

Technical note

ZrO₂-doped Y₂O₃ transparent ceramics via slip casting and vacuum sintering

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Abstract

Commercial Y₂O₃ powder was used to fabricate highly transparent Y₂O₃ ceramics with the addition of ZrO₂ via slip casting and vacuum sintering. The effects of ZrO₂ addition on the transparency, grain size and lattice parameter of Y₂O₃ ceramics were studied. With addition of ZrO₂ the transparency of Y₂O₃ ceramics increased markedly and the grain size of Y₂O₃ ceramics decreased markedly by cation diffusivity mechanism and the lattice parameter of Y₂O₃ ceramics slightly decreased. The highest transmittance (at wavelength 1100 nm) of the 5.0 mol% ZrO₂-Y₂O₃ ceramic (1.0 mm thick) sintered at 1860 °C for 8 h reached 81.7%, very close to the theoretical value of Y₂O₃.

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1. Introduction

Y₂O₃, as a promising optical material, has excellent physical and chemical properties such as high melting point (2430 °C), broad range of transparency (0.2–8 μm), and high corrosion resistance. Y₂O₃ ceramics have been developed for laser host materials,¹ infrared-domes,² nozzles,³ refractories⁴ and components of semiconductor devices.⁵

Generally, it is not easy to produce transparent Y₂O₃ ceramics due to its high melting point. To decrease the sintering temperature and improve the transparency of Y₂O₃ ceramics, sintering aids and/or special sintering process such as hot pressing and hot isostatic pressing (HIP) were employed. For example, LiF,⁶ Al₂O₃,⁷ BeO,⁸ HfO₂,⁹ ThO₂¹⁰ and La₂O₃¹¹ have been respectively added to remove pores for high optical quality of Y₂O₃ ceramics during the past 40 years. However, the formation of a transient second solid-phase or a liquid-phase by addition of La₂O₃, LiF, Al₂O₃ or BeO is a disadvantage for optical applications. On the other hand, hot pressing is not suitable to prepare transparent Y₂O₃ ceramics with complex shape. Recently, Bernard-Granger et al.¹² fabricated transparent Y₂O₃ ceramics via HIP method with the addition of 300 ppm ZrO₂. The transmittance of their sample reached 70%

at 1100 nm. They focused on the investigation of grain growth and densification kinetics and did not discuss the effect of ZrO₂ concentration on the optical property of Y₂O₃ transparent ceramics.

Our aim is to develop a simple and cheap process to produce Y₂O₃ ceramics with high optical quality. ZrO₂-doped Y₂O₃ transparent ceramics have been prepared using commercial Y₂O₃ powders via slip casting and vacuum sintering. The effects of ZrO₂ concentration and sintering temperature on the optical property and microstructure of Y₂O₃ transparent ceramics were evaluated.

2. Experimental procedure

Commercial Y₂O₃ powder (5N purity, Jiangyin Jiahua Advanced Material Resources Co., Ltd., China) consists of agglomerated platelet particles (Fig. 1(a)) with a mean particle diameter of 2.0 μm and a BET surface area of 3.44 m²/g. The Y₂O₃ powder, adding different concentrations of ZrO₂ sintering aid (3N purity, Shanghai Di Yang Chemical Ltd., China), was milled with ZrO₂ balls for 12 h in ethanol. Then the milled slurry was dried at 60 °C for 24 h. The so-obtained powders were calcined at 1000 °C for 2 h. Fig. 1(b) shows the morphology of the calcined powder. Its mean particle diameter was 0.48 μm and BET surface area was 5.40 m²/g. It indicated that ball-milling effectively changed the morphology and particle size of the commercial powder.

