the Y_2O_3 ceramics was closely related to the purity and agglomeration degree of raw powders. However, without proper sintering mechanisms, ceramics cannot achieve full densification. In this chapter, the influence of sintering parameters on the densification of Y_2O_3 transparent ceramics was explored, trying to make clear what factors played the critical role during sintering.

Heating rate (HR) is considered to be one of the most important sintering parameters. Rapid rate sintering (RRS), with a HR of ≥ 10 °C/min, has been widely used to enhance densification and suppress grain growth of various ceramics. It is well known that surface diffusion for coarsening is dominant as compared with grain boundary or lattice diffusion for densification at low temperatures. Therefore, RRS can be used to achieve densification directly at a high temperature without too much grain growth.

Various ceramics, including ZrO_2 ¹¹⁹, $SrA(O,N)_3$ ($A=Mo, W$)¹²⁰, ZnO ¹²¹ and Al_2O_3 ^{100, 122–124}, with sufficiently high relative density (>99%) and small grain size, have been obtained by using this sintering technique.

However, in most cases, the success of RRS is actually limited to a few novel sintering technologies, such as microwave sintering (MS)^{121, 125} and spark plasma sintering (SPS)^{100, 119–120}. Moreover, the efficiency of RRS in fabricating transparent ceramics has not been clarified up to now, because different conclusions have been reported in the open literature. For instance, Li et al.¹¹⁸ concluded that a low heating rate (≤ 1 °C/min) was helpful to improving transparency of Y_2O_3 ceramics, due to the homogeneous densification. Similarly, Pan et al.¹²⁶ found that a rapid heating (≥ 5 °C/min) obstructed pore exclusion and atom diffusion of YAG ceramics. On the contrary, García et al.¹²² reported that submicron grained (1.2 μm) Al_2O_3 ceramics with high relative density (99%) could be fabricated by using RRS (HR >100 °C/min). In addition, Yang et al.¹²³ found the driving force for densification of Al_2O_3 ceramics could be increased by using RRS. In that study, Al_2O_3 ceramics with a relative density of 99.998% were fabricated successfully by using pressure-less vacuum sintering with HR = 100 °C/min.

It has been suggested that, during the conventional pressure-less sintering, the presence of temperature gradient is unavoidable, especially when using RRS. Such a temperature gradient resulted in a difference in densification, where the densification rate at the near surface area is slightly higher than that at the center area of the compact. Once the near surface region is nearly fully or fully densified, the pores in the center area cannot escape. Such an effect could be negligible in ceramics for other applications, because some properties, such as mechanical strength and electrical conductivity, are not so sensitive to porosity, especially when the porosity is at a very low level. However, in sharp contrast, optical transmittance is extremely sensitive to porosity^{86, 127, 128}. Therefore, the application of RRS to transparent ceramics is not very successful, although limited number of examples is present.

In this section, $Ho:Y_2O_3$ ceramics were sintered by using different sintering profiles. The temperature range in which differentiation of densification was observable has been identified. Within this temperature range, a two-step RRS was proposed, by including an intermediate temperature thermal treatment. By using this strategy, high quality $Ho:Y_2O_3$ transparent ceramics could be obtained.

5.1.2 Experimental Procedure

5.1.2.1 Ceramic Fabrication

$Y(NO_3)_3$, $Ho(NO_3)_3$ and $ZrOCl_2 \cdot 8H_2O$ solutions were mixed according to the chemical formula of $(Ho_{0.005}Y_{0.965}Zr_{0.03})_2O_3$ (described as Ho:Y₂O₃ in short), with Y³⁺ concentration of 0.5 mol/L. Yttrium precursor was precipitated by dropping a mixed $NH_4OH + NH_4HCO_3$ solution (molar ratio of 1:0.9) into the mother solution under stirring until the pH value reached 8-9. After aging for 4 h, the slurry was filtered, washed five times with pure water and twice with ethanol. Then the precursor was dried and calcined at 1300 °C for 5 h in air. The handling of the powders is similar to that reported by Zhang et al³⁹. The obtained powder was dry-pressed into pellets of 22 mm in diameter, followed by cold isostatic pressing (CIP) at 200 MPa. After CIP, thickness of the green bodies was 4.90 mm. The compacts were vacuum sintered at a vacuum level of $\leq 10^{-3}$ Pa, during which the HR was fixed at 10 °C/min from room temperature to 1300 °C. After holding at 1300 °C for 1 h, different heating rates (HR=40, 20, 10, 2 and 0.5 °C/min) were used. The ceramics were then annealed in air at 1400 °C for 10 h to remove oxygen vacancies. After annealing, the Ho:Y₂O₃ ceramics were mirror polished on both surface to about 2.5 mm.

5.1.2.2 Characterization

Bulk densities of the ceramics were determined by using the Archimedes method. In-line transmittance of the Ho:Y₂O₃ transparent ceramics was measured by using a UV-VIS-NIR spectrometer (Carry 5000, Agilent, Santa Clara, CA, USA). Microstructures of the ceramics were recorded by using a scanning electron microscopy (JSM-6360A, JEOL, Tokyo, Japan) and an optical transmission microscopy (Olympus BX53-P, Japan). If not otherwise specified, the SEM and optical images were recorded at near center area of the samples.

5.1.3 Results and Discussion

5.1.3.1 Estimation of Temperature Gradient

For a given compact, the temperature difference during constant heating between the surface and center is given by²⁸:

$$\Delta T_{sc} = T_s - T_c = \frac{L^2 \left(\frac{dT}{dt} \right)}{8\alpha}, \quad 5.1$$

Where L is sample thickness, dT/dt is heating rate and α is the thermal diffusivity that is given by¹¹⁹:

$$\alpha = \frac{\lambda_e}{\rho C}, \quad 5.2$$

Where C is material specific heat capacity, ρ is sample density and λ_e is effective thermal conductivity of the compact. Combining Eqs. 5.2 with 5.1, ΔT_{sc} can be expressed as:

$$\Delta T_{sc} = \frac{\rho C L^2 \left(\frac{dT}{dt} \right)}{8\lambda_e}. \quad 5.3$$

The specific heat capacity of Y_2O_3 is increased linearly with temperature by¹²⁹:

$$C \text{ (J/g} \cdot \text{K)} = 0.441 + 1.284 \cdot 10^{-4} \cdot T. \quad 5.4$$

During vacuum sintering, effective thermal conductivity of the compact is given by^{130, 131}:

$$\lambda_e = (1 - \delta') \alpha_r D_p + \delta' \lambda_p, \quad 5.5$$

Where δ' is a dimensionless parameter, which represents the effective contact area rate of the particles for a given compact, α_r is the heat transfer coefficient for thermal radiation, D_p is the particle diameter and λ_p is the thermal conductivity of Y_2O_3 , whose value can be determined from the thermal conductivity of a fully dense Y_2O_3 ceramic. It is related to temperature ($300 \text{ K} < T < 2000 \text{ K}$) through¹²⁹:

$$\lambda_p \text{ (W/m} \cdot \text{K)} = 85660 \cdot T^{1.577} + 2.86. \quad 5.6$$

Although λ_p decreases with increasing temperature, in the temperature range between 1573 and 2000 K, its value is actually quite stable, which is only decreased from 3.64 W/m·K at 1573 K to 3.39 W/m·K at 2000 K. Therefore, the value of λ_p can be approximately taken as 3.64 W/m·K.

The term $(1 - \delta')\alpha_r D_p$ represents heat transfer through radiation, while $\delta'\lambda_p$ represents thermal conduction through the particles and their contacting area.¹³⁰ α_r is given by¹³⁰:

$$\alpha_r = 4\sigma \frac{1}{\frac{2}{\varepsilon_r} - 1} T^3, \quad 5.7$$

Where ε_r is the particle emissivity ($=0.60$ for Y_2O_3 ¹³²), T is the absolute temperature, σ is the Stefan-Boltzmann constant ($5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$). With Eq. 5.7 and $D_p = 130 \times 10^{-9} \text{ m}$, $\lambda_p = 3.64 \text{ W/m}\cdot\text{K}$, Eq. 5.5 can be simplified as:

$$\lambda_e = (1 - \delta')(1.26 \times 10^{-14} T^3) + 3.64 \cdot \delta'. \quad 5.8$$

As the contribution of solid conduction to thermal conductivity ($3.64 \text{ W/m}\cdot\text{K}$) is much higher than that of radiation ($1.26 \times 10^{-14} T^3 \text{ W/m}\cdot\text{K}$), it is expected that the effective thermal conductivity would increase linearly with the value of δ' , which is a direct reflection of the contact area of the particles (sintering necks). According to Londry and Slavin, the value of δ' for ZrO_2 green body (relative density of 52%) was thought to be much lower than 0.05 ¹³⁰. In the present work, the value of 0.05 was used for our Y_2O_3 green bodies (relative density of 55%) to estimate the ΔT_{SC} .

At the beginning of constant rate sintering, temperature gradient from the surface to the center was directly related to the heating rate. At 1300°C , the value of ρ , C and λ_e is 2.77 g/cm^3 , $0.64 \text{ J/g}\cdot\text{K}$ and $0.182 \text{ W/m}\cdot\text{K}$, respectively. By using these values, the temperature gradients for different heating rates can be obtained with Eq. (3). The values of ΔT_{SC} ($^\circ\text{C}$) were 19.5 ($HR=40^\circ\text{C/min}$), 9.8 ($HR=20^\circ\text{C/min}$), 4.9 ($HR=10^\circ\text{C/min}$), 1.0 ($HR=2^\circ\text{C/min}$) and 0.25 ($HR=0.5^\circ\text{C/min}$). It is obvious that the temperature gradient is increased linearly with increasing heating rate. According to Chen and Mayo¹¹⁹, during the rapid rate sintering of ZrO_2 ceramics, an initial temperature gradient of 14°C was sufficiently high to produce differentiation in densification.

5.1.3.2 Microstructure Evolution during RRS

Fig. 5.1 shows fracture surface of the $Ho:Y_2O_3$ ceramics sintered at temperatures of 1450 – 1760°C with $HR=40^\circ\text{C/min}$. The sintering time was 0 minute at each sintering temperature. In order to check difference in densification between the surface and center of the samples, images of the near surface (NS) and near center (NC) areas were

recorded for each sintering temperature. The NS area represents the location of 10-200 μm away from the sample edge (surface), while the NC area represents the location of 1.8-2.2 mm away from the surface. At 1450 $^{\circ}\text{C}$, there was no significant difference in microstructure between the NC and the NS area (Fig. 5.1 (a) and (b)), because densification of the compact just started, as evidenced by the relative density data shown in Fig. 5.2. When the sintering temperature was increased to 1550 $^{\circ}\text{C}$, microstructure of the NC area (Fig. 5.1 (c)) was quite similar to that of the 1450 $^{\circ}\text{C}$ sintered sample (Fig. 5.1 (a)), while noticeable densification could be observed in the NS area (Fig. 5.1(d)). It means that densification behaviors of the surface and the center begun to be different. This difference was more pronounced as the sintering temperature was increased to 1650 $^{\circ}\text{C}$ (Fig. 5.1 (e, f)). Microstructures of the samples sintered at this temperature were typical features of intermediate stage sintering²³. This is consistent with the relative density data shown in Fig. 5.2. As the sintering temperature was further increased to 1760 $^{\circ}\text{C}$, relative density of the ceramic was increased drastically to 92.4%. Only closed pores were detected at the NS area (Fig. 5.1 (h)), while a certain number of open pores were observed at the NC area (Fig. 5.1 (g)). Therefore, differentiation of densification became very serious at this temperature.

Fig. 5.1 SEM images of the Ho:Y₂O₃ ceramics at the NC (a, c, e, g) and the NS (b, d, f, h) area with HR=40 °C/min.

Fig. 5.2 Relative density versus sintering temperature of the Ho:Y₂O₃ samples with HR=40 °C/min.

5.1.3.3 Effect of HR on the Final-stage Sintering

Fig. 5.3 shows grain size and relative density of the Ho:Y₂O₃ ceramics sintered at 1760 °C with different HRs at the final stage sintering, as a function of sintering time. As demonstrated in Fig. 5.3 (a), the samples with higher HR (40 °C/min) had smaller grain size than those with lower HR (2 °C/min), as the sintering times were ≤ 2 h. Because of their smaller average grain size, densification of the higher HR samples was faster, when entering the final-stage sintering (Fig. 5.3 (b)). For example, after sintering for 1 h, relative density of the sample with HR=40 °C/min reached 99.6%, while that of the one with HR=2 °C/min was 99.4%. However, as the sintering time was increased to be ≥ 2 h, full densification of the ceramics with HR=40 °C/min could not be obtained, in terms of high optical properties, which will be discussed in details in the following section. In addition, as the sintering time was above 4 h, the samples with different HR values exhibited almost same average grain size.

