

分散剂浓度对真空热压烧结 Y_2O_3 透明陶瓷显微结构和光学性能的影响

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摘 要: 以硝酸钇为原料, 采用沉淀法成功制备出 Y_2O_3 纳米粉体, 通过真空热压烧结工艺制备出 Y_2O_3 透明陶瓷。沉淀法是制备 Y_2O_3 粉体的常用方法, 具有反应条件温和、粉体纯度高、成本低等优点, 但由于粉体在沉淀过程中容易发生团聚现象, 导致陶瓷的透明性降低。为了解决这一问题, 在沉淀溶液中添加 PEG4000 作为分散剂, 期望改善其粉体的分散性。同时, 在真空热压烧结过程中, 用钼箔包裹样品, 有效地防止了碳污染的发生。本工作研究了 PEG 添加量对 Y_2O_3 粉体和陶瓷的影响, 并找到最佳工艺参数。结果表明, 当 PEG 添加量为 0.9% (摩尔分数), 烧结温度为 1 500 °C 时制备的 Y_2O_3 陶瓷具有最高的透明性, 其在 1 100 nm 处的直线透过率为 48.4%, 在 600 nm 处也达到了 18.0%。

关键词: 氧化钇; 透明陶瓷; 沉淀法; 透过率; 热压烧结

中图分类号: TQ174.758.23

文献标志码: A

文章编号: 0454-5648(2024)03-0774-09

网络出版时间: 2024-02-05



1 Introduction

Yttria (Y_2O_3) ceramic is an optical material with a great application potential due to its transparency in the wavelength range of 0.2–8.0 μm and outstanding thermophysical properties^[1–2]. These properties (*i.e.*, high melting point, low vapor pressure, high corrosion resistance, high thermal conductivity, low thermal expansion coefficient, low phonon energy and low infrared emissivity at a high temperature^[3]), make yttria ceramic suitable for various applications^[4]. For instance, yttria ceramic can be used as high-temperature transparent windows, missile domes, bulb envelopes and laser hosts^[5–6]. Moreover, this ceramic is especially suitable as a main material for scintillators and solid-state lasers, which requires high optical quality and stability^[7–8].

Researchers employed different methods, such as sol-gel combustion^[9], electrospray pyrolysis^[10], hydrothermal synthesis^[11], precipitation^[12], *etc.*, to prepare high-activity yttria nanocrystalline powders. Among these methods, the precipitation method is a simple, low-cost and environmentally friendly method that can produce yttria powders with a good

performance^[13]. However, it has a drawback, *i.e.*, the particles of precipitates tend to agglomerate, which affects the dispersibility and sinterability of the powder^[14]. To address this issue, some dispersants, such as ammonium sulfate^[15], polyethylene glycol^[16], *etc.*, are usually added to inhibit or minimize the interaction between the particles of precipitates. Moreover, the freeze-drying method is applied in drying process, preserving the structure and particle size of the precipitates during drying^[17].

To fabricate a highly transparent yttria ceramic, it is essential to completely eliminate residual pores, which is a challenge, because yttria has a high melting point (*i.e.*, 2 430 °C)^[18]. Researchers employed different sintering methods and additives to accelerate the densification of yttria. Pressureless sintering methods, such as hydrogen atmosphere sintering and vacuum sintering, can speed up the ceramic densification and prevent contamination from heating or insulating elements on the samples^[19–20]. However, these methods require high sintering temperatures (*i.e.*, 1 750–1 940 °C) and long holding durations (*i.e.*, 12–20 h), which significantly increase the cost. On the other hand, pressure sintering techniques, such as hot

收稿日期: 2023-08-25。 修订日期: 2023-10-16。

基金项目: 国家自然科学基金(51972245)。

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Received date: 2023-08-25. Revised date: 2023-10-16.

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pressing^[21–22], spark plasma sintering^[23–24], and hot isostatic pressing (HIPing)^[25], are known to provide more driving force to eliminate pores, and thus may improve the transparency, compared with the pressureless methods. Moreover, applying mechanical pressure can reduce the sintering temperature and shorten the holding time, resulting in transparent ceramics with suppressed grain growth and enhanced mechanical properties^[26]. Among these techniques, the hot pressing method is widely applied in the sintering process of ceramics due to its lower sintering temperature and shorter hot pressing holding time.

Dutta and Gazza prepared transparent Y_2O_3 specimens by vacuum hot pressing for 1–2 h in graphite molds at 1 300–1 500 °C. The prepared samples had a grain size of less than 1 μm , and an optical transmittance of more than 80% in the infrared range, although the transparency in the visible range was quite limited^[27]. Majima et al. used the vacuum hot pressing method to prepare transparent Y_2O_3 in graphite molds with stepwise loading at 1 300 °C, 44 MPa, and 1.0% (mole fraction) LiF content^[28]. The transmittance at 644 nm was 78%. Liu et al. used commercial powders and ZrO_2 sintering additives as raw materials, and prepared highly transparent, submicron-grained $\text{Yb}:\text{Y}_2\text{O}_3$ ceramics by the hot pressing method at 1 600 °C for 3 h. The average grain size was less than 1 μm , and the transmittance at 600 nm ranged from 72.7% to 77.7%^[29].

This work attempted to fabricate transparent yttria ceramics by a conventional hot-pressing method at 1 500 °C. It is noteworthy that the reaction between yttria and graphite at a high temperature, which causes the opacity of yttria, must be prevented^[30]. Therefore, this work employed a simple hot-pressing method with tantalum foil shielding to prepare highly transparent yttria ceramics, which effectively avoided carbon contamination from graphite mold^[31]. Furthermore, this work also doped sintering additives such as ZrO_2 to suppress the grain growth and facilitate the pore elimination of yttria ceramics, thereby enhancing their optical transmittance. This work prepared a low-agglomerated, small-sized, and high-active yttria nanopowder by a precipitation method using ammonia as a precipitant, anhydrous ethanol as a solvent, and PEG as a dispersant. This work also fabricated highly transparent yttria ceramics by a vacuum hot-pressing method under the protection of tantalum foil, and investigated the effects of PEG amount and sintering temperature on the transmittance of ceramics.

2 Experimental section

2.1 Synthesis of yttrium oxide powder

Zirconium oxynitrate ($\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ 99.5%) and yttrium nitrate hexahydrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 99.99%) were dissolved in anhydrous ethanol (AR) to prepare dilute solutions as reaction materials. Two salt

solutions were mixed according to a stoichiometric ratio of $(\text{Y}_{0.97}\text{Zr}_{0.03})_2\text{O}_3$. Ammonium hydroxide (NH_4OH AR 25% (mass fraction)) was dissolved in 100 mL of anhydrous ethanol as a precipitant, and to investigate the effect of the addition amount of polyethylene glycol 4000 (PEG4000) as a dispersant on the dispersion of samples, and PEG4000 with different molar amounts of 0, 0.1% (mole fraction), 0.3%, 0.6%, 0.9% of Y^{3+} content was added to the precipitant, respectively, which were abbreviated as P0, P1, P3, P6, P9. Note that 0.9% PEG4000 reached a solubility limit in 100 mL of ethanol.

