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Effect of calcination temperature on the fabrication of transparent lutetium titanate by spark plasma sintering

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Abstract

Transparent lutetium titanate ($Lu_2Ti_2O_7$) bodies were fabricated by spark plasma sintering using Lu_2O_3 and TiO_2 powders calcined from 700 °C to 1200 °C. No solid-state reaction was identified after calcination at 700 °C, whereas single-phase $Lu_2Ti_2O_7$ powder was prepared at 1100 and 1200 °C. The calcination at 700 °C promoted densification at the early stages of sintering, whereas residual pores at grain boundaries resulted in $Lu_2Ti_2O_7$ bodies with low transparency. Low-density and opaque $Lu_2Ti_2O_7$ bodies formed owing to the coarsening of the powder calcined at 1200 °C. The $Lu_2Ti_2O_7$ body sintered using the powder calcined at the moderate temperature of 1100 °C had a density of 99.5% with the highest transmittances of 41% and 74% at wavelengths of 550 nm and 2000 nm, respectively.

Keywords: A. Sintering; B. Microstructure-final; Transparent ceramics

1. Introduction

Polycrystalline transparent ceramics are of great interest for their optoelectronic properties and wide applications [1,2]. They are fabricated by powder densification processes including powder preparation, cold forming and sintering. High transparency requires a fully dense body having clean grains and grain boundaries, free from pores and secondary phases. Because the morphology, particle size and size distribution of the starting powder influence the microstructure of the sintered body [3], its preparation and calcination would significantly affect the transparency of sintered body.

Lutetium titanate ($Lu_2Ti_2O_7$) has the cubic pyrochlore structure (space group: $Fd\bar{3}m$; $a = 1.0019$ nm) and is a promising transparent ceramic. Because $Lu_2Ti_2O_7$ powder is not commercially available, it is synthesized by solid-state reaction [4], coprecipitation [5], sol-gel technique [6], the Pechini process [7] and the molten salt method [8]. Among the powder preparation techniques, the solid-state reaction method is the simplest and most convenient. However, insufficient reaction at low calcination temperatures causes compositional and microstructural inhomogeneity in the sintered bodies, whereas high calcination temperatures often result in the formation of coarse aggregates with pores at the triple junctions of grain boundaries [9,10]. Therefore, the calcination temperature should be optimized to successfully prepare fully dense transparent ceramics.

In the present study, Lu_2O_3 and TiO_2 powders were premixed by ball milling and calcined at temperatures from 700 °C to 1200 °C. The resultant powders were sintered by spark plasma sintering (SPS). In addition, the effect of the calcination temperature on the sintering behavior, microstructure and transparency of $Lu_2Ti_2O_7$ bodies was investigated.

2. Experimental procedure

Lu_2O_3 (99.99%; Shin-Etsu Rare Earth, Tokyo, Japan) and rutile TiO_2 (99.9%; Kanto Chemical, Tokyo, Japan) were used as starting materials. The Lu_2O_3 powder is spherical and slightly agglomerated with an average particle size of 30 nm, whereas the TiO_2 powder has a polyhedral shape approximately 500 nm in size [11]. These powders were stoichiometrically mixed (Lu:Ti = 1:1). The mixed powders were ball milled with zirconia balls in ethanol for 12 h. Then, they were dried at 60 °C

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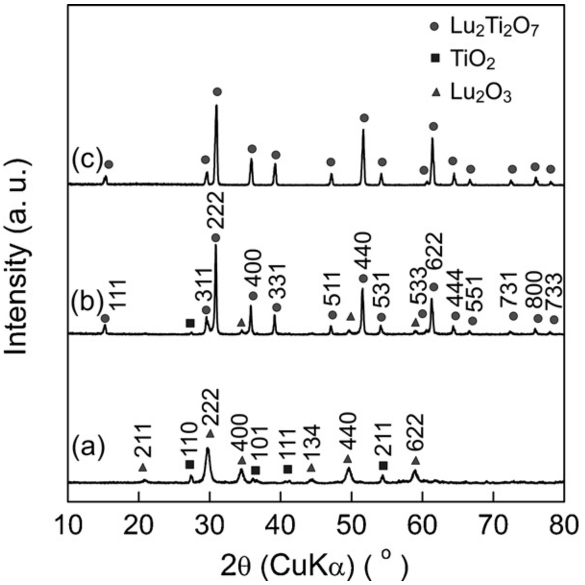