Fig. 5.3 Average grain size (a) and relative density (b) of the $\text{Ho:Y}_2\text{O}_3$ ceramics as a function of sintering time at 1760 °C with different HR values.

Fig. 5.4 shows SEM images of the $\text{Ho:Y}_2\text{O}_3$ ceramics sintered with $\text{HR}=40\text{ }^\circ\text{C/min}$ at 1760 °C for 1 min and 1 h, recorded at the NC and NS areas. Relative density of the sample sintered for 1 min was 95%, but there were many residual pores observed at the NC area (Fig. 5.4 (a)), while the NS area was nearly dense (Fig. 5.4 (b)). After sintering for 1 h, the NS area has been fully sintered (Fig. 5.4(d)), whereas the NC area had an estimated porosity of 0.4% (Fig. 5.4(c)).

Fig. 5.4 SEM images of the Ho:Y₂O₃ ceramics sintered at 1760 °C with HR=40 °C/min for 1 min (a, b) and 1 h (c, d).

5.1.3.4 Optical Transmittance

Fig. 5.5 shows SEM images of the Ho:Y₂O₃ ceramics sintered at 1760 °C for 13 h with different heating rates. Secondary phases were not detected in all the samples. Average grain size of the samples was about 2.5 μm. However, grain boundary pores were still observed occasionally in the samples with HR≥10 °C/min, as shown in Fig. 5.5 (a) and (b). It is generally believed that grain boundary pores can be easily eliminated along with grain growth during the final-stage sintering, given that they are not trapped by the fast grain growth to become the intragranular pores. However, these grain boundary pores of our Ho:Y₂O₃ ceramics were much stable than expected, which could be readily attributed to the presence of the hard shell in the NS area. According to Kingery, once a hard shell is formed during the sintering, chemical potential of the boundary is reduced, so that further material transport from grain boundary to pore becomes difficult.²⁸ As a result, the pores in the interior area were prevented from

escaping. A similar observation was reported by Chen et al.¹¹⁹, when they sintered ZrO_2 ceramics using RRS (HR=20 °C/min). After a hard shell was formed, densification of the interior of the samples was retarded. As shown in Fig. 5.5 (c) and (d), the Ho:Y₂O₃ ceramics sintered with HR=2 and 0.5 °C/min were nearly pore-free, because of the very small temperature gradients during sintering. The difference in densification was effectively suppressed.

Fig. 5.5 SEM images of the Ho:Y₂O₃ ceramics sintered at 1760 °C for 13 h at different heating rates.

In-line optical transmittance of the corresponding samples, together with their photographs, is presented in Fig. 5.6. With decreasing heating rate from 40 to 2 °C/min, optical transmission of the samples was increased monotonically. In addition, the samples with HR ≥ 10 °C/min exhibited obvious transparency gradient in between the NS and NC areas, due to the differentiation of densification, as revealed in Fig. 5.6 (b). The in-line transmittances of the ceramics with HR=2 and 0.5 °C/min were both reaching 80.2% at 1100 nm, which was about 98% of the theoretical transmittance of Y₂O₃ single crystal. The theoretical value was calculated to be 81.7%, based on the

formula of $T=100[1-((n-1)/(n+1))^2]^2$, where n is the refractive index of Y_2O_3 single crystal¹³³.

Fig. 5.6 In-line optical transmittance (a) and photograph (b) of the $Ho:Y_2O_3$ ceramics sintered at 1760 °C for 13 h with different heating rates.

Fig. 5.7 shows the microstructure and in-line optical transmittance of the $Ho:Y_2O_3$ ceramics sintered with different HRs at 1760 °C for 20 h. It can be seen that the sample sintered with HR=2 °C/min exhibited almost pore-free microstructure (Fig. 5.7 (a)), while many scattering centers could be observed in the sample with HR=40 °C/min (Fig. 5.7 (b)). It was confirmed by the SEM image that these scattering centers were the residual grain boundary pores (Fig. 5.7 (c)). As illustrated in Fig. 5.7 (d), in-line transmittance of the ceramic with HR=2 °C/min was further improved after sintering for 20 h, as compared with that of the one sintered for 13 h (Fig. 5.6 (a)). Specifically, at the

wavelength of 600 nm, in-line transmittance of the ceramic was increased from 76% to 79%. In contrast, for the sample sintered at HR=40 °C/min, almost no improvement in transparency was achieved by prolonging the sintering time, implying that once the pores were ‘trapped’ they would be very stable in the samples.

Fig. 5.7 Optical transmission micrographs (a, b), SEM image (c) and in-line optical transmittance (d) of the Ho:Y₂O₃ ceramics sintered at 1760 °C for 20 h.

5.1.3.5 Two-step RRS

As discussed above, at a given HR, the temperature gradient formed in a compact is closely associated with its effective thermal conductivity. Therefore, it is reasonable to expect that if the effective thermal conductivity of the compact is increased, the temperature gradient will be reduced, so that the difference in densification could be suppressed. In this section, we tried to verify this hypothesis. To do this, a two-step sintering route was proposed, with details shown schematically in Fig. 5.8. Two intermediate temperatures (1415 and 1530 °C) were studied, corresponding to R1 and R2. HR was fixed at 40 °C/min.

Fig. 5.8 Two-step RRS (T-RRS) sintering profiles.

Fig. 5.9 shows SEM images of the $Ho:Y_2O_3$ ceramics sintered with the two different routes. As shown in Fig. 5.9 (a), after being kept at 1415 °C for 218 min, particle sintering necks were formed, although the relative density of the sample was only 8% higher than that of the green body. This means initial stage sintering started at this temperature. According to Coble²³, during the initial stage sintering, the effective particle contact area rate could be increased from 0 to 0.2, due to the formation of sintering necks. Such an increase in particle contact area rate means that the thermal conductivity of the compact could be enhanced accordingly. If δ' was taken to be 0.2, the initial temperature gradient from the surface to the center (ΔT_{SC}) during the subsequent RRS was estimated to be merely 4.9 °C, which was much lower than that of the one without the use of the pre-sintering. Similarly, after pre-sintering at 1530 °C for 218 min, the compact should have even higher thermal conductivity, because more sintering necks were formed (Fig. 5.9 (b)). As a result, much lower temperature gradient would be formed during the subsequent RRS. This sample had obvious open pore channels, with a relative density of 75%, a typical microstructure of the intermediate stage sintering. Average grain size of the sample was estimated to be 220 nm after the pre-sintering, which was only 90 nm larger than that of the initial powder. In addition, the use of the pre-sintering step has another advantage. According to the relative density

curve in Fig. 5.2, densification rate of the ceramics was quite low at the temperatures below 1530 °C. Therefore, it can be inferred that when the samples were heated from 1300 to 1530 °C, the difference in densification was not so serious. The pre-sintering step at 1530 °C provided enough time for the compact to achieve homogeneous densification. Once the density of the compact reached a certain value, where the sample had sufficiently high thermal conductivity to avoid the temperature gradient, difference in densification could be effectively suppressed during the subsequent RRS process. This is supported by the SEM images of the ceramics sintered with R1 and R2, as shown in Figs. 5.9 (c) and (d). Porosity of the two samples was much lower than that of the one sintered by using the one-step RRS (Fig. 5.5(a)).

Fig. 5.9 SEM images of the Ho:Y₂O₃ ceramics sintered with different conditions: (a) 1415 °C/218 min, (b) 1530 °C/218 min, (c) R1 and (d) R2. Heating rate was 40 °C/min for all the samples.

Fig. 5.10 (a) shows the in-line optical transmittance of the Ho:Y₂O₃ ceramics sintered with R1 and R2 routes. Both samples exhibited much better in-line transmittance as compared with the one sintered by using the one-step RRS (40 °C/min) shown in Fig. 5.6. Interestingly, the R1 sample had a transmittance comparable to that of

the one sintered with $HR=10\text{ }^{\circ}\text{C}/\text{min}$ (Fig. 5.6). In addition, the value of ΔT_{SC} of both samples during heating was estimated to be $4.9\text{ }^{\circ}\text{C}$, suggesting a close relationship between the value of ΔT_{SC} and the final transmittance. On the other hand, the transmittance of the R2 sample was much higher than that of the R1 sample, because the former had a much better thermal conductivity than the latter after the pre-sintering step. Remarkably, the in-line optical transmittance of the R2 sample reached 81.7% at the wavelength of 1100 nm, which is almost same as the theoretical transmittance of Y_2O_3 single crystal.

Fig. 5.10 In-line optical transmittance curves (a) and photographs (b) of the $\text{Ho:Y}_2\text{O}_3$ ceramics sintered by using the T-RRS routes, with $HR=40\text{ }^{\circ}\text{C}/\text{min}$.

5.1.3.6 Discussion

With the above discussion, it is concluded that the effect of heating rate on densification in RRS process can be understood in terms of microstructural development, and thus thermal conducting behavior of the compact. Although RRS can be used to acquire ceramics with relatively small grain size for given high relative density, it is not suitable for transparent ceramics that require a relative density of $>99.95\%$, because optical transmittance is more sensitive to the presence of residual porosity^{86, 127, 128} than those for non-optical applications, such as microwave dielectric ceramics and piezoelectric ceramics^{134, 135}. For example, in the present work, the Ho:Y₂O₃ ceramics can readily reach a relative density of 99.6% within 72 min during the RRS (HR=40 °C/min). However, it was difficult to further densify to near 100%. According to the open literature, a successful implementation of RRS to fabricate transparent ceramics is usually combined with the utilization of other novel sintering technique such as microwave sintering, due to the absence of large temperature gradient¹²⁵. This could be the reason why RRS is not very successful in preparing transparent ceramics by using the conventional pressure-less sintering technique. In fact, large temperature gradients can also exist in ceramics during SPS, though the mechanism of heat conduction during SPS is different from that during the conventional pressure-less sintering. Although Yang et al.^{123, 124} successfully obtained Al₂O₃ transparent ceramics with a heating rate of as high as 100 °C/min, it should be careful to elucidate the underlying reasons. Firstly, Al₂O₃ has a relatively high thermal conductivity (≈ 6.5 W/m·K at 1200-1500 °C¹³⁶), which is nearly twice that of Y₂O₃ in the same temperature range¹⁶. More importantly, a pre-sintering thermal treatment was used in that study. Before vacuum sintering, the Al₂O₃ green bodies were calcined at 1200 °C for 2 h in a muffle furnace. Although no detailed information about the calcined sample was presented, such as relative density and microstructure, it is believed that 1200 °C should be sufficiently high to initiate the initial stage sintering, so that particle neck growth was facilitated¹³⁷. As a result, that process is similar to our two-step RRS in the present study, i.e., temperature gradient and thus the difference in densification has been prevented.

5.1.4 Conclusions

By using Ho:Y₂O₃ as an example, the reason why high quality transparent ceramics

cannot be obtained by using the conventional pressure-less vacuum sintering at high heating rates was explored. During the rapid rate sintering, i.e., HR=40 °C/min in this study, difference in densification was generated during the heating process above a certain temperature, which then led to the formation of a hard shell that prohibited the full densification of the interior of the compacts. A two-step RRS was proposed, in which the samples were treated at an intermediate temperature for a certain time duration before they were heated to the final sintering temperatures. After the intermediate temperature treatment, the samples reached a microstructure with appropriate particle contact area rate through the neck growth, which prevented the occurrence of temperature gradient and thus difference in densification. The Ho:Y₂O₃ ceramics pre-sintered at 1530 °C for 218 min and finally sintered at 1760 °C for 13 h exhibited an excellent in-line optical transmittance of 81.7% at 1100 nm.