The precipitant solution was gradually added to the reactants at 4 mL/min under vigorous stirring until the pH reached 9. The resulting precipitates were aged at room temperature for 4 h, then washed for 4 times with deionized water to remove impurity ions, and collected by centrifugation. The washed precipitates were freeze-dried for 10 h to obtain well-dispersed precursor powders. An appropriate calcination temperature was explored to completely eliminate organic components, impurity ions and obtain high-purity yttria powders. The precursor powders were calcined in a muffle furnace at 400, 600 °C and 850 °C for 4 h, respectively.

2.2 Preparation of ceramic

The calcined yttria powders were wrapped with tantalum foil and then loaded into a customized graphite mold ($\phi 16$ mm). The graphite mold was then placed in a vacuum hot-pressing furnace and the temperature was gradually increased at a heating rate of 15 °C/min. A stepwise pressure application was adopted during the pressurization, and a uniaxial pressure of 20 MPa was applied when the temperature reached 950 °C, and the pressure was increased to 30 MPa when the temperature reached 1 100 °C. Afterwards, the temperature increased to different sintering temperatures (*i.e.*, 1 450–1 600 °C) under a pressure of 30 MPa, and held for 2 h, with a vacuum degree of 9.0×10^{-3} Pa.

After the holding period, the sintered samples were cooled to 1 200 °C at 5 °C/min, and the pressure was gradually released during this process to prevent the sample cracking due to thermal stress. The samples were allowed to cool naturally to room temperature. Another ceramic sample without tantalum foil shielding was also sintered using the same process for comparison. After the hot-pressing step, the Ta foil was removed, and the samples were annealed at 900 °C in air for 2 h and then ground and polished for the coming characterizations.

2.3 Characterizations

The thermal decomposition behavior of the precipitated precursors in air at a heating rate of 10 °C/min was analyzed by a model multi-sample X3 DSC thermogravimetric-differential scanning calorimeter (TG–DSC, TA Instruments, USA). The group of

absorption peaks in the infrared bands of the precipitated precursors and the yttria powders calcined at 400, 600 °C and 850 °C were tested by a model Nexus Fourier transform infrared spectroscope (FT-IR, Thermo Nicolet, USA) in the range of 400–4 000 cm^{-1} . The phase composition of the synthesized precursors and the Y_2O_3 powders calcined at 400, 600 °C and 850 °C was characterized by a model D/Max-RB X-ray diffractometer (XRD, Rigaku, Japan) using nickel-filtered $\text{Cu K}\alpha$ radiation in the range of 10° – 80° . The microstructure of the yttria powders prepared with different PEG additions and the fractured/cross-sectional microstructure of the yttria ceramics were analyzed by a model SU8010 field emission scanning electron microscope (FE-SEM, Hitachi, Japan). The optical transmittance of the yttria transparent ceramics in the wavelength range of 200–2 500 nm was measured by a model UH4150 ultraviolet-visible-infrared spectrophotometer (UV-VIS-IR, Hitachi, Japan).

3 Results and discussion

3.1 Thermal analysis and XRD of the powder

The precursor prepared by the precipitation method was analyzed by simultaneous TG-DSC to investigate its thermal decomposition process. In Fig. 1, the sample loses 5.882% of its mass from room temperature to 145 °C mainly due to the evaporation of physically adsorbed water and a small amount of residual water on the surface, as manifested by an endothermic peak at 76.4 °C in the TG-DSC curves^[32]. Subsequently, the mass loss rate is 8.384% at 145–290 °C, corresponding to a broad endothermic peak at 259.8 °C, which is attributed to the elimination of molecular water in the precursor. The mass loss is 6.004% at 290–396 °C, showing an exothermic peak at 348.8 °C in the TG-DSC curve, resulted from the oxidation of residual organic matter in the powder^[33]. Also, a large mass loss of 10.517% occurs at 396–507 °C, showing an exothermic peak at 468.8 °C, which is caused by the decomposition of the precursor. The weight loss is rather small at 507–900 °C, with a small exothermic peak at 643.9 °C, which is due to the crystallization of yttria. Since there is no obvious weight loss at >800 °C, Y_2O_3 is completely crystallized at 800 °C. Therefore, the calcination temperature should be chosen at >800 °C to ensure the complete crystallization of Y_2O_3 .

Fig. 2 shows the FT-IR spectra of the precipitation precursor before and after calcination at different temperatures. In Fig. 2, the absorption peaks centered at 3 566 cm^{-1} and 1 641 cm^{-1} can be attributed to the symmetric stretching vibration of O—H group and the bending vibration of H—O—H, which are caused by a small amount of water in the powder. The absorption bands at 2 410, 1 384 cm^{-1} and 1 355 cm^{-1} correspond to the stretching and bending vibrations of C—H bond,

which originate from the CH_3 group in ethanol or PEG^[34]. Two peaks at 820 cm^{-1} and 631 cm^{-1} appear due to the stretching vibration of N—O in the residual NO_3^- ^[35].

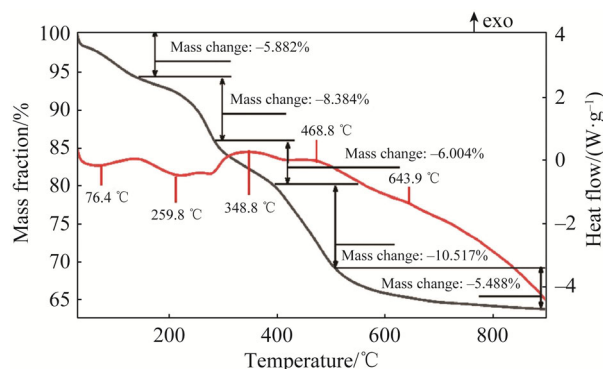


Fig. 1 TG-DSC analysis of Y_2O_3 precursor

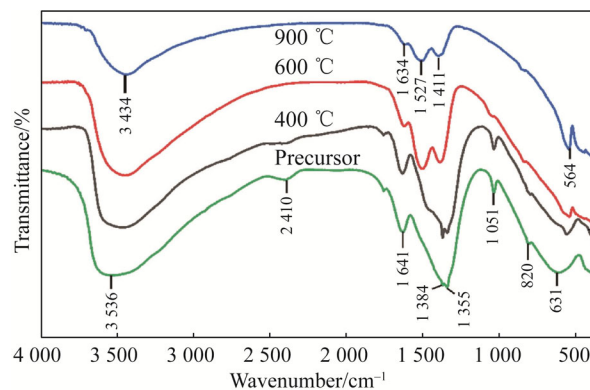


Fig. 2 FT-IR spectra of yttria precursor and the powders calcined at different temperatures