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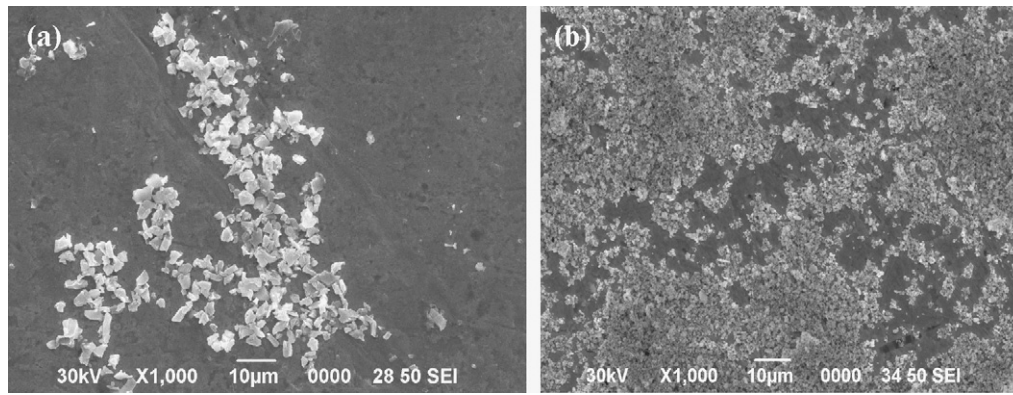


Fig. 1. Scanning electron micrograph of received commercial Y₂O₃ powder before (a) and after (b) ball-milling.

Suspensions with 30 vol% Y₂O₃ solids were prepared by ball-milling the calcined powder, deionized water and dispersant. The detail of this process can be found in a previous report.¹³ The prepared suspensions were slip-casted into a gypsum mold. After demolding and drying, the green bodies were heat treated at 900 °C for 2 h in order to burn out the organic additives.

The green bodies with a relative density of about 45% were sintered at 1730–1900 °C for 5–15 h under vacuum of 2×10^{-3} Pa in a furnace with tungsten heating element. The sintered samples were then annealed at 1500 °C for 10 h in air. Finally, the obtained samples were ground and polished.

The optical transmittance was measured by a spectrophotometer (Model U-2800, Hitachi, Japan). Microstructure and grain size of the samples were observed by scanning electron microscopy (SEM, JXA-8100, JEOL, Japan). X-ray diffraction (XRD) was performed on the ZrO₂-doped Y₂O₃ ceramics using a diffractometer (Model D/MAX-2550 V, Rigaku, Japan). Guinier-Hagg camera (XDC-1000, Stockholm, Sweden) was used to precisely characterize lattice parameters of the ceramics.

3. Results and discussion

Fig. 2 shows XRD patterns of the Y₂O₃ ceramics doped with different ZrO₂ concentrations sintered at 1860 °C for 8 h

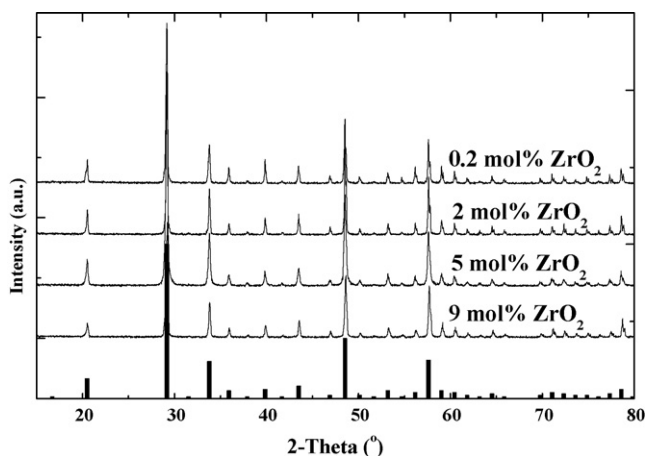


Fig. 2. X-ray diffraction patterns of Y₂O₃ ceramics doped with different ZrO₂ concentrations sintered at 1860 °C for 8 h in vacuum atmosphere.

Table 1

The lattice parameter ($a=b=c$) of Y₂O₃ doped with different ZrO₂ concentrations.

ZrO ₂ concentrations (mol%)	a axis of Y ₂ O ₃ (nm)
0.2	1.05994
2	1.05949
5	1.05948
9	1.05841

in vacuum. All the samples exhibit a pure cubic phase of Y₂O₃ structure without the presence of ZrO₂ phase or other impurities. It indicated that ZrO₂ was soluble in Y₂O₃ within the composition range of 0–9 mol% ZrO₂. This result is in agreement with the phase diagram of ZrO₂–Y₂O₃ system presented by Duwez¹⁴. Though the stoichiometric composition of Y₂O₃ is not the same as that of ZrO₂, they have the similar crystal structure. Y₂O₃ can be pictured as a modified fluorite-type cubic structure with one-fourth of the anion sites vacant and regularly arranged. In other words, it could be considered that the unit cell of Y₂O₃ is made up of eight cells of ZrO₂ in which the yttrium atoms replace zirconium atoms and only three-fourths of the oxygen positions are occupied. So it is easy to understand that ZrO₂ is soluble in Y₂O₃ over a wide range of concentrations.