Fig. 1. XRD patterns of the powder mixture of Lu_2O_3 and TiO_2 calcined at (a) 700 °C, (b) 1000 °C and (c) 1100 °C for 7.2 ks.

for 86.4 ks and passed through a 200-mesh sieve. Finally, they were calcined in an electric furnace at 700–1200 °C for 7.2 ks in air before sintering.

The calcined powder was poured into a graphite die of 10 mm diameter and sintered using an SPS apparatus (SPS-210 LX, Fuji Electronic Industrial, Japan) in vacuum. The sintering temperature was increased to 600 °C in 180 s and 1000 °C in 300 s and then held there for 300 s. The sintering temperature was further increased to 1450 °C at 0.17 °C s^{-1} and maintained for 2.7 ks. The specimens were preloaded with a pressure of 10 MPa until the temperature reached 1000 °C. Then, the pressure increased to 100 MPa within 60 s when the sintering temperature was increased beyond 1000 °C. Specimen shrinkage during the SPS process was continuously monitored by the displacement of the punch rod. After sintering, these specimens were annealed at 750 °C in air for 21.6 ks and both sides were mirror-polished with diamond slurry. The final thickness of these specimens were approximately 1 mm.

The final density was measured in distilled water by the Archimedes method. The crystal phase was investigated with X-ray diffractometer (XRD; RAD-2C, Rigaku, Japan) at 30 kV and 15 mA using a graphite monochromator and Cu Kα radiation ($\lambda = 0.154$ nm). The mirror-polished surface was thermally etched at 1300 °C in air for 3.6 ks. The morphology of the calcined powders and the microstructure of the sintered bodies were observed with a field emission scanning electron microscope (FESEM, JSM-7500F, JEOL, Japan) and a scanning electron microscope (SEM, S-3100H, Hitachi, Japan). From the SEM micrographs, the average grain size was determined as the mean linear intercept length for at least 250 grains multiplied by 1.56 [12]. The inline transmittance in the visible and infrared regions was measured with a spectrophotometer (UV-3101PC, Shimadzu, Japan) at wavelengths of 190–2500 nm.