In Fig. 2, after calcination at a high temperature of >600 °C, the peaks of C—H bond from organic matter completely disappear due to the decomposition and oxidation, and the relative intensity of the absorption peaks of O—H and N—O groups also decrease significantly, indicating that the organic matter in the powder is completely eliminated after calcination. Meanwhile, a series of absorption bands appear in a low frequency region, among which the absorption band at 564 cm^{-1} is the most obvious, which is caused by the vibration of Y—O bond in yttrium oxide^[35]. In addition, two peaks appear at 1 527 cm^{-1} and 1 411 cm^{-1} due to the asymmetric stretching and bending vibrations of the C—O bond. The reason that there are still peaks in the region of 3 434–1 411 cm^{-1} after high-temperature calcination is that yttrium oxide powder and KBr substrate absorb CO_2 and H_2O in air. Yttrium oxide powder synthesized by a chemical method has such bands at a higher temperature^[32]. In summary, pure yttrium oxide can be obtained by calcining the precursor at a high temperature of >600 °C.

Fig. 3(a) shows the XRD pattern of the yttrium

precursor prepared at 0.9% PEG addition. The peaks of the precursor powder correspond to a basic yttrium nitrate- $\text{Y}_2(\text{OH})_{5.14}(\text{NO}_3)_{0.86} \cdot \text{H}_2\text{O}$ (PDF 32-1435), and no impurity peaks are detected^[36]. Fig. 3(b) shows the XRD patterns of the precursor calcined at 400, 600 °C and 850 °C for 3 h, respectively. Clearly, the precursor does not completely transform into cubic Y_2O_3 when the calcination temperature reaches 400 °C (see Fig. 1). The diffraction peaks of the Y_2O_3 samples obtained at ≥ 600 °C represent a standard cubic Y_2O_3 phase (PDF: 41-1105), and no impurity peaks appear in the diffraction patterns, indicating that there are no impurities in the final powder. Although the powder calcined at 600 °C exhibits a typical yttria phase, it is actually a partially decomposed product, as evidenced in the presence of O—H and N—O groups in Fig. 2(b). When the calcination temperature increases to 850 °C, the precursor almost completely decompose and well crystallize into yttria powder, which is in reasonable agreement with the results of TG-DSC (see Fig. 1) and FT-IR analysis (see Fig. 2).

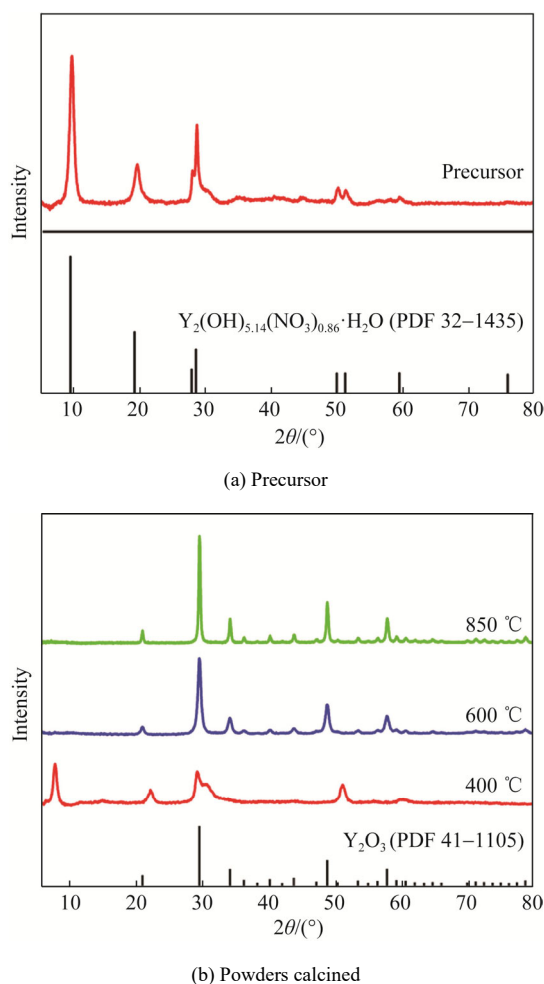


Fig. 3 XRD patterns of the precursor and powders calcined at different temperature for 3 h

3.2 Microstructural analysis of the powders

Fig. 4(a) shows the FESEM micrograph of the

yttrium precursor prepared with 0.9% PEG addition. The precursor is a yttrium hydroxynitrate flake, which is stacked together in a roof-tile-like manner^[37]. Figs. 4(b)–4(f) show the Y_2O_3 nanopowders obtained after calcined at 850 °C. The average particle sizes of all the powders are from 20 nm to 30 nm, indicating that the PEG addition has a slight effect on the grain growth. However, the PEG addition can affect the particles agglomeration in the powder. When the PEG addition is lower (see Figs. 4(c) and 4(d)), the powder surface charge imbalance is enhanced, resulting in the agglomeration of particles due to their van der Waals forces or electrostatic forces from the inability of PEG molecules to form a uniform and sufficiently thick adsorption layer on the particle surface. This agglomeration reduces the energy input required for sintering the nanopowder at high temperatures, and also causes the microstructural inhomogeneity in the green body^[38]. When the PEG addition is high (see Figs. 4(e) and 4(f)), due to the ability of PEG molecules to form a uniform and sufficiently thick adsorption layer on the particle surface, effectively isolating the particle surface charge from the agglomeration effect, while also providing the steric hindrance and solvation effects, preventing the particles in the powder from approaching and bonding. In Fig. 4(f), the large agglomerates disappear in the powder prepared at 0.9% PEG addition, and the shape and edge of the yttrium nanoparticles are clearer and rounder, which is beneficial to improving the sintering activity of the powder.

3.3 Sinterability of the powders

Fig. 5 shows the images of the hot-pressed samples with and without tantalum foil shielding. All the samples are polished in both sides. The samples have a diameter of 16 mm and a thickness of 2 mm. Clearly, the shielded sample exhibits a good transparency, and the text underneath can be clearly seen. In contrast, the unshielded sample is mainly black and opaque due to severe carbon contamination, so tantalum foil is an effective approach to shield the carbon contamination during the hot-pressing process^[39].