5.2 The first room temperature lasing on $Ho:Y_2O_3$ ceramics

5.2.1 Introduction

In section 5.1, the influence of vacuum sintering conditions on the densification of $Ho:Y_2O_3$ transparent ceramics was studied. It was found that to prevent the differentiate densification, a low heating rate or a pre-sintering process at an appropriate sintering temperature should be used. After that, the $Ho:Y_2O_3$ transparent ceramics with relatively high optical transmittance could be fabricated. However, it was found that the ceramics still could not meet the requirement of laser application, as a certain amount of residual pores could still be detected. For example, from the transmittance curve shown in Figs. 5.6 and 5.10, it can be noticed that the transmittance curve decreased obviously at the short wavelength range (300 to 800 nm). Therefore, in order to obtain $Ho:Y_2O_3$ transparent ceramics suitable for laser applications, HIP sintering technique was used to further decrease the porosity of $Ho:Y_2O_3$ transparent ceramics

2 μm eye-safe lasers have many important applications, such as the remote sensing of atmospheric CO_2 and H_2O , medical treatment, LIDAR systems, and pump sources for mid-IR OPOs.^{138, 11} Trivalent holmium (Ho^{3+}), as a promising active ion for 2 μm lasers, has attracted great attention thanks to its 1.9-2.1 μm transition from the excited state (5I_7) to the ground state (5I_8).⁷⁴ In recent years, Ho^{3+} doped single crystals, such as YVO_4 ^{139, 140}, KREW (RE=Lu, Gd, and Y)¹⁴¹, YAG¹⁴², and sesquioxides (Y_2O_3 , Lu_2O_3 , and Sc_2O_3),^{143, 144} have been fabricated and their laser oscillation at 2 μm has been demonstrated. However, considering the relatively high cost and difficulty of making large size single crystals, transparent ceramics are regarded as a highly attractive alternative host materials for high power solid-state lasers.^{1, 145} It is to note that the 100 kW level solid-state lasers have been achieved using Nd:YAG ceramics as the laser gain media, confirming the great potential of transparent ceramics for high power laser applications.⁹

More recently, Y_2O_3 and other sesquioxide ceramics (e.g., Lu_2O_3 , Sc_2O_3) have attracted much attention for high power laser applications, because of their relatively high thermal conductivity and high emission cross sections.^{74, 143} However, laser operation of the holmium doped sesquioxide ceramics has been less addressed. There

has been no report on room temperature laser oscillation of $Ho:Y_2O_3$ ceramics at 2 μm . To the best of our knowledge, the only laser operation of $Ho:Y_2O_3$ transparent ceramics were carried out by Newburgh et al. in 2011¹¹, at liquid nitrogen temperature (77 K). In 2013, Kim et al.⁷⁴ reported the first room temperature laser oscillation of $Ho:Lu_2O_3$ transparent ceramics, which were fabricated by using the combination of hot pressing and hot-isostatic pressing (HIP) techniques. The samples had average grain sizes of 40-50 μm . However, due to the presence of small amount of scattering, lasing performance of the $Ho:Lu_2O_3$ ceramics was not promising.⁷⁴ For example, a maximum output power of 182 mW and a slope efficiency of 1% were obtained by using the $Ho:Lu_2O_3$ ceramics.

In this section, $Ho:Y_2O_3$ transparent ceramics were fabricated by using the three step vacuum sintering plus HIP technique. By precisely controlling the sintering profile, the $Ho:Y_2O_3$ transparent ceramics exhibited excellent optical quality with relatively fine grains, with which room temperature laser oscillation was demonstrated for the first time.

5.2.2 Experimental Procedure

5.2.2.1 Ceramic Fabrication

$Ho(NO_3)_3$, $Y(NO_3)_3$, and $ZrOCl_2 \cdot 8H_2O$ solutions were mixed according to the formula $(Ho_{0.015}Y_{0.955}Zr_{0.03})_2O_3$ (denoted as 1.5 at.% $Ho:Y_2O_3$ in short). Then, mixed solution of $NH_4HCO_3 + NH_4OH$ was added dropwise into the mother solution at a constant rate of 6 mL/min, until the PH value reached 8-9. After aging for 4 h, the precipitate was washed with ultra-pure water for five times and ethanol for two times. After that, it was dried at 60 °C for 24 h and then calcined at 1300 °C for 5 h in air to obtain 1.5 at.% $Ho:Y_2O_3$ powder. The obtained powder was dry-pressed into pellets of 22 mm in diameter, followed by cold isostatic pressing (CIP) at 200 MPa. Detailed processing has been previously reported¹⁴⁵. The green bodies were vacuum sintered in a three-step manner, in order to obtain compacts with relatively high relative density and small grain size. The sintered ceramics were HIPed at 1775 °C for 4 h at 198 MPa in argon (Ar). Finally, the ceramics were annealed at 1400 °C for 10 h in air to remove the color centers.

5.2.2.2 Characterization

Bulk densities of the ceramics were measured by using the Archimedes method. Transmittance spectra of the ceramics were measured by using a UV-VIS-NIR spectrometer (Carry 5000, Agilent, Santa Clara, CA). Surface morphologies of the ceramics were examined by using a scanning electron microscope (JSM-6360A, JEOL, Tokyo, Japan). Average grain size and grain size distribution were obtained by using a statistical method, with the Nano Measure software, with at least 300 grains counted for each sample. Thermal conductivity of the samples was measured by using the laser flash method (Laser Flash:DLF 1200, TA Instruments, USA). Thermal expansion was recorded by using a thermo-mechanical analyzer (TMA:Q400, TA Instruments, USA).

5.2.3 Results and Discussion

5.2.3.1 Densification during HIP

It is well known that HIPing is a very effective technique to approach the ultimate densification of ceramics during the final-stage sintering. In this sintering stage, pores have been isolated and the porosity has been very low ($\leq 6\%$). Because of the limiting porosity, densification should be governed by grain boundary diffusion or lattice diffusion, or the combination of both mechanisms.³⁰ It is also known that the relative contributions of grain boundary and lattice diffusions to the final densification are closely related to the grain size, i.e., the reduction in grain size could enhance the relative contribution of grain boundary diffusion over lattice diffusion.³⁰ In the case of grain boundary diffusion, the densification rate can be expressed as²¹:

$$\frac{d\rho}{dt} = \frac{101D_b\delta_bV_mP_{appl.}}{RTG^3} (1 - \rho)^{\frac{1}{3}} \quad 5.9$$

If the densification is governed by lattice diffusion, the densification rate is expressed as²¹:

$$\frac{d\rho}{dt} = \frac{61D_lV_mP_{appl.}}{RTG^2} (1 - \rho)^{\frac{2}{3}} \quad 5.10$$

Where D_b is the grain boundary diffusion coefficient, δ_b represents the grain boundary thickness, D_l is the lattice diffusion coefficient, V_m is the mole volume of the solid, G is the grain size, T is the absolute temperature and $P_{appl.}$ is the effective applied

pressure:

During pressure-less vacuum sintering, the driving force for pore removal is capillary pressure, which is given by⁸⁰:

$$P = \frac{2\gamma_s}{r} \quad 5.11$$

Where γ_s is the specific surface energy of the solid, r is the radius of the neck curvature, $2\gamma_s/r$ is the capillary pressure due to pore curvature. Since the exact surface energy of Y_2O_3 is not available, we assume $\gamma_s = 1.5 \text{ J/m}^2$, a typical value for ceramics.¹⁴⁶ Taken $r = 0.8 \text{ }\mu\text{m}$, the value of $2\gamma_s/r$ is calculated to be 3.75 MPa. Therefore, during the final-stage of pressureless sintering, this capillary pressure (3.75 MPa) is the main driving force for the final densification. However, if an external applied pressure (e.g. 200 MPa) is applied during the sintering, while the other parameters are not changed, the driving force for densification would be about 53 times greater.

In addition, according to Eqs. 5.9 and 5.10, a reduction in grain size could also lead to great enhancement in the densification rate. For example, in the case of grain boundary diffusion, densification rate could be increased by 8 times, as the grain size is only reduced from 2 to 1 μm . Therefore, in order to maximize the efficiency of HIPing, it is essential to suppress the grain growth. On the other hand, in order to minimize the penetration of Ar gas during HIPing, a dense compact with only closed pores and relative density of above 98% are required to produce the self-encapsulation of the ceramic.^{80, 84} However, during the final-stage sintering, the enhancement of relative density is generally accompanied by rapid grain growth. As a result, the sintering profiles should be precisely controlled.

5.2.3.2 Microstructure and Optical Property

In order to obtain ceramics suitable for HIPing, a three-step vacuum sintering process was utilized, as shown in Fig. 5.11. The green bodies were first vacuum sintered at 1530 °C for 218 min, aiming to initiate neck growth of the particles and thus enhance the effective thermal conductivity of the pellets.¹⁴⁷ This is to avoid the differentiate densification during the subsequent rapid rate heating. After this step, relative density of the ceramics was about 75%, with an average grain size of 220 nm. Then, the ceramics were fast heated to 1750 °C, at a high heating rate of 44 °C/min. Relative density of the ceramics was increased significantly during the rapid rate sintering from 75% to 93%,

but the grain size was only increased to 500 nm due to the high heating rate, so that the surface diffusion for coarsening was restraint. Without holding at 1750 °C, the samples were fast cooled (30 °C/min) to 1630 °C and held for 20 h to achieve close porosity. After this step, the ceramics exhibited a sufficiently high relative density of 99.5%, together with a relatively small average grain size of about 800 nm.

Fig. 5.11 Sintering profile of the three-step vacuum sintering process.

Figure 5.12(a) shows SEM image of the $Ho:Y_2O_3$ ceramics after the three-step vacuum sintering process. It can be seen that open porosity has been eliminated almost completely, leaving very small amount of isolated grain boundary pores, so that the penetration of Ar gas into the sample could be minimized. In addition, grain size distribution of the sample approximately complies with the normal distribution, without the presence of abnormal grain growth and intragranular pores. After HIPing at 1775 °C for 4 h, the ceramic exhibited homogeneous and dense microstructure, with an average grain size of 1.5 μm (Fig. 5.12(b)).

Fig. 5.12 SEM images of the Ho:Y₂O₃ ceramics after vacuum sintering (a) and vacuum sintering plus HIPing (b), with insets showing particle size distributions of the two samples.

Figure 5.13 shows the in-line optical transmittance of the HIPed Ho:Y₂O₃ ceramic with a thickness of 3.34 mm. The main absorption peaks are attributed to the trivalent

holmium absorption transitions of $^5I_8 \rightarrow ^5I_7$ (1760-2180 nm), $^5I_8 \rightarrow ^5I_6$ (1070-1240 nm), $^5I_8 \rightarrow ^5F_5$ (610-690 nm), and $^5I_8 \rightarrow ^5F_4 + ^5S_2$ (515-580 nm), respectively.¹⁴⁸ The ceramics after HIPing exhibited excellent in-line optical transmittance ($> 80\%$) through the entire wavelength range, even in the short wavelength range (< 800 nm). In fact, as compared with the pressure-less vacuum sintered samples, the HIPed ceramics in this work showed a much better transparency in the short-wavelength range. For example, the vacuum sintered samples had a maximum in-line optical transmittance of just 79% at 600 nm, which is about 2% lower than that of Y_2O_3 single crystal. The transmittance of Y_2O_3 single crystal was calculated to be 80.9% (at 600 nm) based on the formula of $T = 100[1 - ((n-1)/(n+1))^2]^2$ (n is the refractive index of Y_2O_3 single crystal)¹⁴⁹. The value at the wavelength of above 1000 nm was close to the theoretical value.^{147, 150}

In comparison, our present HIPed samples achieved a transmittance of 80.6% at 600 nm, reaching 99.6% of the theoretical value. According to the Rayleigh scattering theory, the scattering intensity is decreased significantly with increasing wavelength (in λ^{-4}), which means that the transmittance at the short wavelength range should be a better indicator of optical quality for transparent ceramics.¹⁶ Based on the Rayleigh scattering theory, Harada and co-workers¹⁵¹ proposed and verified that if the size of scattering centers was 20 times smaller than wavelength, scattering effect could be neglected. For example, if the size of a scattering center is 40 nm, it will scatter light at wavelengths near 800 nm. Therefore, the nano-sized residual pores, which cannot be completely removed only by using the pressure-less vacuum sintering, have been eliminated by using the HIPing process.

Fig. 5.13 In-line optical transmittance of the Ho:Y₂O₃ ceramics after HIP, with the inset showing the corresponding photograph.

Thermal properties of the ceramics are important because they determine the cooling properties during lasing. Figure 5.14(a) shows the thermal conductivity (TC) of the Ho:Y₂O₃ ceramics as a function of temperature. Compared with pure Y₂O₃ ceramics, the room temperature thermal conductivity of the Ho:Y₂O₃ ceramic is $11.1 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, which is superior to that of YAG ($10.8 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)⁹. However, this value is slightly lower than that of pure Y₂O₃ ceramics ($13.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$), due to the doping of ZrO₂ and Ho₂O₃. Figure 5.14(b) shows the thermal expansion (TE) and thermal expansion coefficient (TEC) of the Ho:Y₂O₃ ceramics versus temperature. Both the thermal expansion and thermal expansion coefficient are increased almost linearly with increasing temperature up to 900 °C. At 900 °C, the values of TE and TEC are 0.0071 and $8.3 \cdot 10^{-6} \text{ K}^{-1}$, respectively, in good agreement with the literature data.¹⁵²

Fig. 5.14 (a) Thermal conductivity and (b) Thermal expansion and thermal expansion coefficient of the Ho:Y₂O₃ ceramics as a function of temperature.