3. Results and discussion

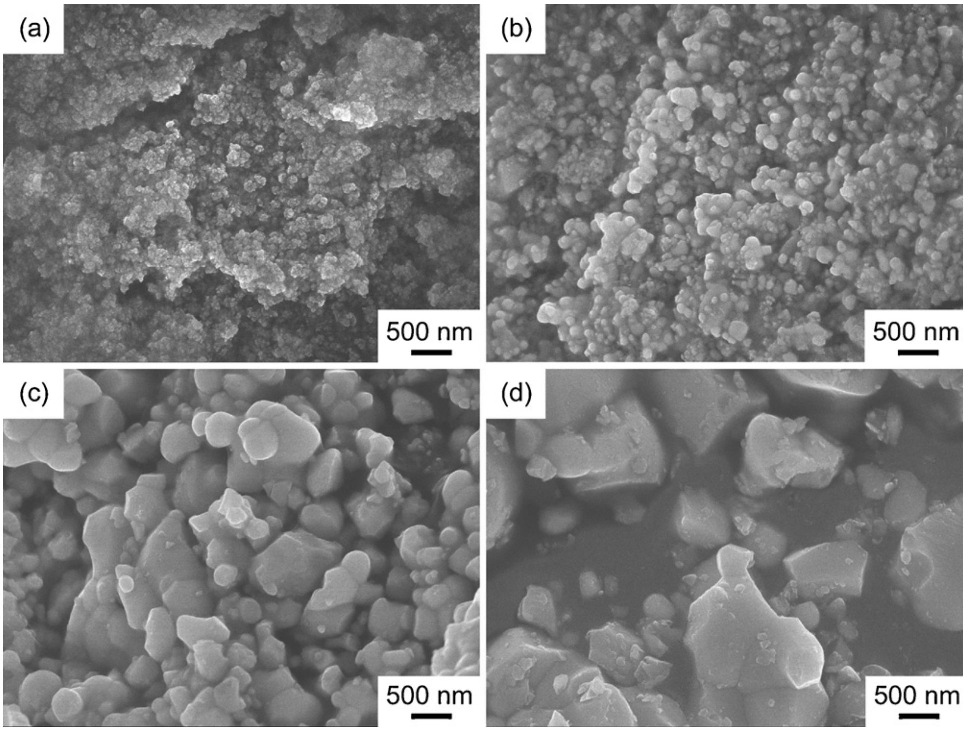

Fig. 2. Morphologies of the powder mixture of Lu_2O_3 and TiO_2 calcined at (a) 700 °C, (b) 1000 °C, (c) 1100 °C and (d) 1200 °C for 7.2 ks.

Fig. 1 shows the effect of the calcination temperature on the phase evolution of the powder mixture of Lu_2O_3 and TiO_2. No solid-state reaction was identified at the calcination temperature

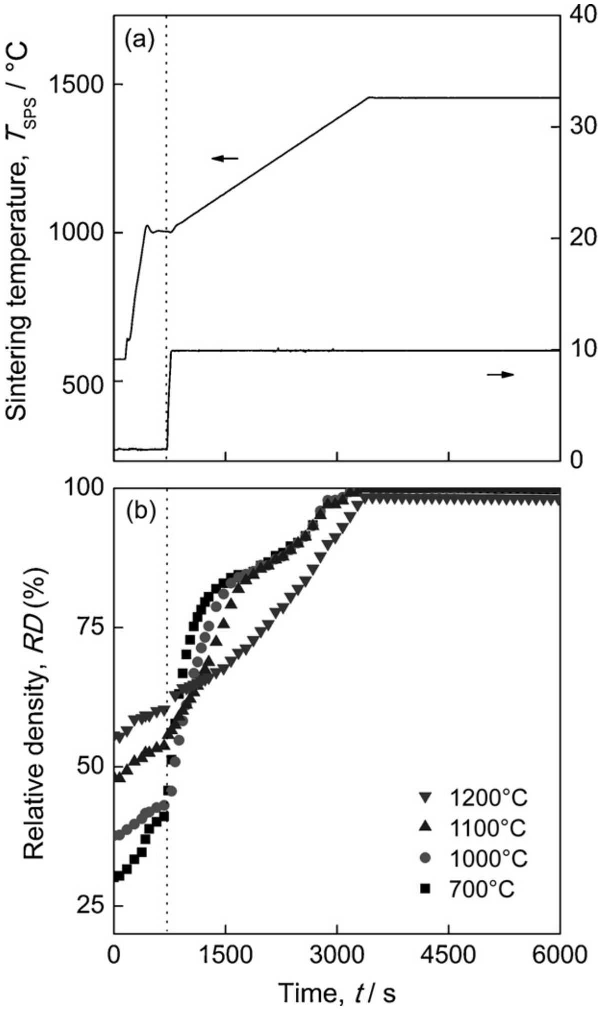

Fig. 3. (a) The sintering temperature and pressure profile as a function of time (t) and (b) sintering curves of $Lu_2Ti_2O_7$ bodies sintered using the powder mixture calcined at 700–1200 °C. Dotted line refers to the application of the final pressure.

of 700 °C (Fig. 1a). At 1000 °C, the $Lu_2Ti_2O_7$ pyrochlore phase (JCPDS #23-0375) formed with a small amount of Lu_2O_3 and TiO_2 phases (Fig. 1b). Single-phase $Lu_2Ti_2O_7$ was obtained at 1100 (Fig. 1c) and 1200 °C. The temperature for single-phase $Lu_2Ti_2O_7$ was comparable to that reported with the Pechini process [7] and coprecipitation method [13] and lower than that reported with the solid-state reaction (1400 °C for 14.4 ks) [14]. The high reactivity of the Lu_2O_3 and TiO_2 powders with nano and submicron particles may be attributed to the relatively low-temperature synthesis of $Lu_2Ti_2O_7$.