From Table 1, it can be seen that with the increase of ZrO₂ concentration, lattice parameters of the sintered Y₂O₃ ceramics decreased slightly. This is due to that the radius of Zr⁴⁺ (0.79 Å) is smaller than that of Y³⁺ (0.89 Å).

Fig. 3 shows the pictures of Y₂O₃ transparent ceramics doped with different ZrO₂ concentrations sintered at 1860 °C for 8 h in vacuum atmosphere. All Y₂O₃ ceramics were 1 mm in thickness. It can be seen that the undoped Y₂O₃ ceramic was opaque. The optical quality of Y₂O₃ ceramic doped with 0.2 mol% ZrO₂ was

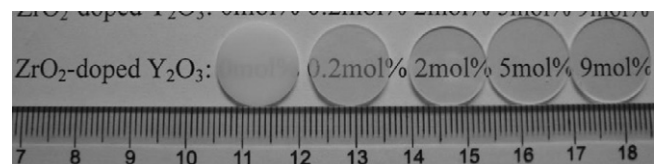


Fig. 3. Photographs of Y₂O₃ ceramics doped with different ZrO₂ concentrations.

a little better than that without ZrO_2 . And the other three Y_2O_3 ceramics exhibited high optical transmittance.

Fig. 4 shows the in-line transmittance of 1 mm thick Y_2O_3 transparent ceramics doped with different ZrO_2 concentrations sintered at $1860^\circ C$ for 8 h in vacuum atmosphere. With the doping concentration of ZrO_2 increased from 0 mol% to 5 mol%, the transmittance of Y_2O_3 ceramics at 1100 nm was improved from 8.34% to 81.7%. The theoretical transmittance of Y_2O_3 is 81.93% at 1100 nm. It is worth to notice that the Y_2O_3 ceramics doped with 5 mol% ZrO_2 shows quite a good optical transmittance even at 400 nm.

Fig. 5 (a)–(e) shows fracture surfaces of ZrO_2 -doped Y_2O_3 transparent ceramics sintered at $1860^\circ C$ for 8 h in vacuum atmosphere. It can be seen that large pores were visible for Y_2O_3 ceramics doped with 0 mol% (Fig. 5 (a)) and 0.2 mol% (Fig. 5 (b)) ZrO_2 . Due to the presence of pores, light scattering and absorption occurred in the two samples, which resulted in a lower transmittance. For the 5 mol% ZrO_2 -doped sample, it was fully densified and it is hard to observe any pore in the sintered body. Therefore, it had a higher transparency (Fig. 4). The grain

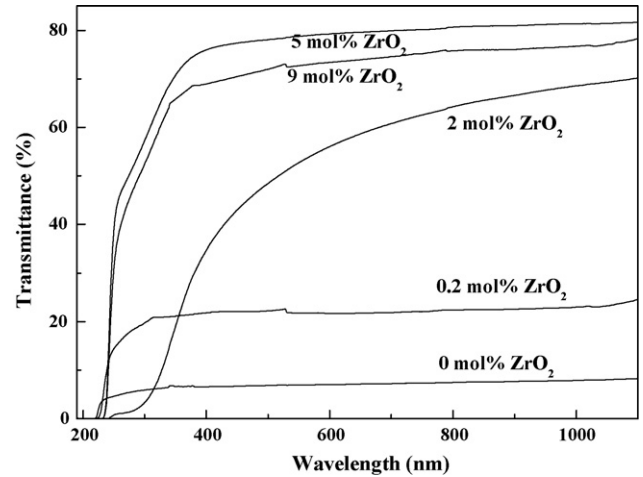


Fig. 4. In-line transmittance of Y_2O_3 ceramics doped with different ZrO_2 concentrations sintered at $1860^\circ C$ for 8 h in vacuum atmosphere.