5.2.3.3 Room temperature laser oscillation

In order to investigate the laser performance of the Ho:Y₂O₃ transparent ceramics, a two-mirror cavity with total cavity length of about 25 mm was employed in the lasing experiment. The pump source used in our experiment is a Tm: fiber laser at the wavelength of about 1930 nm, whose spot radius was fixed at 230 μm. The dimension of the Ho:Y₂O₃ ceramic slab was 2 mm × 3 mm × 15 mm. Both end surfaces of the ceramic slab were antireflection coated at 1800-2100 nm. The input plano-plano mirror M1 was dichroic coated with high reflection at 2050-2250 nm and high transmission at 1850-1960 nm. Two different output couples (M2) with transmission of 6% and 10%

were utilized in the experiment to investigate the output performance of the laser. To remove the generated heat, the ceramic was wrapped with indium foil and tightly mounted in a copper block at 15.0 °C, which was controlled by water- cooling. The laser output power was measured with a laser power/energy meter (NOVAII, OPHIR).

Room temperature laser performance of the 1.5 at.% Ho:Y₂O₃ ceramic was first evaluated. The CW laser output power as a function of the incident pump power at different cavity output couplings (OC) are shown in Fig. 5.15 (a). The laser threshold for the OC with transmission of 6%, and 10% were about 6.7 W and 9.2 W, respectively. By using the 6% output coupler, a maximum output power of 1.1 W were achieved at an incident pump power of 16.6 W, corresponding to an optical-to-optical efficiency of 10%. The output power was increased linearly with increasing the absorbed pump power, while no power saturation was observed. Figure 5.15 (b) shows the typical optical spectrum under the maximum output power of 1.1 W. It can be seen that the center wavelength of the laser was about 2116.5 nm measured with an optical spectrum analyzer (AQ6375, Yokogawa Electric, Tokyo).

Fig. 5.15 (a) CW laser output power as a function of the incident pump power with

different cavity output couplers (OC). (b) Optical spectrum under the maximum output power of 1.1 W.

5.2.4 Conclusions

Highly transparent 1.5 at.% Ho:Y₂O₃ ceramics have been fabricated by using a three-step vacuum sintering process plus HIPing. The ceramics after the vacuum sintering reached a relative density of 99.5%, with a sub-micron grain size of 800 nm. After HIPing at 1775 °C for 4 h, the samples had an in-line transmittance of 80.9% at 600 nm, with a relatively fine average grain size of 1.5 μm. For the first time, room temperature laser oscillation of the Ho:Y₂O₃ transparent ceramics was demonstrated. A maximum output power of about 1.1 W with an optical-to-optical efficiency of 10% was achieved at the 2.1 μm.

Chapter 5 Sintering controls on Y_2O_3 transparent ceramics

6

TOWARD LOW LEVEL SINTERING ADDITIVES

In chapter 5, Ho: Y₂O₃ transparent ceramics were fabricated and their laser oscillation was achieved successfully thanks to their very good optical quality. 3 at.% ZrO₂ was utilized as the sintering additive. The purpose is to promote the densification during sintering and lower the numbers of scattering sources, such as pores in particular. To develop high performance sesquioxide ceramics, it is necessary to use sintering aids to improve densification without exaggerated grain growth. For example, various sintering aids, such as ThO₂⁵⁵, ZrO₂^{34, 41, 58}, La₂O₃^{56, 87, 153}, and ZrO₂-La₂O₃¹⁵⁴, have been utilized in the last 50 years. To obtain ceramics with maximum transparency, the amount of sintering aids should be sufficiently high to achieve maximum densification, if a single sintering aid is used. For example, the doping amount of ZrO₂ is usually ≥ 3 at.% (3.3 wt.%), while that of La₂O₃ is ≥ 8 at.% (11.1 wt.%). It is well recognized that thermal conductivity tends to decrease with increasing content of foreign ions.^{14, 16} However, for high-power solid-state lasers, efficient heat removal is critical, because the rise in temperature increases the population of the terminal laser level, which decreases the lasing efficiency. Moreover, the temperature gradient in laser rods, associated with nonradiative relaxation of the active ions, induces thermal lensing effects,¹⁴ which is

detrimental to the laser operation. In this respect, thermal conductivity of the ceramics should be as high as possible for effective heat removal. Therefore, such high doping concentrations are undesirable for transparent ceramics for high powder laser applications.

To reduce the amount of sintering additives, pressure-assisted sintering methods could be utilized to improve their densification. For instance, Kim and colleagues⁸⁵ prepared Yb:Lu₂O₃ transparent ceramics with small amount of LiF as the sintering aid through the combination of hot-pressing (HP) and hot-isostatic pressing (HIP) sintering methods. The resultant Yb:Lu₂O₃ ceramics had excellent transparency, with promising laser performance.⁹ The applied high pressure (>100 MPa) during sintering provided strong driving force for densification, thus enabling the ceramics to be densified at a relatively low sintering temperature, so that exaggerate grain growth was prevented. Similarly, by using high-pressure assisted spark plasma sintering (SPS), transparent yttria ceramics could also be fabricated without using sintering aids.¹⁵⁵ In-line transmittance of the yttria reached 68% at 700 nm. Table 6.1 lists some of the works on sesquioxide ceramics in the last five years. It is clearly demonstrated that either sufficient amount of sintering aids or pressure-assisted sintering methods should be used to obtain high quality sesquioxide transparent ceramics. In this chapter, the effort was made to decrease the amount of sintering additives, either by using vacuum sintering or HIP.

Table 6.1 Representative transparent sesquioxide ceramics.

Powder synthesis	Sintering aids	Sintering methods	In-line transmittance (at 1100 nm)	References
Combustion	5 at.% ZrO ₂	Pressureless sintering	70%	Wang et al. ⁴¹
Solid-state reaction	3 at.% ZrO ₂ + 10 at.% La ₂ O ₃	Pressureless sintering	80.5%	Pan et al. ¹⁵⁴
Solid-state reaction	3 at.% ZrO ₂	Pressureless sintering	78%	Zhou et al. ¹⁵⁶
Co-precipitation	None	Pressureless sintering plus HIP	76%	Serivalsatit et al. ⁴⁹

Flame spray pyrolysis	None	Pressureless sintering plus HIP	Not reported	Seeley et al. ¹⁵⁷
Co-precipitation	None	Pressureless sintering plus HIP	80%	Ballato et al. ¹²
Solid-state reaction	None	SPS	79%	Ito et al. ¹⁵⁸

6.1 Activated sintering

In this section, the fabrication of highly transparent 0.5 at.% Tm:Y₂O₃ ceramics was reported. 1 at.% ZrO₂ and very small amount of Al₂O₃ (~100 ppm level) were used as the sintering aids. The effect of Al₂O₃ on densification, grain growth and transmittance of the Tm:Y₂O₃ ceramics was systematically studied.

6.1.1 Experimental Procedure

6.1.1.1 Ceramic Fabrication

High purity commercial powders of Y₂O₃ (99.999% purity, Jiahua Advanced Material Resources Co., Ltd, China), Tm₂O₃ (99.99% purity, Jiahua Advanced Material Resources Co., Ltd, China) and ZrO₂ (ZrO₂>94.65 wt.%, main impurity Y₂O₃ with 5.15 wt.%, Tosoh, Japan) were mixed, according to the composition of (Tm_{0.005}Y_{0.985}Zr_{0.01})₂O₃, with xAl₂O₃ as sintering additive (x = 0, 49.1, 81.8, 163.5, 273, 546, 1090 and 4360 wt ppm). The (Tm_{0.005}Y_{0.985}Zr_{0.01})₂O₃ was described as Tm:Y₂O₃ in short hereafter. To ensure homogeneity, Al₂O₃ was introduced by using AlCl₃ solution. The mixtures of Y₂O₃, Tm₂O₃ and ZrO₂ powders and AlCl₃ solution were ball milled for 15 h, with high purity zirconia balls and ethanol (99.99% purity; Merck, Darmstadt, Germany) as ball milling media. The rotation speed was fixed at 140 rpm (rotation per minute). The milled slurries were dried at 80 °C for 24 h to remove the ethanol. After sieving, the powders were calcined at 1000 °C for 3 h in air to remove chlorine through the decomposition of AlCl₃, and then uniaxially pressed into 20 mm diameter pellets at 15 MPa. The pellets were then cold isostatically pressed (CIPed) at 200 MPa. The green bodies were sintered in vacuum ($p \leq 10^{-3}$ Pa) at temperatures from 1450 to 1860 °C. Cooling rate was fixed to be 30 °C/min after the vacuum sintering. Then the ceramics

were annealed in air at 1400 °C for 10 h (Nabertherm LHT 04/17) to eliminate oxygen vacancies. Finally, both surfaces of the ceramics were fine polished, with thickness of about 2.58 mm, by using a Hyprez precision lapping machine (Model: EJW400-IN-D, Engis, Japan).

6.1.1.2 Characterization

Morphologies of the raw powders and the ball-milled powders were observed by using a Leo 1550 field emission scanning electron microscope (SEM, Leo 1550, Cambridge, Cambridgeshire, UK). Brunauer-Emmett-Teller (BET) surface area of the powders was measured by using a Micromeritics Tristar II-3020 nitrogen absorption apparatus. Bulk densities of the sintered samples were measured by using the Archimedes method. Transmittance spectra of the ceramics were recorded with a UV-VIS-NIR spectrometer (Carry 5000 Spectrophotometer, Varian, USA). Phase compositions of the ceramics were identified by using an X-ray diffraction device (XRD, Bruker D8 Advance). Microstructure of the ceramics was examined by using a scanning electron microscopy (SEM, JSM-6360A, JEOL, Tokyo, Japan). Energy-dispersive X-ray spectroscopy (EDX) analysis was conducted by using the same scanning electron microscopy, at an accelerating voltage 15 kv with a spot size of 69 nm. Before microstructural observation, the ceramics were thermally etched in air for 1 h at temperatures that were 100 °C lower than the sintering temperatures.

6.1.2 Results and Discussion

6.1.2.1 Morphology of powders

Figure 6.1(a) shows FESEM images of the Y_2O_3 raw powder. The commercial powder had an average particle size of $>1\ \mu\text{m}$, with a BET surface area of merely $2.4\ \text{m}^2/\text{g}$, implying that the commercial powder was strongly agglomerated. The image of the powder after ball milling is shown in Fig. 6.1(b). Individual particle was highly distinguishable after the ball milling, implying that the agglomeration degree of powder had been greatly decreased. BET surface area of the ball milled powder reached $5.6\ \text{m}^2/\text{g}$.

Fig. 6.1 FESEM images of the Y_2O_3 raw powder before (a) and after ball milling (b).

6.1.2.2 Densification and microstructure evolution

Figure 6.2 shows relative densities versus sintering temperature of the $\text{Tm}:\text{Y}_2\text{O}_3$ ceramics with different levels of Al_2O_3 . It is noticed that the doping of Al_2O_3 had a great influence on densification of the Y_2O_3 ceramics. Relative density of the ceramics rose gradually with increasing content of Al_2O_3 . For example, at 1450°C , relative density of the undoped Y_2O_3 was merely 66%, while that of the sample with 4360 wt. ppm Al_2O_3 reached 82.5%. With increasing sintering temperature, relative density of all the samples increased, but the variation trend in densification was different. The higher the doping level of Al_2O_3 , the lower the sintering temperature would be, at which the ceramics achieved full densification. At the sintering temperature of 1800°C , relative densities of

the 0 and 49.1 wt. ppm Al_2O_3 doped samples were 95% and 98%, respectively, while those of the samples doped with ≥ 81.8 wt. ppm Al_2O_3 all reached above 99%. This implies that the addition of Al_2O_3 has greatly enhanced the densification of the Y_2O_3 ceramics.

Fig. 6.2 Relative densities of the $\text{Tm}:\text{Y}_2\text{O}_3$ ceramics with different levels of Al_2O_3 as a function of sintering temperature.

