Fabrication of transparent La-doped Y₂O₃ ceramics using different La₂O₃ precursors

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Despite being the most common sintering additive of transparent Y₂O₃ ceramics, La₂O₃ still suffers from weight changes when used in manufacturing processes due to its absorption of moisture and carbon dioxide. In the present work, two stable precursors, La(OH)₃ and La₂O₂CO₃, were proposed for use as sintering additives for transparent Y₂O₃ ceramics; La₂O₃ powder was used for comparison. A series of experiments were conducted to investigate the influences of La₂O₃, La(OH)₃ and La₂O₂CO₃ on the optical properties of Y₂O₃ ceramics by comparing the properties of mixed powders, green bodies and their sintering behaviors. Samples using La(OH)₃ or La₂O₂CO₃ as sintering additives exhibited more favorable optical properties at similar sintering temperatures compared to those using La₂O₃. Transmittances close to the theoretical value at 4 μm were achieved for samples doped with La(OH)₃ or La₂O₂CO₃ sintered at 1800 °C.

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1. Introduction

Yttria is one of the most promising materials for use in 3–5 μm infrared transmitting applications because of its long wavelength transmittance [1–3]. Owing to their low infrared emissivity at both ambient and elevated temperatures, Y₂O₃ ceramics are considered as a candidate material for use in hypersonic guided-missile windows and domes [4–7]. The use of La₂O₃ permits the attainment of ceramics with high optical quality and good mechanical properties by eliminating pores and inhibiting grain growth during the Y₂O₃ ceramic sintering process [8–10]. However, La₂O₃ rapidly absorbs moisture and carbon dioxide from air to form hydroxides and hydroxy carbonates [11,12], which makes it more difficult to maintain an exact weight during the weighing process. The absorption of H₂O and CO₂ leads to a weight increase and composition variation, resulting in the fluctuation of the sintering behavior and refractive index, among others [4]. In order to insulate against H₂O and CO₂ absorption, such procedures have to be carried out under N₂, which increases the production cost, especially in the case of industrial production [11].

When needing to work with an oxide material, using its precursors instead is a commonly used technique to obtain the same material with greater ease; for example, tetraethyl orthosilicate (TEOS) is often used instead of SiO₂ as the sintering additive in YAG ceramics [12–14]. In the present work, the stable La(OH)₃ and La₂O₂CO₃ compounds, which decompose to La₂O₃ at elevated temperatures [15,16], are introduced as La₂O₃ sources in the preparation of Y₂O₃ ceramics. The influence of La₂O₃, La(OH)₃ and La₂O₂CO₃ additives on the sintering behavior and optical property of transparent yttria ceramics is investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetry analyses (TG), shrinkage curves and transmittance spectra.

2. Experimental

High-purity commercial powders of Y₂O₃ (99.99%, Alfa Aesar), La₂O₃ (99.99%, Jiangyin Jiahua Advanced Material Resources Co. Ltd., China), La(OH)₃ (99.99%, Shanghai Diyang Chemical Co. Ltd., China) and La₂O₂CO₃ (99.99%, Huizhou Ruier Chemical Science and Technology Co. Ltd., China) were used as raw materials. The Y₂O₃ and La₂O₃ powders were calcined at 800 °C to remove possible absorption and kept in a desiccator before usage. Powders with the designed formula (Y₉₄La₅)₂O₃ were weighed immediately after their removal from the desiccators so as to maintain constant weight over a short time [11]. The weighted powders were ball milled in zirconia jars using a planetary milling machine for 24 h at a rotation speed of 256 rpm (rotation per minute). Anhydrous ethanol and zirconia balls with the diameter of 5 mm were added as the milling media, with the weight ratio of powders: ethanol: balls = 1: 1: 5. After drying and sieving, the mixtures were further calcined at 1200 °C for 5 h in order to dissolve La³⁺ into the Y₂O₃ lattice. The calcined powders were pressed into discs of ø20 mm in...
diameter and subsequently cold isostatic pressed under 210 MPa pressure. The green bodies were sintered at different temperatures (1000–1880 °C) for 5 h under high vacuum (≤ 10⁻³ Pa).

Air exposure experiments were carried out to measure the weight changes of the powders before and after exposure to air for fixed amounts of time. Phase identification was performed using XRD with an Empyrean powder diffractometer (PANalytical X’Pert Pro, Netherlands). The morphologies of the powders were viewed using field emission scanning electron microscopy (ZEISS, Germany). Thermal decomposition behavior of the powders was tested using a SII TG/DTA7300 thermogravimetric apparatus (EXSTAR, Japan) at a heating rate of 10 °C/min. Shrinkage curves were determined by measuring the diameter changes of the green bodies before and after sintering at different temperatures (1000–1800 °C). The transmittance spectra of the polished ceramics were measured using a Lambda 750 UV/VIS/NIR spectrophotometer (Perkin Elmer, America) over a range of 0.2–2.5 μm and a Nicolet 6700 Fourier-transform infrared (FT-IR) spectrometer (Thermo Nicolet, America) over a wavelength range of 2.5–10 μm. The microstructures of the thermally etched ceramics were characterized using a BX-RLA2 optical microscope (OLYPMUS, Japan).