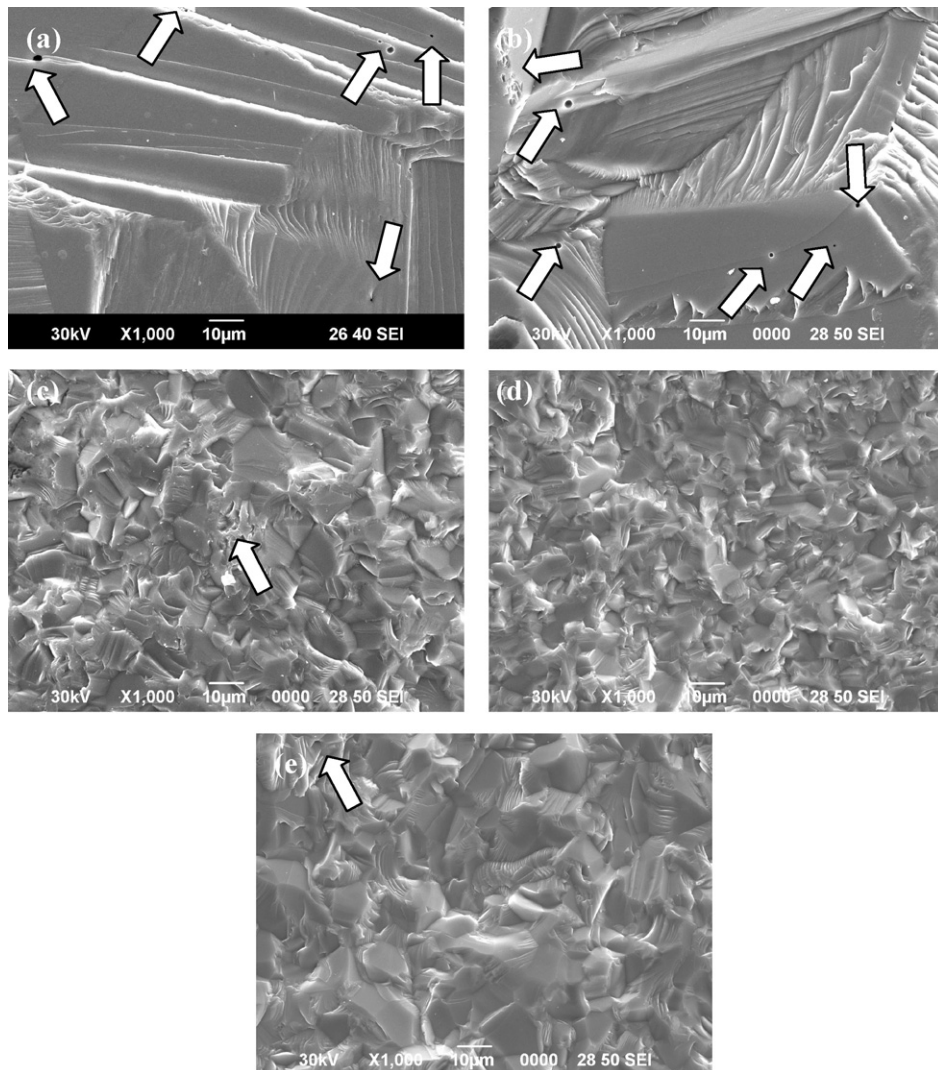


Fig. 5. Fracture surfaces of Y_2O_3 ceramics doped with (a) 0 mol%, (b) 0.2 mol%, (c) 2 mol%, (d) 5 mol%, and (e) 9 mol% ZrO_2 .

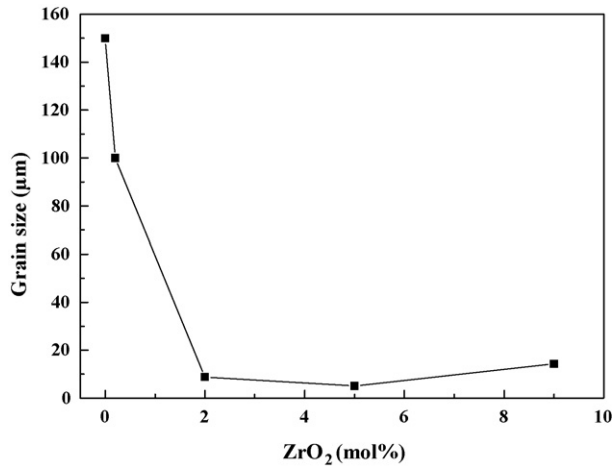


Fig. 6. Relationship between ZrO₂ concentration and grain size of Y₂O₃ ceramics sintered at 1860 °C for 8 h in vacuum atmosphere.