Fig. 6 shows the XRD patterns of the ceramic samples obtained after sintering at 1 500 °C for 2 h. Clearly, all the diffraction peaks of Y_2O_3 are consistent with the cubic phase Y_2O_3 in the standard card (PDF 41-1105), indicating that Y_2O_3 does not undergo a phase transition during the high-temperature sintering process. Moreover, no diffraction peaks of other elements or compounds appear in the patterns, indicating that no impurities or secondary phases occur in the samples. These results demonstrate that the synthesis method in this work can effectively prepare pure cubic phase Y_2O_3 ceramics.

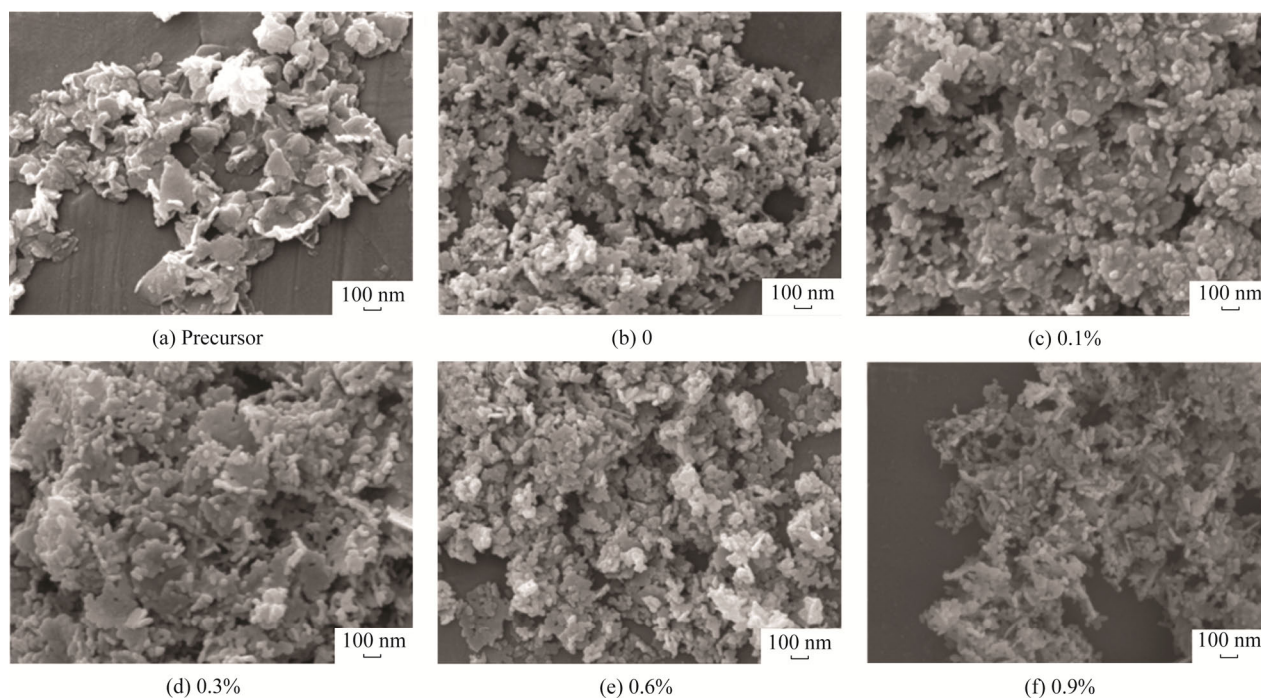


Fig. 4 FESEM micrographs of the precursor and Y_2O_3 powders prepared with different PEG additions after calcined at $850\text{ }^\circ\text{C}$

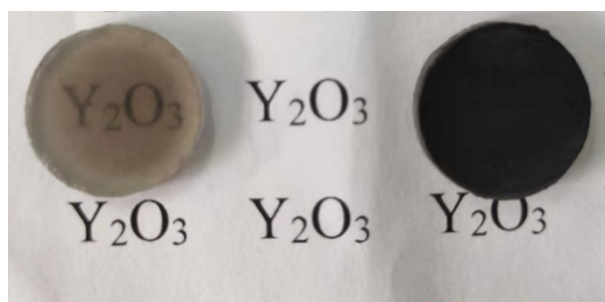


Fig. 5 Photograph of hot-pressed samples with (left) and without (right) tantalum foil shielding

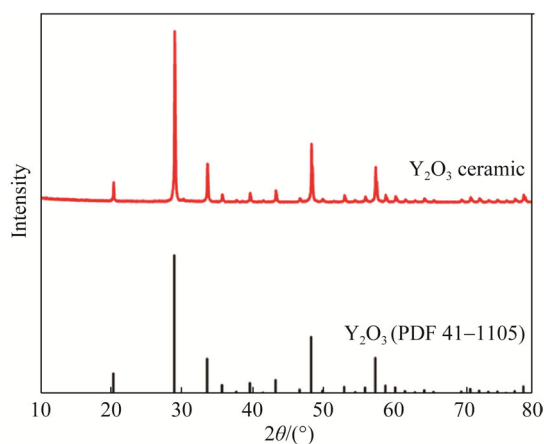


Fig. 6 The XRD pattern of the Y_2O_3 ceramic sample sintered at $1500\text{ }^\circ\text{C}$

1) Effect of hot-pressing temperature

Fig. 7 shows the appearance of the ceramic

samples obtained by sintering the powders prepared with 0.9% PEG addition at different hot-pressing temperatures. The samples have the same size of 16 mm in diameter and 2 mm in thickness. In Fig. 7, all the samples have a certain degree of transparency, but some cracks appear in the sample hot-pressed at $1600\text{ }^\circ\text{C}$, due to the excessive thermal expansion of the ceramic caused at a high temperature, resulting in uneven internal stress distribution and microcrack propagation in stress content regions.

Fig. 8 shows the transmittance of the powder prepared at 0.9% PEG addition, hot-pressed at 30 MPa for 2 h and different temperatures. Clearly, the transmittance of the samples firstly increases and then decreases with increasing hot-pressing temperature, and the sample hot-pressed at $1500\text{ }^\circ\text{C}$ has the maximum transmittance, reaching 48.4% at 1100 nm and 18.0% at 600 nm. This indicates that $1500\text{ }^\circ\text{C}$ is a relatively suitable hot-pressing temperature, which can achieve a sufficient densification of the sample and avoid cracks and defects caused by excessive sintering.