Fig. 2 shows the morphologies of the powder mixture calcined at 700–1200 °C for 7.2 ks. The particles were nearly spherical and steadily grew when the calcination temperature increased from 700 °C to 1100 °C (Fig. 2a–c). At 1200 °C, these particles became coarse and polygonal (Fig. 2d).

The calcined powders were sintered by SPS at 1450 °C for 2.7 ks, and all specimens exhibited the cubic pyrochlore $Lu_2Ti_2O_7$ structure after sintering. Fig. 3a shows the sintering temperature and pressure profile as a function of sintering time (t). The dotted line refers to the application of the final pressure in the two-step pressure profile. Fig. 3b shows the sintering curves of the $Lu_2Ti_2O_7$ bodies using the powder mixture of Lu_2O_3 and TiO_2 calcined at 700–1200 °C. It can be observed that lower the calcination temperature, lower the initial packing density ($t = 0$). When the final pressure of 100 MPa was applied ($t = 720$ s; dotted line in Fig. 3), the relative density significantly increased using the powders calcined at 700–1100 °C and this increase was more pronounced at the lower calcination temperature. Therefore, the solid-state reaction involving Lu_2O_3 and TiO_2 could have promoted densification. The sintering curves almost coincided after $t = 1830$ s regardless of the calcination temperature. Furthermore, the densification process was complete at $t = 3100$ s (approximately 1400 °C), resulting in nearly full densities before the dwelling time ($t > 3100$ s). The relative density of the $Lu_2Ti_2O_7$ body using the powder calcined at 1200 °C gradually changed and was slightly lower than that calcined from 700 °C to 1100 °C.

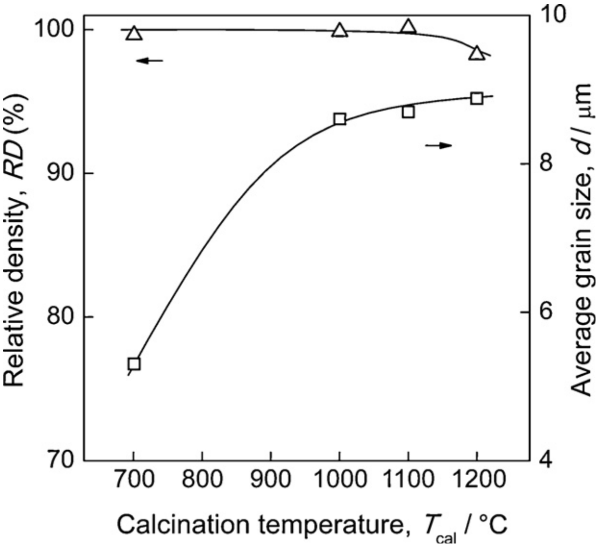

Fig. 4. Effect of calcination temperature on the relative density and average grain size of $Lu_2Ti_2O_7$ bodies sintered at 1450 °C for 2.7 ks.

Fig. 4 shows the effect of the calcination temperature on the relative density and the average grain size of the $Lu_2Ti_2O_7$ bodies. The relative density of the $Lu_2Ti_2O_7$ body sintered using the powder calcined at 700–1100 °C and 1200 °C was 99.5% and 98.3%, respectively. The average grain size significantly increased from 5.3 μm to 8.6 μm with increasing calcination temperature from 700 °C to 1000 °C and reached 8.9 μm at 1200 °C.