3. Results and discussion

Fig. 1 shows the weight changes of the La₂O₃, La(OH)₃ and La₂O₂CO₃ powders exposed to air. The weight of La₂O₃ increases continuously up to about 12 wt% after 24 h, and becomes stable after this time. This weight increase comes from the absorption of moisture and carbon dioxide, as reported by Neumann and Bernal [15,16]. On the contrary, the weight variations of La(OH)₃ and La₂O₂CO₃ powders are only 0.1 wt% and 0.4 wt% after 48 h, much smaller than that of La₂O₃ powder. Such weight stability in La(OH)₃ and La₂O₂CO₃ is beneficial for the preparation of V₂O₅ ceramics in ambient conditions [17].

Fig. 2 shows the XRD patterns of the La₂O₃, La(OH)₃ and La₂O₂CO₃ powders after exposure to air for about 24 h and the corresponding standard cards of No. 05–0602, No. 36–1481 and No. 48–1113 (JCPDS data base). The peaks at 27.35° and 27.95° in the pattern of the La₂O₃ powders, as shown in Fig. 2a, confirm the existence of La(OH)₃ impurity, while no impurity phase is found in that of calcined La₂O₃ powders as shown in Fig. 2d. Such impurity is attributable to the moisture absorption during the exposure period [15]. The diffraction peaks in Fig. 2b are consistent with the standard peak positions of hexagonal La(OH)₃. The XRD pattern shown in Fig. 2c is indexed to a pure monoclinic phase of La₂O₂CO₃. The pure crystalline phases of La(OH)₃ and La₂O₂CO₃ correspond to the results of Fig. 1, in which the weights are almost unchanged after prolonged exposure to air.

The morphologies of the La₂O₃, La(OH)₃ and La₂O₂CO₃ powders at different magnifications are presented in Fig. 3. The polycrystalline La₂O₃ powder shown in Fig. 3a contains aggregated particles with an average diameter of approximately 20 microns, and the block-like particles are composed of closely packed micron-sized grains. Fig. 3b shows the presence of smaller particles, only a few microns in size, in La(OH)₃ powder. The particle size of the
La$_2$O$_2$CO$_3$ powder in Fig. 3c is similar to that of La$_2$O$_3$, and features particles with porous nanostructures. Compared with the micron-sized La$_2$O$_3$ grains, the submicron-sized and nano-sized La(OH)$_3$ and La$_2$O$_2$CO$_3$ grains are loosely arranged, which are shown in the inset morphologies of Fig. 3b and c.

Fig. 4 shows the thermal behavior of the La$_2$O$_3$, La(OH)$_3$ and La$_2$O$_2$CO$_3$ powders. As seen in Fig. 4a and b, La$_2$O$_3$ and La(OH)$_3$ present similar TG curves with two weight loss regions at around 370 °C and 530 °C, indicating the dehydration of La(OH)$_3$ to La$_2$O$_3$ through the LaO(OH) intermediate phase; these results are in good agreement with previously published data [15,17,18]. The smaller weight loss values in Fig. 4a result from the presence of La(OH)$_3$ impurity, since pure La$_2$O$_3$ has no weight loss, theoretically. The total weight loss of the oxycarbonate sample is 11.61 wt%, which is consistent with the theoretical result of La$_2$O$_2$CO$_3$ decomposition (11.90 wt%) [17].

Fig. 5 shows the SEM micrographs of the mixed yttria powders with different dopants before and after heat treatment. Fig. 5a–c depict the morphologies of the powders prepared by ball milling with La$_2$O$_3$, La(OH)$_3$ and La$_2$O$_2$CO$_3$ powders; it is clear from these images that the particles are finely ground together by ball milling. Compared with the micron-sized raw materials, the ball-milled powders have a much smaller and more uniform size distribution, with the majority of the particles ranging from 100 to 400 nm. After calcination at 1200 °C, the smaller particles diminish in size or adhere to the large particles as shown in Fig. 5d–f. Heat treatment leads to the growth of particles with well-crystallized polyhedron morphology.

The XRD patterns of all three calcined powders shown in Fig. 6 reveal sharp well-defined peaks of pure Y$_2$O$_3$ structures without any detectable secondary phases. There is a clear shift in 2θ values to smaller angles because of the expansion of the host lattice. The lattice parameters are calculated using the following formula [11]:

\[
\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}
\]

where \(d_{hkl}\) is the distance between adjacent planes, and \(h, k, \) & \(l\) are the Miller indices. The value of \(d_{hkl}\) is calculated using the Bragg equation: \(2d_{hkl} \sin \theta = \lambda\), in which \(\theta\) and \(\lambda\) are the Bragg angle and wavelength of an X-ray (1.540598 Å), respectively. The corresponding calculated results are 10.62532 Å, 10.62739 Å and 10.62891 Å, which are larger than that of pure Y$_2$O$_3$ (10.604 Å), demonstrating the substitution of larger La$^{3+}$ ions (\(R = 1.06\) Å) to Y$^{3+}$ ions (\(R = 0.89\) Å) [19] and the formation of a La$_2$O$_3$-Y$_2$O$_3$ solid solution. As Mao et al. [11] noted, La$_2$O$_3$ diffusion decreases the humidity absorption capability of the Y$_2$O$_3$ lattice, which is favorable for the sintering of large-sized transparent ceramics as it avoids the formation of cracks.