2) Effect of PEG addition

Fig. 9 shows the photographs of samples prepared with different PED additions, hot-pressed at $1500\text{ }^\circ\text{C}$ for 2 h and 30 MPa. Clearly, all the samples show a certain degree of transparency, but the color of the samples is somewhat darkened. This may be attributed to the formation of some oxygen vacancies in the yttria ceramic during the vacuum sintering process, resulting in the blackening of the samples. Although we anneal the samples to try to eliminate the oxygen vacancies, the effect is not satisfactory, and this phenomenon needs a further investigation.

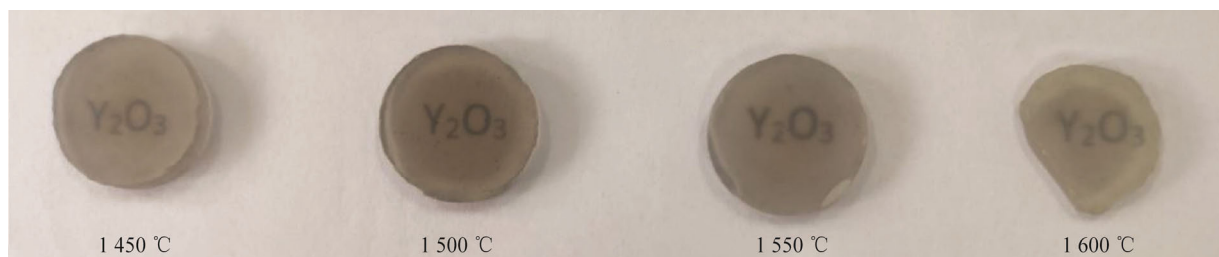


Fig. 7 Photograph of the ceramic samples hot-pressed at 30 MPa for 2 h from the powders prepared by adding 0.9% PEG at different sintering temperatures

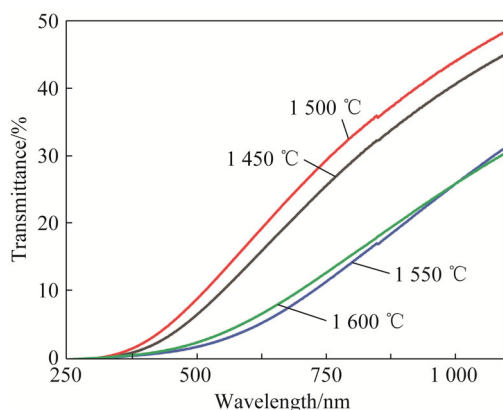


Fig. 8 Transmittance of the powder prepared with 0.9% PEG, hot-pressed at 30 MPa for 2 h at different sintering temperatures

Fig. 10 shows the in-line transmittance of samples prepared with different PEG additions, hot-pressed at 1 500 °C for 2 h and 30 MPa. Clearly, the ceramic sample without PEG addition has a transmittance of 40.0% at 1 100 nm and 12% at 600 nm. The transmittance of the samples slightly decreases at a lower PEG addition. When the PEG addition increases to 0.9%, which is the limit content of PEG in ethanol, the transmittance of the samples slightly increases, reaching 48.4% and 18.0% at the wavelengths of 1 100 nm and 600 nm, respectively. However, the transmittance of all the samples in the visible light range is still not high, which may be related to the oxygen vacancies and carbon impurities in the samples.

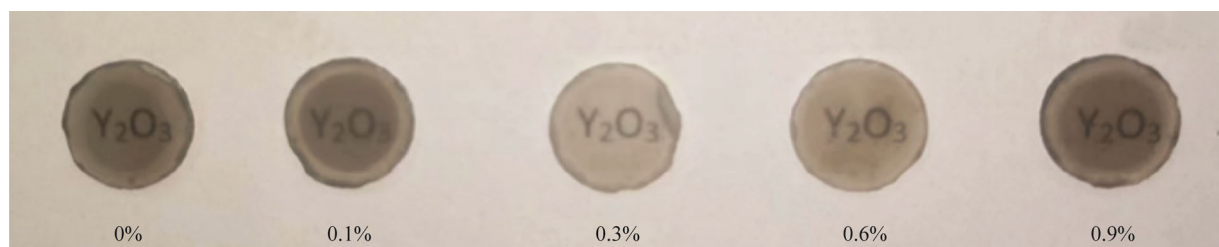


Fig. 9 Photographs of samples prepared with various PEG additions, hot-pressed at 1 500 °C for 2 h and 30 MPa

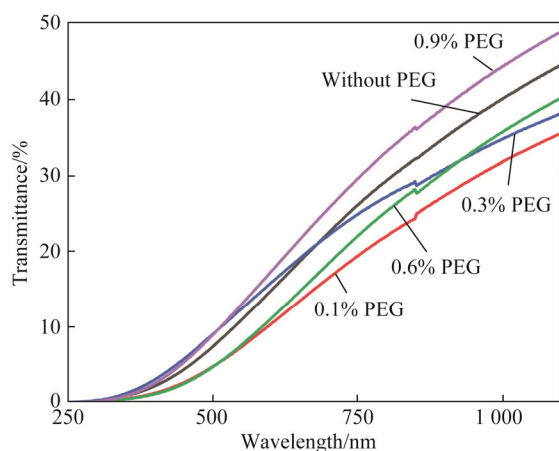


Fig. 10 In-line transmittance of samples prepared with various PEG additions, hot-pressed at 1 500 °C for 2 h and 30 MPa

Fig. 11 shows the SEM images of the fracture surfaces of the hot-pressed ceramic samples prepared with different PEG contents of at 1 500 °C. Clearly, the samples P0 and P9 (see Figs. 11 (a) and 11(e)) have a high density without obvious pores, so their transmittance is also high. The samples P1, P3 and P6 (see Figs. 11(b)–11(d)) have a few tiny pores (indicated by circles), which cause an intense light scattering and reduce the transmittance of the samples. In addition, PEG content also has a significant effect on the grain size of the ceramic samples. The average grains size of sample P0 is approximately 2 μm , while the average grains size of sample P1 increases to 3–4 μm . This is due to the agglomeration of yttria powder caused by a small amount of PEG addition, which affects the forming, sintering and densification of the ceramic^[40]. The agglomeration degree of yttria powder decreases, and the ceramic grain size also

gradually decreases with the increase of PEG content, reaching the minimum value of approximately 1–2 μm when the transmittance of the sample reaches the

maximum value. However, the grain size of all the samples is still large, which may be a main factor limiting the improvement of sample transmittance.