Fig. 5 shows the SEM images of the thermally etched surfaces of the $Lu_2Ti_2O_7$ bodies sintered using the powder mixture calcined at 700–1200 °C. Pores were observed at the triple junctions of the grain boundaries in all specimens (white circles in Fig. 5). Elongated pores were observed in the powder mixture calcined at 1200 °C (Fig. 5d). For a longer holding time, it would yield the elimination of porosity, resulting in high transparency. However, an increase in defects or contamination from the die would result from the prolonged holding time. These could be another source of scattering. Thus, a short

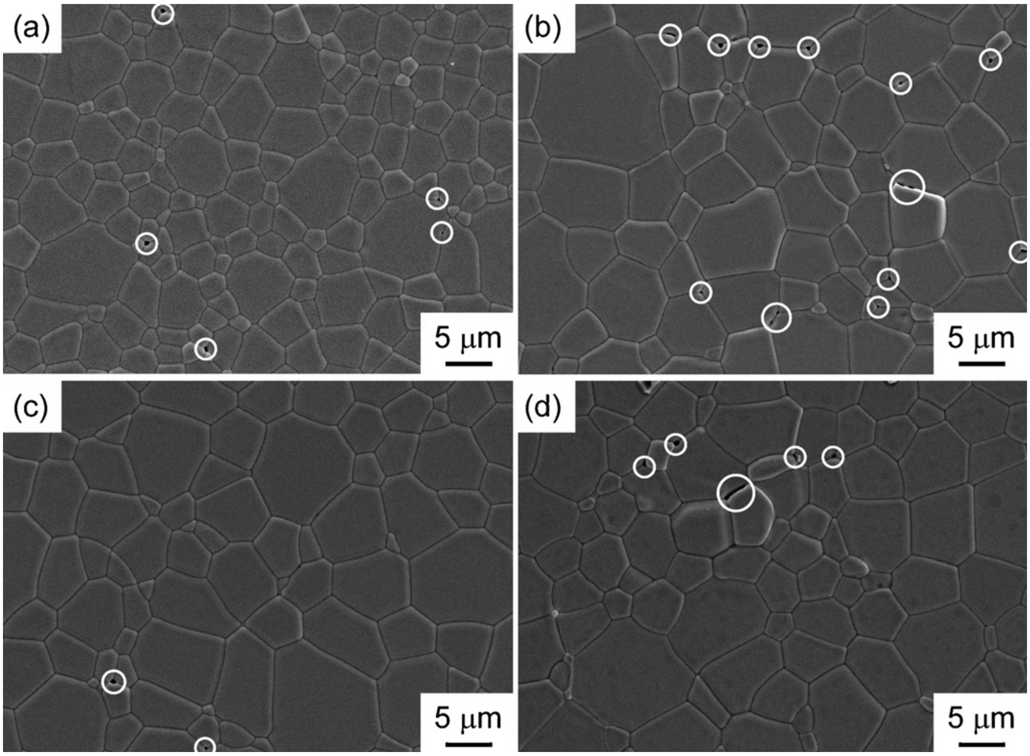

Fig. 5. SEM images of the thermally etched surfaces of $Lu_2Ti_2O_7$ bodies sintered using the powder mixture of Lu_2O_3 and TiO_2 calcined at (a) 700 °C, (b) 1000 °C, (c) 1100 °C and (d) 1200 °C. White circles indicate pores.

holding time is preferable for preparing transparent body by SPS [15]. Porosity was the lowest in the $Lu_2Ti_2O_7$ body sintered using the powder mixture calcined at 1100 °C (Fig. 5c).

The dark color of the $Lu_2Ti_2O_7$ bodies might have resulted from partial reduction during sintering in vacuum as the specimens were in direct contact with the graphite die and punch rods. After annealing at 750 °C in air for 21.6 ks, all specimens became colorless. The $Lu_2Ti_2O_7$ bodies sintered using the powder mixture calcined at 700–1100 °C were transparent and those sintered using the powder mixture calcined at 1200 °C were opaque as shown in Fig. 6. Fig. 7 shows the inline transmittance spectra of the $Lu_2Ti_2O_7$ bodies after annealing. For the $Lu_2Ti_2O_7$ bodies sintered using the powder calcined at 700, 1000 and 1100 °C, the transmittances at the wavelength of 550 nm were 34%, 30% and 41%, whereas those at the wavelength of 2000 nm were 71%, 70% and 74%, respectively. A slight increase in transmittance in the entire wavelength range was observed for the powder calcined at 1100 °C owing to low porosity, as shown in Fig. 5 [16]. For the