Figure 6.3 shows SEM images of the $\text{Tm}:\text{Y}_2\text{O}_3$ ceramics doped with different amounts of Al_2O_3 . As the tetravalent cations, such as Zr^{4+} , Hf^{4+} and Th^{4+} , are very effective to reduce the grain boundary mobility and prevent exaggerate grain growth of Y_2O_3 ⁶⁰, it is not surprised that intra-granular pores were not detected in all the samples. However, grain boundary pores were easily observed in the sample without Al_2O_3 , as shown in Fig. 6.3 (a). When the amount of Al_2O_3 was increased to 81.8 wt. ppm, a microstructure without the presence of pores and inclusions was obtained (Fig. 6.3(b)). It is also noticed that there was significant grain growth after doping with Al_2O_3 . For example, average grain size of the undoped sample was only about 5.3 μm , but it was fast increased to 9.5 and 11.4 μm when the Al_2O_3 doping amount reached 81.8 and 137 wt. ppm, respectively. Interestingly, when the doping amount of Al_2O_3 was further increased to 191 wt. ppm, the enhancing effect on grain growth was retarded and it was merely increased to about 11.9 μm . In addition, small inclusions were detected in the

137 and 191 wt. ppm doped samples, as shown in Fig. 6.3 (c) and (d). Average particle size of these inclusions was about 800 nm, which was much smaller than the average grain size of the ceramics. The presence of the inclusions could act as the ‘pinning centers’ that suppressed the grain boundary migration and inhibited the further increase in grain size. EDX analysis of the inclusions confirmed that they were Al-rich secondary phases, with Al and Y to about 5.7 and 70.2 wt.%, respectively. However, because the inclusions were relatively smaller (~800 nm in diameter) as compared with the penetration depth of the X-ray (1-2 μm) during the EDX analysis, it is suspected that the actual weight percentage of Al in the inclusions had been underestimated. In other words, the content of Al could be higher than 5.7 wt.%. Therefore, this result was not in any contradiction with the XRD results of the sample with high content of Al, as discussed later. These inclusions were not detected in pure and 81.8 wt. ppm doped samples.

Fig. 6.3 SEM images of the Tm:Y₂O₃ ceramics sintered at 1860 °C for 13 h, with different contents of Al₂O₃: (a) 0 wt ppm, (b) 81.8 wt ppm, (c) 137 wt ppm and (d) 191 wt ppm.

Considering that the addition of the small amount of Al₂O₃ has greatly improved densification and grain growth, it is reasonably suggested that, a certain secondary phase

or liquid phase, with much lower melting point than that of Y_2O_3 , should have been formed during sintering at high temperatures. According to the phase diagram of Y_2O_3 - Al_2O_3 - ZrO_2 system reported by Fabrichanaya et al¹⁵⁹, Al_2O_3 is not soluble in Y_2O_3 . In the Al_2O_3 - Y_2O_3 system, both cubic Y_2O_3 and monoclinic $Y_4Al_2O_9$ (YAM) phases would be present when the mole fraction of Y_2O_3 was higher than 67%. Though the solubility of Al_2O_3 in ZrO_2 is closely related to the sintering temperature, it is as high as about 4.6 and 15.4 at.% at 1500 and 2136 K, corresponding to the weight percentage of 1.9 and 6.5 wt.%, respectively. In this case, it is unlikely to form Al-Zr eutectic compounds. As a result, it is reasonable to conclude that YAM eutectic compound was formed during the sintering. Because YAM has a much lower melting point (≈ 2020 °C¹⁶⁰) than Y_2O_3 (≈ 2430 °C¹⁰), it has weaker interatomic electron bonds and thus higher mass transport rate.¹⁶¹ Therefore, the presence of this eutectic phase resulted in a significant increase in ionic diffusion rate.¹⁶² In addition, the increased ionic diffusion rate at the grain boundaries also contributed to higher grain-boundary mobility, which led to faster grain growth.¹⁶¹ This is the reason why densification and grain growth of the Y_2O_3 ceramics were greatly enhanced with the presence of the small amount of Al_2O_3 . This effect is quite similar to activated sintering, which has been observed during the sintering of various materials, such as Bi_2O_3 doped ZnO ceramics¹⁶³. It was found that densification and grain growth of ZnO ceramics could be greatly enhanced when small amount of Bi_2O_3 was added. The enhanced mass transport of ZnO was attributed to the formation of bismuth-rich grain boundary phase during sintering. Nevertheless, it should also be noted that as the amount and size of the inclusions increased, mobility of the inclusions was decreased and their dragging effect on grain boundary was enhanced. That should be the reason why the grain size did not increased consistently with the increasing doping amount of Al_2O_3 , though the relative density was enhanced monotonically. Excess YAM cannot consolidate into the host material and thus segregated at grain boundaries/junctions as a secondary phase.

In order to better identify the secondary phase, SEM image and XRD pattern of the 4360 wt. ppm Al_2O_3 doped Tm: Y_2O_3 ceramics are presented in Fig. 6.4. Compared with the inclusions observed in Figs. 6.3(c) and (d), size of the inclusions shown in Fig. 6.4 was much larger. Average particle size of the inclusions was 2.4 μm . EDX result indicated that, weight percentages of Y and Al in the inclusions were about 64.7% and 8.7%, respectively (Table 6.2), corresponding to a mole ratio of 2.3:1. It is very close to

the stoichiometry of $\text{Y}_4\text{Al}_2\text{O}_9$ (YAM). It is also interesting to note that a certain amount of intra-granular inclusions were detected. According to Kingery et al., inclusions can either move along with grain boundaries or be trapped by grains. When their size is small, the inclusions tend to move along with grain boundaries, because mobility of the small inclusions is generally larger than that of the grain boundaries. However, as grain growth proceeds, small inclusions may agglomerate into larger ones, thus leading to a decrease in their mobility. In this case, the inclusion-boundary separation will inevitably occur. As is revealed by Fig. 6.4 (a), the smaller inclusions were located at grain boundaries, while some larger ones have been already trapped by the grains. The XRD patterns exhibited in Fig. 6.4(b) confirmed that YAM (JCPDS 34-0368) was detected in the sample doped with 4360 wt. ppm Al_2O_3 . One of the main peaks located at $2\theta=30.8^\circ$ matched perfectly with that of YAM, which did not match with that of Y_2O_3 .

Fig. 6.4 (a) SEM image of the 4360 wt ppm Al_2O_3 doped $\text{Tm}:\text{Y}_2\text{O}_3$ sample and (b) XRD patterns of the 81.8 and 4360 wt ppm Al_2O_3 doped $\text{Tm}:\text{Y}_2\text{O}_3$ ceramics.

Table 6.2 EDX points analyses of different areas labeled as 1, 2, 3, 4, and 5 for the 4360 wt ppm Al_2O_3 doped $\text{Tm}:\text{Y}_2\text{O}_3$ ceramics.

Element wt.%	Point 1	Point 2	Point 3	Point 4	Point 5
O	25.43	25.47	25.57	10.75	10.39
Y	65.08	64.61	64.42	85.73	85.93
Al	8.55	8.64	8.92	ND	ND

Zr	ND	ND	ND	2.01	2.05
Tm	0.94	1.28	1.09	1.51	1.63

*ND means the corresponding element was not detected.

6.1.2.3 Optical quality

Figure 6.5 shows photographs of the Tm:Y₂O₃ ceramics with different doping concentrations of Al₂O₃ sintered at 1860 °C for 13 h. It is clearly demonstrated that the sample without Al₂O₃ was opaque. Transparency of the ceramics was gradually increased with increasing content of Al₂O₃, which reached the highest at 81.8 wt. ppm. As the doping amount of Al₂O₃ was further increased, transparency of the ceramics began to decrease. The variation in optical transmittance with the content of Al₂O₃ is shown in Fig. 6. Considering that the transmittance at short wavelengths is more sensitive to scattering, the transmittance at 600 nm was utilized to characterize optical quality of the samples. It can be seen that transmittance of the 54.6 wt. ppm Al₂O₃ doped sample was merely 56.8%, but it jumped to 76.6% at 81.8 wt. ppm. However, the transmittance started to decline with further increasing content of Al₂O₃, which was attributed to the increased amount of the YAM secondary phase, as discussed earlier. Compared with the host Y₂O₃, YAM has a different crystal structure (monoclinic, space group P2_{1/c}) and different refractive index, so that its presence would definitely degrade the optical quality of the Y₂O₃ ceramics.

Fig. 6.5 Photographs of the Tm:Y₂O₃ ceramics with different contents of Al₂O₃. From left to right: 0, 27.3, 54.6, 81.8, 109, 137, 164 and 191 wt ppm Al₂O₃.

Fig. 6.6 Optical transmittance spectra of the Tm:Y₂O₃ ceramics with different doping amounts of Al₂O₃.

6.1.3 Conclusions

The addition of small amount of Al₂O₃ could greatly enhance the sinterability of Y₂O₃ ceramics. Eutectic YAM phase was formed during the sintering process, which was responsible for the enhanced densification in the system. As the concentration of Al₂O₃ was increased to 137 wt ppm, second phase (YAM) began to segregate at grain boundaries. The optimized concentration of Al₂O₃ was 81.8 wt. ppm, at which both densification and grain growth of the ceramics were greatly increased, whereas the secondary phase was not detected. After sintering at 1860 °C for 13 h, in-line transmittance of the Tm:Y₂O₃ ceramics with 81.8 wt. ppm Al₂O₃ reached 83.0% at 2000 nm and 76.5% at 600 nm. It is believed that this simple method should be applicable to other transparent ceramics.

6.2 Yb:Y₂O₃ transparent ceramics processed with hot isostatic pressing

6.2.1 Introduction

In section 6.1, Tm:Y₂O₃ ceramics were used as an example to explore the possibility of decreasing the doping amount of ZrO₂ during vacuum sintering. It was found that with 1 at.% ZrO₂ and 81.8 wt. ppm Al₂O₃ as the combined sintering additives, Y₂O₃ ceramics with high optical quality could be fabricated. The small amount Al₂O₃ could improve grain boundary diffusion and enhance densification of Y₂O₃ ceramics. In this section, Yb:Y₂O₃ transparent ceramics, with 1 at.% ZrO₂ as the sintering aid, were fabricated by using vacuum sintering followed by HIP. In order to obtain the Yb:Y₂O₃ ceramics capable for high efficiency laser oscillation, microstructure without residual pores must be achieved. Meanwhile, smaller grain size is more favorable in order to ensure higher thermal shock resistance and higher mechanical strength.⁴⁸

6.2.2 Experimental details

6.2.2.1 Ceramic fabrication

First, yttrium and ytterbium nitrate solutions were prepared by dissolving the corresponding oxide (purity > 99.99%) in hot nitric acid solution. Then, the yttrium nitrate, ytterbium nitrate and zirconium oxychloride octahydrate solutions were stoichiometrically mixed according to the composition of (Y_{0.94}Yb_{0.05}Zr_{0.01})₂O₃. The mother solution was diluted by using de-ionized water until the concentration of Y³⁺ reached 0.5 mol/L. The mixture of NH₄OH and NH₄HCO₃, with molar ratio 1:0.9, was used as the precipitant. Yb:Y₂O₃ precursor was produced by dripping the precipitant solution into the mother solution at a rate of 6 ml/min under mild stirring at room temperature until the PH value reached 8-9. The resultant precursor, after being aged for 1 day, was filtered by using a suction filter and then washed six times with de-ionized water and two times with alcohol. The wet precursor was completely dried at 75 °C for 48 h and then calcined at 1300 °C for 5 h. The calcined powders were first uniaxially pressed into pellets of 22 mm in diameter at 15 MPa and the pellets were cold-isostatic

pressed at a pressure of 200 MPa. After that, the pellets were vacuum sintered at 1700 °C for 2 h at vacuum of $\leq 10^{-3}$ Pa, followed by hot isostatic pressing (HIPing) at 1700-1775 °C for 4 h at 198 MPa in argon (Ar). Finally, the sintered samples were annealed at 1400 °C for 10 h in air to remove the color centers.

6.2.2.2 Characterization

Morphologies of the precursors and calcined powders were observed by using a Leo 1550 field emission scanning electron microscope (SEM, Leo 1550, Cambridge, Cambridge shire, UK). In-line optical transmittance of the ceramics was measured by using a UV-VIS-NIR spectrometer (Carry 5000, Agilent, Santa Clara, CA, USA). Relative density of the ceramics was determined using the Archimedes method. Microstructure of ceramics was examined by using a scanning electron microscope (SEM, JSM-6360A, JEOL, Tokyo, Japan). Thermal conductivity was measured by using a physical property measurement system (Quantum Design, USA).