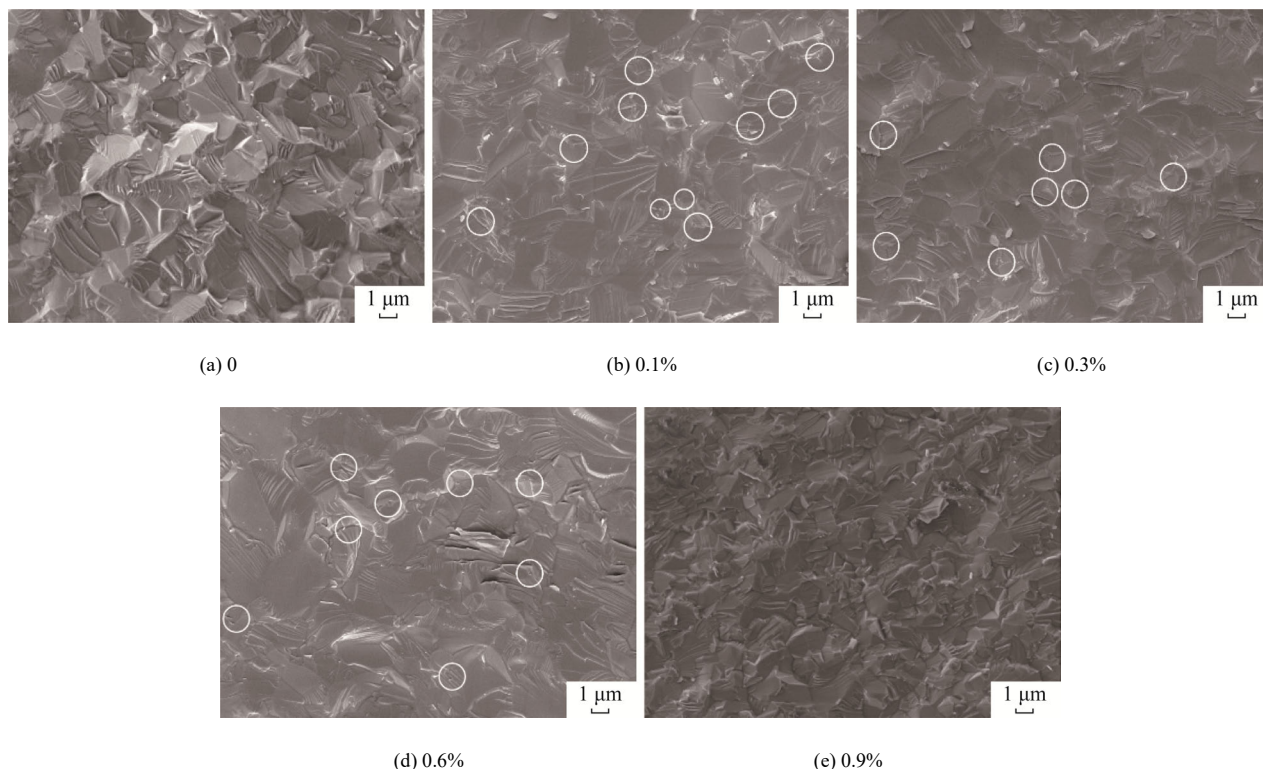


Fig. 11 SEM images of fracture surface of Y_2O_3 ceramics sintered for 2h at 1500 $^{\circ}\text{C}$ by nano-powders prepared with different PEG contents.

4 Conclusions

Yttria nanopowders were synthesized by a precipitation method in ethanol solvent with ammonia as a precipitant, PEG as a dispersant, and 3% ZrO_2 as a sintering aid. The optimal calcination temperature of the precursor was determined to be 850 $^{\circ}\text{C}$ by thermal analysis, at which a high purity cubic yttria phase could be obtained. Y_2O_3 ceramics were prepared by a vacuum hot-pressing sintering technique at 1450–1600 $^{\circ}\text{C}$ under 30 MPa, and the samples were wrapped with tantalum foil to prevent carbon contamination. The results showed that 1500 $^{\circ}\text{C}$ was the optimal sintering temperature, at which Y_2O_3 ceramic had the maximum optical transparency, with a linear transmittance of 48.4% at 1100 nm wavelength for samples with the thickness of 2 mm. In addition, the PEG addition also affected the microstructure and optical properties of Y_2O_3 ceramic, and when the PEG content was 0.9%, Y_2O_3 ceramic had uniform and fine grains, which was beneficial to improving the transparency. This work could provide a reference for the effective preparation of a high-performance Y_2O_3 ceramic.

参考文献:

- [1] HOU X R, ZHOU S M, LI Y K, et al. Effect of ZrO_2 on the sinterability and spectral properties of $(\text{Yb}_{0.05}\text{Y}_{0.95})_2\text{O}_3$ transparent ceramic[J]. *Opt Mater*, 2010, 32(9): 920–923.
- [2] PARKHOMENKO S, BALABANOV A, KRYZHANOVSKA O, et al. Effect of green body annealing on microstructure and optical properties of $\text{Y}_2\text{O}_3\text{:Yb}^{3+}$ ceramics[J]. *Ceram Int*, 2023, 49(17): 29048–29054.
- [3] CHERNOMORETS D G, PIANCASTELLI A, ESPOSITO L, et al. Effect of milling parameters on the morphology and sinterability of the yttrium oxide powders for transparent ceramics[J]. *Open Ceram*, 2023, 15: 100391.
- [4] KEAR B H, COLAIZZI J, MAYO W E, et al. On the processing of nanocrystalline and nanocomposite ceramics[J]. *Scr Mater*, 2001, 44(8/9): 2065–2068.
- [5] YIN D L, WANG J, WANG Y, et al. Fabrication of $\text{Er:Y}_2\text{O}_3$ transparent ceramics for 2.7 μm mid-infrared solid-state lasers[J]. *J Eur Ceram Soc*, 2020, 40(2): 444–448.
- [6] BALABANOV S, PERMIN D, EVSTROPOV T, et al. Hot pressing of $\text{Yb:Y}_2\text{O}_3$ laser ceramics with LiF sintering aid[J]. *Opt Mater*, 2021, 119: 111349.
- [7] ZHANG L, YANG J, YU H Y, et al. Highly efficient up-conversion in $\text{Nd:Y}_2\text{O}_3$ transparent ceramics[J]. *Scr Mater*, 2020, 178: 281–284.
- [8] ZHU L L, PARK Y J, GAN L, et al. Effects of the Zr content on transparent Y_2O_3 ceramics fabricated by vacuum pre-sintering and a subsequent HIP treatment[J]. *J Mater Sci Mater Electron*, 2017, 28(11): 7854–7861.