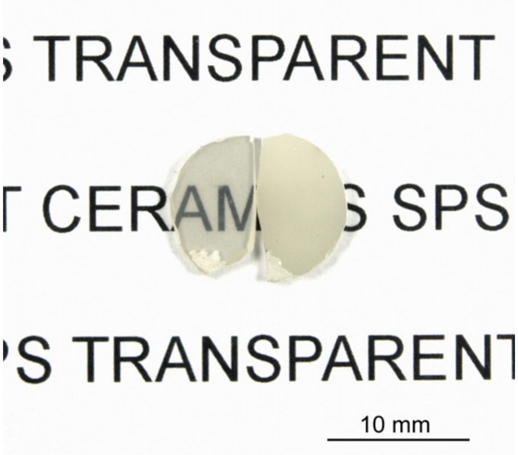

Fig. 6. Photographs of $Lu_2Ti_2O_7$ bodies sintered using the powder mixture of Lu_2O_3 and TiO_2 calcined at 1100 (left) and 1200 °C (right) after annealing at 750 °C in air for 21.6 ks.

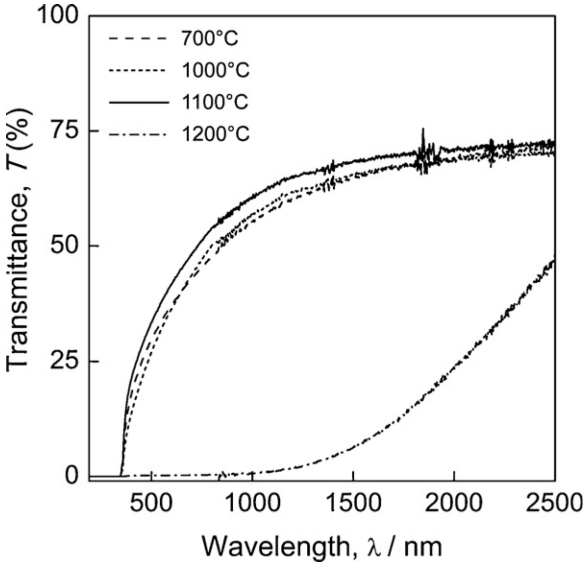

Fig. 7. Transmittance spectra of the $Lu_2Ti_2O_7$ bodies sintered using the powder mixture of Lu_2O_3 and TiO_2 calcined at 700–1200 °C. All specimens were annealed at 750 °C in air for 21.6 ks.

powder calcined at 1200 °C, the transmittances at 500 nm and 2000 nm were 0% and 24%, respectively. The low relative density with large pores (Figs. 4 and 5) due to particle coarsening (Fig. 2d) resulted in low transmittance. Therefore, the calcination temperature of 1100 °C is optimal for fabricating highly transparent $Lu_2Ti_2O_7$ bodies.

4. Conclusions

Transparent $Lu_2Ti_2O_7$ bodies were prepared by SPS using a powder mixture of Lu_2O_3 and TiO_2 calcined at 700–1200 °C. Single-phase pyrochlore $Lu_2Ti_2O_7$ powder was obtained at calcination temperatures as high as 1100–1200 °C. All sintered bodies contained the $Lu_2Ti_2O_7$ pyrochlore phase after sintering at 1450 °C. Solid-state reaction between the remaining Lu_2O_3 and TiO_2 during sintering enhanced densification, whereas the remaining pores at the grain boundaries decreased the transparency of the $Lu_2Ti_2O_7$ body sintered using the powder mixture calcined at 700 °C. Particle coarsening of the starting powder calcined at 1200 °C induced large pores in the sintered body, which resulted in low transmittance. The optimal calcination temperature was 1100 °C that resulted in a fully dense $Lu_2Ti_2O_7$ body with low porosity, which led to the highest transmittances of 41% and 74% at the wavelengths of 550 nm and 2000 nm, respectively.

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