6.2.3 Results and Discussion

6.2.3.1 In-line optical transmittance

Fig. 6.7 shows SEM images of the precursor and the calcined powders. Both the precursor and the calcined powder showed good dispersity. Primary particle size of the precursor was estimated to be below 60 nm, while that of the powders calcined at 1300 °C was about 170 nm.

Fig. 6.7 FESEM images of the precursor (a) and the 1300 °C calcined powders (b).

Fig. 6.8 shows SEM images of the 5 at.% Yb:Y₂O₃ ceramics after vacuum sintering and HIPing. After vacuum sintering at 1700 °C for 2 h, relative density of the sample reached 97.5% without the presence of any open pores. Average grain size of the ceramic was 700 nm, with a narrow grain size distribution. After HIPing at 1700 °C for 4 h, porosity of the ceramic was decreased drastically, with an average grain size of only 1.1 μm, as shown in Fig. 6.8 (b). However, there were still a small number of grain boundary pores, as highlighted by the red circles in Fig. 6.8 (b). When the HIPing temperature was increased to 1740 °C and above, Yb:Y₂O₃ ceramics with fully dense microstructure could be obtained (Figs. 6.8 (c) and (d)). Average grain size of the 1775 °C HIPed sample was increased to 1.9 μm, with no residual pores observed in the SEM image.

Fig. 6.8 SEM images of the 5 at.% Yb:Y₂O₃ ceramics vacuum sintered at 1700 °C/2 h (a), followed by HIPing for 4 h at 1700 °C (b), 1740 °C (c) and 1775 °C (d).

Fig. 6.9 illustrates in-line optical transmittance and photographs of the HIPed Yb:Y₂O₃ transparent ceramics. The absorption peak located at between 800 and 1100 nm is attributed to the $^2F_{7/2}$ - $^2F_{5/2}$ transition. The as-vacuum-sintered sample (Sample A) was totally opaque, because there were still many residual grain boundary pores inside the sample. However, it can be seen that transparency of the ceramics was improved significantly after the HIPing process. As the HIPing temperature was increased from 1700 to 1775 °C, the transmittance of the ceramics was improved gradually. The enhancement in the transmittance should be attributed to the elimination of the residual pores. So far, the best HIPing temperature was 1775 °C, leading to the ceramic with in-line optical transmittances of 83.4% and 78.9% at 2000 and 600 nm, respectively.

Fig. 6.9 In-line optical transmittance (a) and photograph (b) of the Yb:Y₂O₃ ceramics HIPed at different temperatures: A, before HIPing, B, HIPed at 1700 °C, C, HIPed at 1740 °C and D, HIPed at 1775 °C.

6.2.3.2 Hardness and fracture toughness

The Vickers hardness and fracture toughness of the HIPed samples were tested using a digital hardness tester (FV-700e, FUTURE-TECH Co. Ltd, Japan).

Vickers hardness can be calculated from the following equation⁴⁸:

$$H_V = k \left(\frac{P}{d^2} \right) \quad 6.1$$

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).

Fracture toughness can be calculated with the equation⁴⁸:

$$K_{IC} = 0.16(E/H_V)^{1/2} (P/C^{3/2}) \quad 6.2$$

Where E is the Young's modulus (here is 179.8 GPa according to Ballato¹² et al.), C is indentation crack length.

The grain size dependence of hardness and fracture toughness of the Yb:Y₂O₃ ceramics are shown in Fig. 6.10. The hardness increased with decreasing grain size (Fig. 6.10(a)). The relationship between hardness and inverse square root of grain size was found to be linear (Fig. 6.10(b)), which followed the Hall-Petch equation¹⁶⁴. For the dependence of fracture toughness on the grain size, the general tendency was that if with smaller grain size, fracture toughness tends to be higher (Fig. 6.10(c)). It is also revealed

that, from the Fig. 6.10(c), when grain size was decreased to below 2 μm , significant enhancement of fracture toughness could be observed. This can be further verified by the indentation tests shown in Fig. 6.11. It is revealed that the fracture area of the large-grained ceramic sample was very large during the indentation tests. Morphology of the grains could even been seen through the cracks. However, the small-grained ceramic sample exhibited a much lower fracture area during the same test (Fig. 6.11(d)). It illustrates that when the same external stress was applied to the ceramic, it will be much easier to maintain the integrity of samples for the sub-micro grained ceramics. And it is more likely to trigger a massive breakage for the large-grained ceramics. Therefore, the sub-micro grained ceramics exhibited higher strength and higher thermal shock resistance. These ceramics will be more desirable in high energy laser systems where thermal shock resistance is critical.

Fig. 6.10 Hardness of the 5at.%Yb:Y₂O₃ ceramics versus (a) the grain size and (b) the inverse of the square root of the grain size; (c) Fracture toughness of transparent Yb:Y₂O₃ ceramics. versus grain size

Fig. 6.11 Indentation test of the 5 at.% Yb:Y₂O₃ ceramics with grain sizes of: (a, b) 10 μm and (c, d) 1 μm.

6.2.3.3 Thermal conductivity

Thermal conductivity analysis was conducted on the HIPed Yb:Y₂O₃ ceramics. For comparison, the Y₂O₃ ceramics without Yb³⁺ doping were also tested and compared. The details are shown in Table 6.3 and Fig. 6.12. It was found that the thermal conductivity decreased monotonically with increasing doping level of foreign ions. For example, the thermal conductivity of the 1 mol.% ZrO₂ doped ceramics was 9.78 w/(mK), but it decreased to 9.51 w/(mK) when ZrO₂ was increased to 3 mol.%. In addition, the introducing of Yb³⁺ will also lower the thermal conductivity, which is consistent with the result reported by Ikesue¹⁶.

Table 6.3 Thermal conductivity of the Y₂O₃ ceramics.

Y ₂ O ₃ ceramics	Doping details	Total doping amount	Thermal conductivity (W/(mK))
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Fig. 6.12 Thermal conductivity versus doping level of ions of the Y₂O₃ transparent ceramics.

Table 6.4 compares the thermal conductivity values of 5at.% Yb:Y₂O₃ ceramics between this work and the open literatures. Compared with the literatures, the thermal conductivity value in this work was improved thanks to the decrease in the amount of sintering additive.

Table 6.4 Thermal conductivities of Yb:Y₂O₃ transparent ceramics prepared using different methods.

Ceramics	Powder synthesis	Sintering methods	Additives	Thermal conductivity at RT (W/m·K)
5 at.% Yb:Y ₂ O ₃ ³²	Solid-state reaction	Pressureless sintering	3 at.% ZrO ₂ + 9 at.% La ₂ O ₃	6.5
5 at.% Yb:Y ₂ O ₃ ⁵⁹	Solid-state reaction	Pressureless sintering	3 at.% ZrO ₂	6.46

5 at.% Yb:Y ₂ O ₃ [This work]	Co-precipitation	Pressureless sintering plus HIP	1 at.% ZrO ₂	8.84
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6.2.3.4 Laser oscillation

Figure 6.13 shows a setup of the Yb:Y₂O₃ ceramic laser experiment. The pump source used in our experiment is a fiber-coupled laser diode with maximum power of about 25 W at the wavelength of about 940 nm. Collimated by a convex lens (F1) with focus length of 35 mm, the pump beam was then focused into the Yb:Y₂O₃ ceramics with a spot radius of about 140 μm by a spherical convex lens (F2) with focus length of 100 mm. In the experiment, a polished and uncoated Yb:Y₂O₃ ceramic slab was used as the laser gain medium. It was cut into a size of 3.18 mm in length and 4 mm × 4 mm in cross-sectional dimension. To remove the generated heat, the ceramic was wrapped with indium foil and tightly mounted in a copper block whose temperature was water cooled to 18.0 °C. A simple two-mirror cavity with total cavity length of about 12 mm was employed in the experiment. The input plano-plano mirror M1 was dichroic coated with high reflectivity (R>99.7%) for 1000-1100 nm and high transmission for pump wavelength. The M2 mirror was a plano-plano output coupler. Two different output couples (M2) with transmission of 5% and 7.5% were utilized in the experiment to investigate the output performances of the laser.

Fig. 6.13 Schematic diagram of the Yb:Y₂O₃ ceramic laser experiment.

In the experiment, the laser output power was measured with a laser power/energy meter (NOVAII, OPHIR). The CW laser output power as a function of the absorbed pump power with different cavity output couplers (OC) was shown in Fig. 6.14 (a). The laser thresholds for the OC with transmission of 5%, and 7.5% were about 3.46 W and 4.23 W, respectively. By using the 7.5% coupler, the highest slope efficiency of 10.6% and the maximum output power of 0.77 W were achieved in the experiment, corresponding to the absorbed pump power of about 11.5 W. The output power was

increased linearly with increasing absorbed pump power, while no power saturation was observed. Figure 6.14 (b) shows the typical optical spectrum under the maximum output power of 0.77 W. It can be seen that the center wavelength of the laser was about 1076 nm measured with an optical spectrum analyzer (USB4000, Ocean Optics).

Fig. 6.14 Variation of output power as a function of the absorbed power (a) and output spectrum (b) for the 5 at.% Yb:Y₂O₃ ceramic laser at 1076 nm.

6.2.4 Conclusions

Well dispersed Yb:Y₂O₃ nanopowders with an average particle size of 170 nm were synthesized by using chemical co-precipitation process. After vacuum sintered at 1700 °C for 2 h, the ceramic showed a fine-grained microstructure with pores only at grain boundaries. With increasing HIPing temperature from 1700 to 1775 °C, both the grain size and transmittance of the ceramics were increased. The Yb:Y₂O₃ ceramics

HIPed at 1775 °C, with a relatively small average grain size of 1.9 μm , exhibited the highest in-line optical transmittances, which were 83.4% and 78.9% at 2000 and 600 nm, respectively. CW lasing of the 5 at.% Yb:Y₂O₃ ceramic was demonstrated by using a simple two-mirror cavity. A maximum output power of 0.77 W with a slope efficiency of 10.6% was achieved.

Chapter 6 Toward low level sintering additives

7

FABRICATION OF SESQUIOXIDE TRANSPARENT CERAMICS WITHOUT SINTERING ADDITIVES

In chapters 3-6, the conditions of powder preparation, sintering parameters, and sintering additives for making transparent sesquioxide ceramics were discussed. Highly transparent Y_2O_3 ceramics could be fabricated with ZrO_2 as the sintering additive. The continuous wave laser oscillation was also realized on the Zr-doped $\text{Ho:Y}_2\text{O}_3$ and $\text{Yb:Y}_2\text{O}_3$ transparent ceramics. However, the authors found that there were some significant problems with the zirconium doping. In this chapter, the problems with the Zr-doped samples will be discussed and solved.

7.1 Problem with ZrO_2 as the sintering additive

7.1.1 Inclusions

From the transmittance curves shown in Figs. 5.13 and 6.9, it is revealed that there was slight decrease in transmittance at the visible wavelength, which means there still

exists a certain amount of small scatterings. When the Zr-doped Y_2O_3 samples were carefully examined using an optical microscopy (Fig. 7.1), it was found that the inner part of the ceramics was not so 'clean'. Pores were hard to be detected in the samples, but there were a certain amount of inclusions (secondary phases) accumulated.

Fig. 7.1 Optical transmission micrographs of the HIPed 3 at.% ZrO_2 -doped $\text{Ho:Y}_2\text{O}_3$ transparent ceramics.

To further identify their size, the as-sintered Zr-doped Y_2O_3 transparent ceramics were examined using a JEOL JSM-2010 electron microscopy. The measured high-resolution TEM images were displayed in Fig. 7.2. As shown in Fig. 7.2, some grain boundaries with the width of 5-10nm were detected, whose thickness is much larger than the normal boundary thickness of 0.5 nm. It is known that at the sintering temperature of 1800 °C, the solubility of Zr^{4+} into the Y^{3+} lattice is around 4 at. %⁵⁸, just slightly higher than the maximum doping level of the current work (3 at.%). In chapter 3, it has been verified that the grain growth mechanism of the Zr-doped Y_2O_3 ceramics is controlled by the solute drag effect. Therefore, it is very likely that the Zr-rich solutes segregated between grain boundaries after sintering, which leads to the formation of the secondary phases (fluorite type or $\text{Zr}_3\text{Y}_4\text{O}_{12}$)¹⁶⁵.

Fig. 7.2 TEM images for the Zr-doped Y₂O₃ ceramics.