- [9] ZHANG J Y, ZHANG Z T, TANG Z L, et al. Luminescent properties of $\text{Y}_2\text{O}_3\text{:Eu}$ synthesized by sol-gel processing[J]. *J Mater Process Technol*, 2002, 121(2/3): 265–268.
- [10] RULISON A J, FLAGAN R C. Synthesis of yttria powders by electrospray pyrolysis[J]. *J Am Ceram Soc*, 1994, 77(12): 3244–3250.
- [11] DELL'AGLI G, MASCOLO G. Hydrothermal synthesis of $\text{ZrO}_2\text{-Y}_2\text{O}_3$ solid solutions at low temperature[J]. *J Eur Ceram Soc*, 2000, 20(2): 139–145.
- [12] WANG Y, WANG J, NI M, et al. Exploring the evolution of pores in HIPed Y_2O_3 transparent ceramics[J]. *Ceram Int*, 2021, 47(8): 11637–11643.
- [13] WANG H Z, GAO L, NIIHARA K. Synthesis of nanoscaled yttrium aluminum garnet powder by the co-precipitation method[J]. *Mater Sci Eng A*, 2000, 288(1): 1–4.
- [14] YANG Y, XU S M, XIE M, et al. Growth mechanisms for spherical mixed hydroxide agglomerates prepared by co-precipitation method: A case of $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}(\text{OH})_2$ [J]. *J Alloys Compd*, 2015, 619: 846–853.
- [15] SERIVALSATIT K, KOKUOZ B, YAZGAN-KOKUOZ B, et al. Synthesis, processing, and properties of submicrometer-grained highly transparent yttria ceramics[J]. *J Am Ceram Soc*, 2010, 93(5): 1320–1325.
- [16] CHEN P H, WANG Q, HU D J, et al. Fabrication and microstructure evolution of 8 mol% yttria-stabilized zirconia (8YSZ) transparent ceramics from co-precipitated nanopowders[J]. *Opt Mater*, 2023, 142: 113997.
- [17] NIKOLIC N. Preparation of fine oxide ceramic powders by freeze drying[J]. *Ann De Chim Sci Des Matériaux*, 2001, 26(5): 35–41.
- [18] NAJAFZADEHKHOEE A, TALIMIAN A, SEDLÁČEK J, et al. Translucent yttrium oxide ceramics from low-density green bodies shaped by uniaxial pressing[J]. *J Eur Ceram Soc*, 2022, 42(11): 4623–4630.
- [19] CAO Y F, LI H Y, ZHENG X Y, et al. Simultaneous precipitation of Zr^{4+} and Y^{3+} ions induced refinement of precursors and powders in fabrication of Zr^{4+} doped Y_2O_3 transparent ceramics[J]. *Opt Mater*, 2023, 139: 113802.
- [20] ZHANG J A, AN L Q, LIU M, et al. Sintering of $\text{Yb}^{3+}\text{:Y}_2\text{O}_3$ transparent ceramics in hydrogen atmosphere[J]. *J Eur Ceram Soc*, 2009, 29(2): 305–309.
- [21] HUANG Z G, SUN X D, XIU Z M, et al. Precipitation synthesis and sintering of yttria nanopowders[J]. *Mater Lett*, 2004, 58(15): 2137–2142.
- [22] OH H M, PARK Y J, KIM H N, et al. Effect of milling ball size on the densification and optical properties of transparent Y_2O_3 ceramics[J]. *Ceram Int*, 2021, 47(4): 4681–4687.
- [23] KIMURA H, KATO T, YAMAMOTO S I, et al. Influence of Yb doping on optical and upconversion photoluminescence properties of Yb-, Er-co-doped Y_2O_3 transparent ceramics prepared by SPS[J]. *J Mater Sci Mater Electron*, 2021, 32(5): 6304–6311.
- [24] HU Z W, LIU P, WANG X D, et al. Spectroscopic investigations and Judd-Ofelt analysis of Sm^{3+} doped Y_2O_3 transparent ceramics[J]. *Phys B Condens Matter*, 2023, 669: 415283.
- [25] YIN D L, WANG J, NI M, et al. Fabrication of highly transparent Y_2O_3 ceramics with CaO as sintering aid[J]. *Materials*, 2021, 14(2): 444.
- [26] OH H M, PARK Y J, KIM H N, et al. Remarkable plasma-resistance performance by nanocrystalline $\text{Y}_2\text{O}_3\text{:MgO}$ composite ceramics for semiconductor industry applications[J]. *Sci Rep*, 2021, 11(1): 10288.
- [27] DUTTA S K, GAZZAG E. Transparent Y_2O_3 by hot-pressing[J]. *Mater Res Bull*, 1969, 4(11): 791–796.
- [28] MAJIMA K, NIIMI N, WATANABE M, et al. Effect of LiF addition on the preparation of transparent Y_2O_3 by the vacuum hot pressing method[J]. *J Alloys Compd*, 1993, 193(1/2): 280–282.
- [29] LIU C R, ZHOU G H, JIANG J, et al. Fabrication and luminescence properties of highly transparent and submicrometer-grained $\text{Yb:Y}_2\text{O}_3$ ceramics by hot-pressing sintering[J]. *J Alloys Compd*, 2022, 898: 163002.
- [30] GAN L, PARK Y J, PARK M J, et al. Facile fabrication of highly transparent yttria ceramics with fine microstructures by a hot-pressing method[J]. *J Am Ceram Soc*, 2015, 98(7): 2002–2004.
- [31] SAKAJIO M, SHTER G E, MANN-LAHAV M, et al. Carbon contamination prevention during spark plasma sintering[J]. *ACS Appl Mater Interfaces*, 2023, 15(31): 38080–38089.
- [32] KHAJELAKZAY M, RAZAVI R S, BAREKAT M. Synthesis and characterization of yttria nanopowders by precipitation method[J]. *Trans Indian Ceram Soc*, 2015, 74(4): 208–212.
- [33] LIU Z F, JIN Z G, LI W, et al. Preparation of ZnO porous thin films by so-gel method using PEG template[J]. *Mater Lett*, 2005, 59(28): 3620–3625.
- [34] SREENIVASULU G, JAYARAJU N, SUNDARA RAJA REDDY B C, et al. Organic matter from benthic foraminifera (*Ammonia beccarii*) shells by FT-IR spectroscopy: A study on Tupilipalem, South east coast of India[J]. *MethodsX*, 2017, 4: 55–62.
- [35] GONG H, TANG D Y, HUANG H, et al. Effect of grain size on the sinterability of yttria nanopowders synthesized by carbonate-precipitation process[J]. *Mater Chem Phys*, 2008, 112(2): 423–426.
- [36] FROLOVA E A, KONDAKOV D F, YAPRYNTSEV A D, et al. Synthesis of basic yttrium nitrate[J]. *Russ J Inorg Chem*, 2015, 60(3): 259–264.
- [37] IKEGAMI T, LI J G, MORI T, et al. Fabrication of transparent yttria ceramics by the low-temperature synthesis of yttrium hydroxide[J]. *J Am Ceram Soc*, 2002, 85(7): 1725–1729.
- [38] DEARMITT C, ROTHON R. Dispersants and coupling agents[M]// *Applied Plastics Engineering Handbook*. Amsterdam: Elsevier, 2011: 441–454.
- [39] GAN L, PARK Y J, KIM H, et al. The effects of the temperature and pressure on ZrO_2 -doped transparent yttria ceramics fabricated by a hot-pressing method[J]. *Opt Mater*, 2017, 71: 109–116.
- [40] YALU M, YU Z, JUNPING Z. Agglomeration control of ultrafine $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $(\text{MgO}, \text{Y}_2\text{O}_3)\text{-ZrO}_2$ powders synthesized by coprecipitation process[J]. *Transact Tianjin Univ*, 2005, 11(1): 17–21.