sizes of Y₂O₃ ceramics doped with 0 mol%, 0.2 mol%, 2 mol%, 5 mol% and 9 mol% ZrO₂ were 150 μm, 100 μm, 8.8 μm, 5 μm, and 14.4 μm, respectively (Fig. 6). According to Chen et al.,¹⁵ Zr⁴⁺ was the most effective grain growth inhibitor in the sintering of Y₂O₃. Grain boundary mobility of Y₂O₃ was controlled by cation diffusivity, and cation diffusion by an interstitial mechanism can be suppressed by the presence of oxygen interstitials (O_i''). When ZrO₂ is soluble in Y₂O₃, two tetravalent Zr⁴⁺ create one O_i' and a large concentration of ZrO₂ may introduce more O_i'. So ZrO₂ as a dopant inhibited Y³⁺ diffusivity which decreased grain boundary mobility of Y₂O₃ and led to the decrease of grain size. At much higher concentration ZrO₂ doping, such as 9 mol%, the grain boundary mobility was increased, resulting in a slight increase of grain size and embedded pores. Thus, the transmittance of the Y₂O₃ ceramics was decreased. Similar phenomena had been reported in Ti⁴⁺ doped Y₂O₃ ceramics.¹⁴

Fig. 7 shows the effect of sintering temperature on the grain size and transmittance of 2 mol% ZrO₂-doped Y₂O₃ ceramics sintered at different temperatures for 8 h. With the sintering

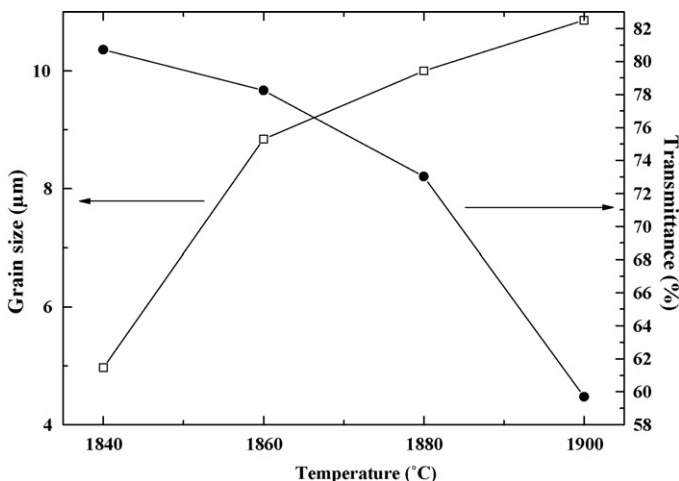


Fig. 7. Effect of sintering temperature on grain size and transmittance of 2 mol% ZrO₂-doped Y₂O₃ ceramics sintered at different temperatures for 8 h.

temperature increasing from 1840 °C to 1900 °C, the transmittance of 1.0 mm thick Y₂O₃ ceramics decreased and the grain size of Y₂O₃ ceramics increased. It indicated that a sintering temperature of 1840 °C was adequate to obtain Y₂O₃ transparent ceramics with a higher transparency and a smaller grain size.

4. Conclusions

Using commercial Y₂O₃ powders as the starting materials, highly transparent Y₂O₃ ceramics with the addition of ZrO₂ were fabricated by slip casting and vacuum sintering at 1730–1900 °C for 5–15 h. The important results are summarized as follows:

- (1) A simple and cheap method, slip casting and vacuum sintering has been successfully developed to prepare ZrO₂-doped Y₂O₃ transparent ceramics.
- (2) Doping with 5 mol% ZrO₂, Y₂O₃ ceramics was pore-free and the grain size was 5 μm. The transmittance was 81.7% which was very close to the theoretical value.
- (3) Due to the radius of Zr⁴⁺ smaller than that of Y³⁺, lattice parameter of Y₂O₃ decreased with increasing the concentration of ZrO₂.

Acknowledgements

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