From the TEM images, some inclusions with the size of 20-40 nm were also detected. Because refractive index of the defects is different with that of the Y₂O₃ host material, the existence of such defects would definitely degrade the transmittance at the wavelength of below 800 nm. This is rightly consistent with the Rayleigh scattering law and the transmittance curves. Rayleigh scattering in polycrystalline ceramics can be expressed by the following equation¹⁵¹:

$$S = \frac{128\pi^5}{3\lambda^4} d^6 \left| \frac{M^2 - 1}{M^2 + 1} \right|^2 \tag{7.1}$$

- M=n₂/n₁,
- n₁: Reflective index of host materials,
- n₂: Reflective index of scattering centers,
- d: Size of scattering media,
- λ: Wavelength,

According to the Rayleigh scattering theory, it can be concluded that if the size of a scattering center is much smaller than the light wavelength, there will be very little scattering effect. Based on the Rayleigh scattering theory, Harada and co-workers¹⁵¹ proposed and verified that if the size of scattering centers was 20 times smaller than wavelength, scattering effect could be neglected. In other words, if, for example, the size of a scattering center is 40 nm, it will only scatter light with the wavelength of ≤800 nm. For our ceramics, the transmittance started to decrease rightly at the 800 nm (Figs. 5.13

and 6.9), implying that the main scattering centers had the size range of ≤ 40 nm, which is consistent with the TEM analysis.

7.1.2 Laser produced color center

In section 6.2, the CW laser oscillation on the Zr-doped Yb:Y₂O₃ transparent ceramics was realized. However, after the lasing experiments, it was found that the color of the ceramic bodies irradiated by the laser beam turned brown, as can be seen in Fig. 7.3(a). When this part was observed under optical transmission microscopy, it was found that there were small brown dots (darkness) produced along the moving direction of the laser beam (Fig. 7.3(b)). It is interesting that the darkness just disappeared after the ceramics were annealed at 500 °C for 2 h in air. This phenomenon is very similar to the generation and elimination of color centers. Actually, in our Zr-doped Nd:Y₂O₃, Zr-doped Ho:Y₂O₃, and Zr-doped Yb:Lu₂O₃ transparent ceramics, the darkness were also generated during lasing.

Fig. 7.3 Photograph (a) and observation under optical microscopy (b) of the 1 at.% Zr-doped Yb:Y₂O₃ transparent ceramics after being excited by 940 nm laser beam.

The possible reason for producing the color centers can be described below. It is originated from the charge imbalance caused by the ZrO₂ additive. The doping of Zr⁴⁺ produces oxygen interstitial:

The oxygen ion loses its charge under pump light excitation, and free electrons are produced:

Free electrons are not stable in the crystal. They tend to be trapped by Y^{3+} , Zr^{4+} , or $V_o^{\bullet\bullet}$. Therefore, color centers are produced:

When the ceramics were re-oxidized at 500 °C for 2 h in air, color centers disappear:

Actually, the generation of color centers would decrease the transmittance greatly.¹⁶⁶ This is the first time that the laser darkness effect was detected in sesquioxide ceramics. Similar phenomena also exist in other materials, such as the solarization in Y_2O_3 doped ZrO_2 crystals/ceramics¹⁶⁷ and Si^{4+} doped YAG ceramics¹⁶⁸.

7.2 Sintering of sesquioxide ceramics without sintering additives

ZrO_2 is very effective to prevent the pore-boundary separation and enhance the densification of Y_2O_3 ceramics, but the Zr^{4+} -doped Y_2O_3 ceramics are not good for the laser applications, as the hetero valence doping introduces color centers under strong light illumination. Therefore, in this section, the possibility of making sesquioxide laser ceramics without using sintering additives was explored. By studying the sintering map of Y_2O_3 and Lu_2O_3 ceramics respectively, the critical temperatures that lead to pore-boundary separation could be located. If ceramics can be densified below this temperature, pore-boundary separation might be able to be prevented and full densification could be achieved.

7.2.1 Microstructural evolution of Y_2O_3 during vacuum sintering

In this section, Y_2O_3 ceramics were fabricated by using co-precipitated powders without any sintering additive. The synthesis method of the powders was similar to that described in chapter 6. Figure 7.4 shows the SEM images of fracture surface of the pure Y_2O_3 ceramics sintered at 1450 to 1600 °C. The ceramic sintered at 1450 °C reached the relative density of 95.7%, with the average grain size of 0.62 μm (Fig. 7.4(a)). Most of the residual pores have been pinched off and become closed pores, implying the final-stage sintering has begun. However, open pores can still be detected occasionally. With the increasing of sintering temperature, both the relative density and grain size were increased. When the sintering temperature was increased to 1520 °C, all the open pores of the ceramic collapsed and became isolated pores (Fig. 7.4(b)). Meanwhile, relative density and average grain size of the ceramic were increased to about 97.8% and 1.1 μm , respectively. When the sintering temperature was further increased to 1550 °C, average grain size of the ceramics was drastically increased to about 12 μm , implying that the grain boundary mobility has been significantly enhanced. Meanwhile, pore-boundary separation occurred due to the significant grain growth, as is revealed in Fig. 7.4(c). When further increased the sintering temperature to 1600 °C, the ceramic exhibited larger average grain size ($\sim 30 \mu\text{m}$) and more intragranular pores (Fig. 7.4(d)).

Fig. 7.4 SEM images of the Y_2O_3 ceramics without sintering additive sintered for 7 h at temperatures of 1450 °C (a), 1520 °C (b), 1550 °C (c), and 1600 °C (d).

Figure 7.5 shows the densification and grain growth behavior of the pure Y_2O_3 ceramics. It can be seen that relative density of the ceramics was increased steadily with the increasing of sintering temperature. At the sintering temperatures between 1400 and 1520 °C, average grain size of the ceramics was relatively small ($<1.5 \mu\text{m}$), implying that the moving velocity of the grain boundary was low enough for the attachment of boundary pores. However, when the sintering temperature was increased to 1550 °C, pore-boundary separation occurred before the completion of densification, due to the fast grain boundary migration rate. After that, densification rate was significantly reduced, making fully densification almost impossible. The abrupt acceleration of the grain boundary migration rate at above 1520 °C can be attributed to the following reasons: (1) the grain boundary diffusion coefficient (D_b) increases exponentially with increasing sintering temperature; (2) during the final-stage sintering, as the densification proceeds, the volume fraction of the grain boundary pores is reduced. In other words, the product of the average pore numbers (N) and the radius (r) of pores surrounded a grain is decreased, meaning the dragging effect of grain boundary pores on grain boundaries is reduced. Therefore, during the final-stage sintering, with the sintering temperature increases, the value of D_b is increased and $N \cdot r$ is decreased. According to the Eq. 2.10, the increasing of D_b and the decreasing of $N \cdot r$ would both lead to the enhancing of grain boundary migration rate.

Fig. 7.5 Densification and grain growth behavior of pure Y_2O_3 ceramics.

In order to achieve full densification of Y_2O_3 , the densification process needs to be completed before the pore-boundary separation occurs, implying that the ceramics should be fully densified below the separation temperature. Figure 7.6 shows the SEM images for the Y_2O_3 ceramics pre-sintered at 1520 °C for 7 h and post-HIP at 198 MPa of argon for 3 h at 1400-1600 °C. It can be noticed that, compared with the vacuum pre-sintered ceramic (Fig. 7.4(b)), the ceramics after HIPing at 1400-1450 °C exhibited little grain growth and significantly decrease of porosity, as is shown in Figs. 7.6(a) and (b). However, when the HIP temperature was increased to 1500 °C, average grain size of the ceramic was abruptly increased to about 22 μm, with a certain number of intragranular pores detected (Fig. 7.6(c)). It means that during HIPing, pore-boundary separation can still occur if high sintering temperature is applied. At high HIPing temperature, pores may have been trapped by grains before they are eliminated.

Fig. 7.6 SEM images for the Y_2O_3 ceramics pre-sintered at 1520 °C for 7 h and post-HIP at 198 MPa of argon for 3 h at: (a) 1400 °C, (b) 1450 °C, (c) 1500 °C, and (d) 1600 °C.

Figure 7.7 shows the in-line optical transmittance of the Y_2O_3 ceramics pre-sintered at 1520 °C for 7 h followed by HIPing at 1400–1500 °C. The sample HIPed at 1400 °C had the transmittance of 78.6% at 600 nm. When the HIPing temperature was increased to 1450 °C, the transmittance was slightly increased to 79.5%, which reaches 98.8% of the theoretical value. The in-line transmittance was slightly decreased at the short wavelength range (<800 nm) due to the existence of nano-sized residual pores (<100 nm). However, further increased the HIPing temperature to 1500 °C, the transmittance was decreased drastically, due to the presence of many intragranular pores.

Fig. 7.7 In-line optical transmittance of the Y_2O_3 ceramics pre-sintered at 1520 °C for 7 h and HIPed at 1400-1500 °C.

Fig. 7.8 shows the photograph of the 1450 °C HIPed Y_2O_3 ceramics, one of which was irradiated by a red laser beam. The sample was about 4 mm above the logo. No obvious scatterings were detected by the laser beam. Meanwhile, the logo under the ceramic could be clearly seen, implying that the ceramics have high optical quality.

Fig. 7.8 Photograph of the 1450 °C HIPed Y_2O_3 ceramics, one of which was irradiated by a red laser beam.

7.3 Laser oscillation on Yb:Y₂O₃ ceramics without sintering additives

In the last section, the sintering behavior of pure Y₂O₃ ceramics was studied. Through controlling the sintering temperature, pure Y₂O₃ ceramics with high transparency could be fabricated. In this section, the laser active ion, Yb³⁺, was doped into Y₂O₃ ceramics. It was found that after doping with Yb³⁺, the densification and grain growth behavior of the 5at.% Yb:Y₂O₃ ceramics were very close to that of the pure Y₂O₃ ceramics. Figure 7.9(a) shows the in-line optical transmittance of the 5 at.% Yb:Y₂O₃ ceramics pre-sintered at 1520 °C/7 h followed by HIPing at 1450 °C/3 h under 198 MPa Ar gas. The in-line transmittance was 82.8% at 1200 nm and remained 76.6% at 600 nm.

Fig. 7.9 In-line optical transmittance (a) and photograph (b) of the 5 at.% Yb:Y₂O₃ ceramics pre-sintered at 1520 °C/7 h followed by HIPing at 1450 °C/3 h under 198 MPa Ar gas.

Figure 7.10 shows the CW laser output power as a function of the absorbed power for the 5 at.% Yb:Y₂O₃ ceramic laser at 1076 nm. The laser setup was similar to that used in the section 6.2.3.4. The laser thresholds for the output couplers (OC) with transmission of 5%, and 13% were about 3.5 W and 5.0 W, respectively. By using the 13% coupler, the highest slope efficiency of 22% and the maximum output power of 2.7 W were achieved, corresponding to the absorbed pump power of about 17.9 W. It is worth clarifying that there was not any laser darkness effect detected during or after the

laser experiment. It verifies that the Zr^{4+} doping was the source for the producing of color centers during lasing.

Fig. 7.10 Variation of output power as a function of the absorbed power for the 5 at.% $\text{Yb:Y}_2\text{O}_3$ ceramic laser at 1076 nm.

Figure 7.11(a) shows the comparison of in-line optical transmittance between the 5 at.% $\text{Yb:Y}_2\text{O}_3$ ceramics with and without ZrO_2 as the sintering additive. It can be seen that their transmittances were very close in the near infrared wavelength range. At the short wavelength range of 230-800 nm, the transmittance of the ZrO_2 doped ceramic was slightly higher thanks to the better boundary controlling effect of Zr^{4+} . However, the laser efficiency of the ZrO_2 doped $\text{Yb:Y}_2\text{O}_3$ ceramic was merely 9%, which was much lower than that of the one without sintering additive (slope efficiency 17%), as is revealed in Fig. 7.11(b). It means that the color centers produced during lasing were detrimental to laser oscillation.

Fig. 7.11 Comparison of in-line optical transmittance (a) and CW laser efficiency (b) between the 5 at.% Yb:Y₂O₃ ceramics with and without ZrO₂ as the sintering additive.

7.4 Yb:Lu₂O₃ ceramics and their laser oscillation

7.4.1 Fabrication of Yb:Lu₂O₃ ceramics without sintering aids

In section 7.2, the densification and grain growth behavior of Y₂O₃ ceramics were studied. The grain boundary migration rate of Y₂O₃ was very sensitive to sintering temperatures. Therefore it is important to control the sintering temperature of Y₂O₃ below the critical temperature to prevent pore-boundary separation. In this section, the sintering behavior of Lu₂O₃ ceramics was studied as well.