Effect of Dispersant Content on Microstructure and Optical Properties of Yttrium Oxide Transparent Ceramics Prepared by Vacuum Hot-Pressing Sintering

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Extended Abstract

Introduction The quality of the powder is crucial for the performance of transparent yttria ceramics. The powder characteristics,

such as size, shape, distribution, and agglomeration, directly affect the densification and microstructure of the ceramics. Co-precipitation is a common method for preparing yttria powder, which has the advantages of simplicity, low cost, and scalability. However, it also has some drawbacks, such as uneven particle size distribution, severe agglomeration, and complicated post-treatment processes. The agglomeration of the powder not only reduces its activity, but also impairs its sinterability. Therefore, how to effectively disperse the powder is one of the key techniques for improving the quality of transparent yttria ceramics. Adding dispersant is a common method for dispersing the powder, among which PEG (polyethylene glycol) is a widely used dispersant, which can form strong hydrogen bonds with the surface of hydroxide colloids, and enhance the stability of the colloids by steric hindrance effect. Moreover, since PEG is an organic substance, it can be completely removed during the high-temperature calcination process, without causing any negative impact on the properties of the ceramics. In this study, we use PEG as the dispersant, and investigate its influence on the optical properties of yttria nanocrystalline powder and its sintered ceramics.

Methods Zirconium oxynitrate and yttrium nitrate hexahydrate were dissolved in anhydrous ethanol to prepare dilute solutions as reaction materials. Two salt solutions were mixed according to a stoichiometric ratio of $(Y_{0.97}Zr_{0.03})_2O_3$. Ammonium hydroxide was dissolved in 100 mL of anhydrous ethanol as a precipitant, and to investigate the effect of the addition amount of polyethylene glycol 4000 as a dispersant on the dispersion of samples, and PEG4000 with different molar amounts of 0, 0.1% (mole fraction), 0.3%, 0.6%, 0.9% of Y^{3+} content was added to the precipitant. The precipitant solution was gradually added to the reactants at 4 mL/min under vigorous stirring until the pH reached 9. The resulting precipitates were aged at room temperature for 4 h, then washed for 4 times with deionized water to remove impurity ions, and collected by centrifugation. The washed precipitates were freeze-dried for 10 h to obtain well-dispersed precursor powders. The precursor powders were calcined in a muffle furnace at 400, 600 °C and 850 °C for 4 h, respectively. The calcined yttria powders were wrapped with tantalum foil and then loaded into a customized graphite mold. The graphite mold was then placed in a vacuum hot-pressing furnace and sintered under vacuum. Another ceramic sample without tantalum foil shielding was also sintered using the same process for comparison. After the hot-pressing step, the Ta foil was removed, and the samples were annealed at 900 °C in air for 2 h and then ground and polished for the coming characterizations.

Results and discussion The precursor was completely decomposed and crystallized into well-crystallized yttria powder with little organic and impurity residues after calcination at 850 °C, as revealed by TG–DSC, FT-IR and XRD analyses. The average particle size of the yttria powder prepared with different dispersant concentrations was in the range of 20–30 nm, indicating that the addition of PEG had little effect on the grain growth. However, the addition of PEG changed the agglomeration state of the particles in the powder. At low PEG addition, the surface charge of the powder was unbalanced, and the particles tended to agglomerate due to van der Waals force or electrostatic force, because PEG could not form a uniform and thick adsorption layer on the particle surface. This agglomeration reduced the energy demand for high-temperature sintering of the nanopowder, but also resulted in the microstructural inhomogeneity of the green body. At high PEG addition, the particles were effectively isolated from the surface charge by the uniform and thick adsorption layer formed by PEG on the particle surface, which suppressed the agglomeration effect of the particles, and also provided steric hindrance and solvation effects, preventing the particles from contacting and bonding.

Yttria transparent ceramics were obtained after sintering the yttria powder. The use of tantalum foil effectively shielded the carbon contamination. The sintering temperature of 1 500 °C was the optimal condition for the sample performance. The density and transmittance of the samples decreased when the PEG addition was low. The transmittance of the samples increased slightly when the PEG addition increased to 0.9% (the content of PEG in ethanol). This was because the addition of a small amount of PEG caused the agglomeration of yttria powder, which affected the forming, sintering and densification processes of the ceramics. With the increase of PEG content, the agglomeration degree of yttria powder decreased, and the ceramic grain size also gradually decreased. When the transmittance of the samples reached the maximum value, the ceramic grain size was 1–2 μm. However, the transmittance of all samples in the visible light range was still not high, which might be related to the oxygen vacancies and carbon impurities in the samples.

Conclusions Yttria nanopowders were synthesized by a precipitation method in ethanol solvent with ammonia as a precipitant, PEG as a dispersant, and 3% ZrO_2 as a sintering aid. The optimal calcination temperature of the precursor was determined to be 850 °C by thermal analysis, at which a high purity cubic yttria phase could be obtained. Y_2O_3 ceramics were prepared by a vacuum hot-pressing sintering technique at 1 450–1 600 °C under 30 MPa, and the samples were wrapped with tantalum foil to prevent carbon contamination. The results showed that 1 500 °C was the optimal sintering temperature, at which Y_2O_3 ceramic had the maximum optical transparency, with a linear transmittance of 48.4% at 1 100 nm wavelength for samples with the thickness of 2 mm. In addition, the PEG addition also affected the microstructure and optical properties of Y_2O_3 ceramic, and when the PEG content was 0.9%, Y_2O_3 ceramic had uniform and fine grains, which was beneficial to improving the transparency. This work could provide a reference for the effective preparation of a high-performance Y_2O_3 ceramic.

Keywords yttrium oxide; transparent ceramics; precipitation method; transmittance; hot pressing sintering