The sintering behavior of the samples doped with La$_2$O$_3$, La(OH)$_3$ and La$_2$O$_2$CO$_3$ is presented in the sintering shrinkage curves shown in Fig. 7. All of the green bodies begin to shrink at around 1200 °C. The shrinkage of the sample doped with La$_2$O$_3$
changes rapidly from 1400 °C to 1700 °C, then slows down naturally with increasing temperature and becomes stable with a final shrinkage of about 23%. The shrinkage curves of samples doped with La(OH)$_3$ and La$_2$O$_2$CO$_3$ are similar to that of the La$_2$O$_3$-doped sample, except for a much narrower shrinkage temperature range of 1200–1600 °C, possibly due to the small particles derived from the decomposition of La(OH)$_3$ and La$_2$O$_2$CO$_3$ speeding up material transport, leading to rapid densification [20,21]. In other words, the latter two samples have densification temperatures around 100 °C lower than that of the La$_2$O$_3$-doped material. This low densification temperature is beneficial for the sintering of transparent ceramics, especially for high melting point ceramics such as Y$_2$O$_3$ [22].

The dependence of optical transmittance on the sintering temperature for the ceramics doped with La$_2$O$_3$, La(OH)$_3$ and La$_2$O$_2$CO$_3$ is shown in Fig. 8. The transmittance of the Y$_2$O$_3$ ceramic doped with La(OH)$_3$ or La$_2$O$_2$CO$_3$ increases from 0% at 1700 °C to around 83% at 1800 °C, and then decreases slightly afterwards. For the La$_2$O$_3$-doped Y$_2$O$_3$ ceramic, the transmittance increases as the sintering temperature increases from 1750 °C to 1880 °C, while the corresponding values are much lower than that of the former two ceramics, due to the higher densification temperature. Even though the transmittance reaches 77.53% at 1880 °C, attempts to use a higher temperature to improve the optical quality of La$_2$O$_3$-doped Y$_2$O$_3$ ceramics may not be advisable due to the high costs of producing ceramics characterized by grain coarsening [23]. This information also helps to explain the experimentally observed detrimental effects that higher temperatures have on the transmittance of Y$_2$O$_3$ ceramics doped with La(OH)$_3$ or La$_2$O$_2$CO$_3$, as shown in Fig. 8a and b.

Fig. 9 shows transmittance curves of ceramics sintered at 1800 °C over a wide transmittance range of 0.2–9.0 μm. Samples doped with La(OH)$_3$ or La$_2$O$_2$CO$_3$ exhibit excellent transmittance values of 82.72% and 83.34% at 4 μm, which approach the theoretical value of the Y$_2$O$_3$ ceramic. The transmittance of the La$_2$O$_3$-doped Y$_2$O$_3$ ceramic is relatively low when compared with those of the other two ceramics. Fig. 10 shows optical microscopy images of the thermal etched ceramics. It is clear that there are more pores in the samples doped with La$_2$O$_3$; these pores within the grains and grain boundaries act as light scattering centers in transparent ceramics, resulting in a decrease of transmittance [24]. On the contrary, fewer pores were observed on the etched surfaces of the samples doped with La(OH)$_3$ and La$_2$O$_2$CO$_3$, which helps to explain their higher optical quality.

4. Conclusion

Two stable La$_2$O$_3$ precursors, La(OH)$_3$ and La$_2$O$_2$CO$_3$, were used as sintering additives for transparent yttria ceramics with La$_2$O$_3$ powder used for a comparison. The results showed that, compared with the negligible weight variations of 0.1 wt% and 0.4 wt% for La(OH)$_3$ and La$_2$O$_2$CO$_3$ respectively, the weight of La$_2$O$_3$ increased up to about 12 wt% after 24 h by the formation of La(OH)$_3$ impurities. TG analysis demonstrated the formation of La$_2$O$_3$ from La(OH)$_3$ and La$_2$O$_2$CO$_3$ after heat treatment. The samples doped with La(OH)$_3$ or La$_2$O$_2$CO$_3$ could be sintered to higher transmittances at lower temperatures than those samples doped with La$_2$O$_3$, which is likely associated with the smaller particles from the thermal decomposition of La(OH)$_3$ or La$_2$O$_2$CO$_3$. Transmittances of 82.72% and 83.34% were achieved for samples doped with La(OH)$_3$ or La$_2$O$_2$CO$_3$ sintered at 1800 °C. The use of stable La(OH)$_3$ and La$_2$O$_2$CO$_3$ precursors permits the accurate control of lanthanum doping concentrations, and offers the ability to deal with unstable oxide powders in the preparation of transparent oxides ceramics.

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References