8 at.% Yb:Lu₂O₃ transparent ceramics were fabricated by using the chemical co-precipitation process without sintering additives. The synthesise process of the Yb:Lu₂O₃ powders was very similar to that of the Yb:Y₂O₃ powders shown in the section 6.2.

Figure 7.12 shows the SEM image of the Yb:Lu₂O₃ powders. Primary particle size of the powders was about 100 nm. In general, the particles were well dispersed without large aggregations.

Fig. 7.12 SEM image of the Yb:Lu₂O₃ powders synthesized by using chemical co-precipitation process.

Figure 7.13 shows the SEM images of fracture surface of the Yb:Lu₂O₃ ceramics sintered at 1530 to 1800 °C for 5 h. All the ceramics exhibited merely closed pores after sintering at above 1530 °C. When sintered at 1530 °C, the ceramic had relative density of 98.1%, with the average grain size of 0.7 μm (Fig. 7.13(a)). When the sintering temperature was increased to 1560 °C, relative density and average grain size of the ceramic were increased to about 98.7% and 1.0 μm, respectively (Fig. 7.13(b)). However, further increased the sintering temperature to 1600 °C, average grain size of the ceramic was increased to above 20 μm. Meanwhile, many intragranular pores were detected in the sample, as is revealed in Fig. 7.13(c).

Fig. 7.13 SEM images of the 8at.% Yb:Lu₂O₃ ceramics sintered at temperatures of 1530 °C (a), 1560 °C (b), 1600 °C (c), and 1800 °C (d).

Figure 7.14 shows the densification and grain growth behavior of the Yb:Lu₂O₃ ceramics. It can be seen that at the sintering temperatures between 1500 and 1560 °C, average grain size of the ceramics was not higher than 1.0 µm. However, when the sintering temperature was increased to 1600 °C, pore-boundary separation occurred due to fast grain growth. This sintering phenomenon is very similar to that of Y₂O₃ ceramics. The critical temperature for the pore-boundary separation of Y₂O₃ ceramics is about 1560 °C, which is 40 °C lower than that of Lu₂O₃ ceramics.

Fig. 7.14 Densification and grain growth behavior of Yb:Lu₂O₃ ceramics.

Figure 7.15 shows the SEM images of the Yb:Lu₂O₃ ceramics pre-sintered at 1530 °C/5 h followed by HIPing at between 1440 and 1500 °C. It can be seen that in the temperature range of 1440-1500 °C, average grain size of the ceramics exhibited little grain growth after HIPing, but residual pores have been greatly removed. For example, average grain size of the 1440 °C HIPed ceramic was about 700 nm, which was identical to that of the one without HIPing (Fig. 7.13(a)). Pores were hardly detected at the grain boundaries. When the HIPing temperature was increased to 1500 °C, average grain size was only increased to around 800 nm, meaning that the pore-boundary separation had not occurred.

Fig. 7.15 SEM images of the Yb:Lu₂O₃ ceramics pre-sintered at 1530 °C/5 h followed by HIPing at: (a) 1440 °C, (b) 1470 °C, and (c) 1500 °C.

Figure 7.16 shows the in-line optical transmittance of the Yb:Lu₂O₃ ceramics pre-sintered at 1530 °C/5 h followed by HIPing at 1440-1500 °C. The ceramic HIPed at 1440 °C had relatively lower optical transmittance, which achieved 76.1% at 600 nm. When the HIPing temperature was increased to 1470 and 1500 °C, the transmittance was significantly increased, reaching just above 80% at 600 nm. The reason was that in the range below the separation temperature, higher HIPing temperature would have faster densification rate.

Fig. 7.16 In-line optical transmittance of the Yb:Lu₂O₃ ceramics pre-sintered at 1530 °C/5 h followed by HIPing at 1440-1500 °C.

7.4.2 CW laser oscillation on the Yb:Lu₂O₃ ceramics

The 8at.% Yb:Lu₂O₃ ceramics were put in a two-mirror cavity for the laser tests. The setup of the cavity is similar to that shown in Fig. 6.13. Figure 7.17 shows the CW laser output power versus the absorbed pump power with different OC value. The highest slope efficiency of 26% and the maximum output power of about 3 W were achieved by using the 5% coupler. The output power was increased linearly with increasing absorbed pump power. Laser darkness effect was not detected during or after the laser experiment. When the absorbed pump power reached 17 W, the power saturation effect was observed due to the accumulated heat.

Fig. 7.17 CW laser output power versus the absorbed pump power for the 8at.% Yb:Lu₂O₃ ceramics with different OC value.

Figure 7.18 shows the typical optical spectrum of the 8 at.% Yb:Lu₂O₃ ceramic under the output power of 3 W. The center wavelength of the laser was about 1079 nm.

Fig. 7.18 Output spectrum for the 8 at.% Yb:Lu₂O₃ ceramic laser at 1079 nm

7.5 Conclusions

The doping of ZrO₂ into Y₂O₃ resulted in the laser darkness effect, which greatly reduces the laser efficiency. The sintering behavior (densification and grain growth) of Y₂O₃ ceramics without sintering additives was studied. The rapid grain growth of Y₂O₃ ceramics did not start until the vacuum sintering and HIPing temperatures reached 1550 and 1500 °C, respectively. Through maintaining the vacuum sintering and HIPing temperatures of Y₂O₃ ceramics below the separation value, nearly fully densified Y₂O₃ ceramics could be achieved. The 5 at.% Yb:Y₂O₃ transparent ceramics fabricated by such method exhibited good in-line transparency and high laser slope efficiency (22%). The sintering behavior of Lu₂O₃ ceramics was similar to that of Y₂O₃. By vacuum sintering at 1530 °C/5 h followed by HIPing at 1470 °C/3 h, 8 at.% Yb:Lu₂O₃ transparent ceramics with an in-line transmittance of as high as 80% at 600 nm could be obtained. The CW laser oscillation was demonstrated on the 8 at.% Yb:Lu₂O₃ transparent ceramics. The central wavelength of the output spectrum was 1079 nm, with the slope efficiency of 26% and the maximum output power of about 3 W.

8

CONCLUSIONS AND FUTURE PLANS

8.1 Conclusions

The fabrication process requirements of transparent ceramics for laser applications are very strict. In order to get transparent ceramics with lasing quality, relative density of the ceramics should reach at least 99.99%. To achieve this goal, the influence of some critical parameters, including the powder synthesis, sintering parameters, and sintering additives on the densification and grain growth of sesquioxide ceramics has been studied in this research.

Ball milling process is a simple route to break the hard agglomeration of commercial raw powders. Morphology and agglomeration degree of Y_2O_3 powders were influenced by ball milling conditions. With optimized slurry concentration (18.4 vol% in the current work), agglomeration of Y_2O_3 powders was minimized, and densification rate of the Y_2O_3 ceramics was maximized. However, agglomeration was not completely eliminated by the current ball milling process, resulting in the incomplete removal of residual pores.

Compared with the ball milling process, the Y_2O_3 powders synthesized by chemical co-precipitation process had more uniform particle size and much lower degree of agglomeration. Agglomeration could be generated during calcination process. The

optimal calcination temperature of the precursor powders was 1300 °C, at which temperature the Y_2O_3 nanopowders had high purity and low degree of aggregation. ZrO_2 , as the sintering additive, was effective in inhibiting the agglomeration of powders during calcination. Meanwhile, it prevented the pore-boundary separation by solute drag mechanism during the sintering process. Therefore, the ZrO_2 -doped $\text{Ho:Y}_2\text{O}_3$ ceramics were able to be densified at very high sintering temperature to achieve high transparency.

During sintering, the uniform heating of the entire ceramic body is very important. This is to prevent the differential densification during sintering. High heating rate (≥ 10 °C/min) generally led to the formation of a hard shell that prohibited the full densification of the interior of the Y_2O_3 ceramics. However, through pre-sintering the Y_2O_3 ceramics at an appropriate temperature and forming moderate neck connection between particles, fast heating could be utilized to speed up the densification of the Y_2O_3 ceramics. By using such sintering technique combined with HIP, $\text{Ho:Y}_2\text{O}_3$ transparent ceramics with high optical quality (80.9% at 600 nm) and fine grain size (1.5 μm) were fabricated. For the first time, in the world, room temperature laser oscillation of the $\text{Ho:Y}_2\text{O}_3$ transparent ceramics was demonstrated. A maximum output power of about 1.1 W with an optical-to-optical efficiency of 10% was achieved at the 2.1 μm .

With the presence of ZrO_2 , addition of Al_2O_3 into the Y_2O_3 ceramics improved densification rate due to the enhancement of grain boundary diffusion rate. It was found that even with very small amount of Al_2O_3 doping (81.8 wt ppm), densification and normal grain growth of Y_2O_3 could be greatly improved. Meanwhile, pore-boundary separation was not detected thanks to the co-doping of ZrO_2 (1 wt.%). Through the moderate boundary controlling from the double sintering additives, Y_2O_3 ceramics with high relative density and good optical quality could be fabricated in vacuum.

However, speaking of grain boundary control, HIP sintering is considered to be the most powerful technique. The applied high pressure during sintering can provide strong driving force for densification, making possible the full densification of sesquioxide ceramics without the assistance of sintering additives. It was found that sintering additives, especially ZrO_2 , were not good for laser applications. On one hand, it led to the decrease in thermal conductivity of Y_2O_3 . More importantly, during laser operation, laser darkness effect was generated due to the charge imbalance between Y^{3+} and Zr^{4+} , which greatly restricted the laser efficiency. Through studying the sintering behaviors of

pure sesquioxide ceramics, fully densification of ceramics is actually possible. For example, the rapid grain growth of Y_2O_3 ceramics did not start until the vacuum sintering and HIPing temperatures reached 1550 and 1500 °C, respectively. Through maintaining the vacuum sintering and HIPing temperatures of Y_2O_3 ceramics below the separation value, nearly fully densified Y_2O_3 ceramics could be achieved. It is worth mentioning that this sintering temperature was about 300 °C lower than that used to sinter ZrO_2 -doped Y_2O_3 ceramics. Similar sintering methods are also applicable to densify the Lu_2O_3 transparent ceramics. The CW laser oscillations were demonstrated both on the 5 at.% Yb: Y_2O_3 and the 8 at.% Yb: Lu_2O_3 transparent ceramics. Without AR coating, the slope efficiency of the 5 at.% Yb: Y_2O_3 and the 8 at.% Yb: Lu_2O_3 ceramics was 22% and 26%, respectively. Laser darkness effect was not detected in both samples.

8.2 Future plans

Although Y_2O_3 and Lu_2O_3 transparent ceramics with high optical transmittance were fabricated, and high efficiency laser output had been obtained on the Ho: Y_2O_3 , Yb: Y_2O_3 , and Yb: Lu_2O_3 ceramics, there is still space to further improve the optical quality of the ceramics, especially at the short wavelength range. Meanwhile, composite structures can be designed to improve the heat removal during lasing. To this end, the following future works are proposed:

Wet forming techniques such as slip casting and tape casting can be utilized to improve the homogeneity of ceramic green bodies. Compared with the current CIP forming technique, forming by slip casting or tape casting is able to obtain green bodies with smaller initial pore size and much narrower pore-size distribution.^{53, 103} The reduction of pore size will result in faster pore elimination rate without pore-boundary separation. In addition, the increase of the particle packing homogeneity would lead to more homogeneous densification of ceramics. In this case, differential densification will be greatly prevented. Therefore, it is reasonable to predict that by using slip casting or tape casting forming technique, complete pore removal is possible.

It is known that, during lasing, efficient heat removal is very important to achieve high power output. For example, as revealed in Fig. 7.17, the possibility of achieving higher output power on the 8 at.% Yb: Lu_2O_3 ceramic was restraint by the thermal lens effect. If there is more efficient heat removal, thermal lens effect will be reduced and

higher laser output power can be achieved. This can be realized by designing composite structure ceramics. Figure 8.1 shows the schematic diagrams of the composite structure of sesquioxide transparent ceramics. With the uniform composite structure shown in Fig.8.1(a), efficient heat removal of ceramics can be greatly improved.¹ Moreover, through the gradient distribution of laser active ions (e.g. Nd^{3+} , Yb^{3+} , Ho^{3+}), the sudden heat generation can be suppressed, which will further enhance the homogeneity of thermal distribution during lasing.

Fig. 8.1 Schematic diagrams of the composite structures of sesquioxide transparent ceramics.

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