This is the accepted version of the article submitted to Key Engineering Materials, which has been published in final form at 10.4028/www.scientific.net/KEM.484.135.

Fabrication of transparent $La_2Zr_2O_7$ by reactive spark plasma sintering

Liqiong An[a], Akihiko Ito[b] and Takashi Goto[c]

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

[a]anlq@imr.tohoku.ac.jp, [b]itonium@imr.tohoku.ac.jp, [c]goto@imr.tohoku.ac.jp

Keywords: Pyrochlore, $La_2Zr_2O_7$, Transparent ceramic, Spark plasma sintering

Abstract. Transparent $La_2Zr_2O_7$ with cubic pyrochlore structure was first fabricated by reactive spark plasma sintering using commercially available La_2O_3 and ZrO_2 powders. Single phase of pyrochlore $La_2Zr_2O_7$ was obtained at a sintering temperature of 1673 K and sintering pressure at 100 MPa for 2.7 ks. The $La_2Zr_2O_7$ sintered body had a uniform grain size of 1.5 μm and exhibited 68% transmittance in the wavelength range of 4–6 μm.

Introduction

Pyrochlore $La_2Zr_2O_7$ has received much attention on the synthesis and investigation of thermal barriers because of its excellent thermal stability, low thermal conductivity and high thermal expansion coefficient [1,2]. Moreover, studies on $La_2Zr_2O_7$ were carried out for ionic conductivity [3,4], catalytic properties [5] and possible application as a host of fluorescence centers [6,7]. $La_2Zr_2O_7$ powder has been prepared by many methods, such as solid-state reaction [8,9], sol-gel [10], nitric dissolution [6,11], coprecipitation-calcination [2] and hydrazine monohydration [3,4]. Among of them, the solid-state reaction is simple and convenient to prepare compound powders. However, the reheating temperature should be above 1723 K to obtain single phase $La_2Zr_2O_7$ powder and much higher temperature (above 1873 K) could be required for sintering to obtain high density $La_2Zr_2O_7$ body because of poor sinterability.

Spark plasma sintering (SPS) is advantageous to obtain a dense sintered body at a lower sintering temperature and shorter sintering time than conventional hot press sintering. We have prepared transparent $Lu_2Ti_2O_7$ by reactive SPS [12]. In this paper, we prepare transparent $La_2Zr_2O_7$ by reactive SPS using commercially available La_2O_3 and ZrO_2 powders and investigated the microstructure and optical property.

Experimental procedure

La_2O_3 (Wako Pure Chemical, Japan, 99.99%) and ZrO_2 (Wako Pure Chemical, Japan, 99%) were used as the starting materials. These powders were mixed in the stoichiometric ratio La:Zr = 1:1 and ball-milled with zirconia balls in ethanol for 12 h. They were dried at 333 K for 24 h and passed through a 200-mesh sieve. The mixed powder was poured into a graphite die with a diameter of 10 mm and then directly reactive-sintered using an SPS apparatus (SPS-210 LX, SPS SYNTEX, Japan) in a vacuum. The sintering temperature was increased to 1373 K in 480 s and then further increased to 1673 K at a rate of 0.17 K s^{-1} and held for 2.7 ks. A pressure of 10 MPa was maintained until the temperature reached 1373 K, and then increased to 100 MPa. After sintering, the specimen was mirror-polished on both sides using a diamond slurry with a final thickness of about 1 mm.

The density was measured by the Archimedes method in distilled water. The crystal phase was

investigated with X-ray diffraction (XRD, RAD-2C, Rigaku, Japan) at 30 kV and 15 mA using graphite monochromatic Cu-Kα radiation (wavelength: 0.154 nm). The sintered bodies were thermally etched at 1573 K for 3.6 ks in air. A field emission scanning electron microscope (FESEM, JSM-7500F, JEOL, Japan) was used to observe the microstructure of the sintered bodies. The average grain size was determined from the average linear intercept length multiplied by a statistical factor 1.56 with at least 250 grains counted [13]. The in-line transmittance in the wavelength range from 190 to 2500 nm was measured with a spectrophotometer (UV-3101PC, Shimadzu, Japan). The transmittance in the range from 4000 to 400 cm^{-1} (2.5–25 μm) was measured with a Fourier transform infrared spectrometer (FT-IR, 460 Plus, Jasco, Japan) without an integrating sphere.

Results and discussion

Figure 1 shows the morphology of starting powders. La_2O_3 and ZrO_2 powders exhibited a nearly spherical shape with an average diameter of 600 and 400 nm, respectively.

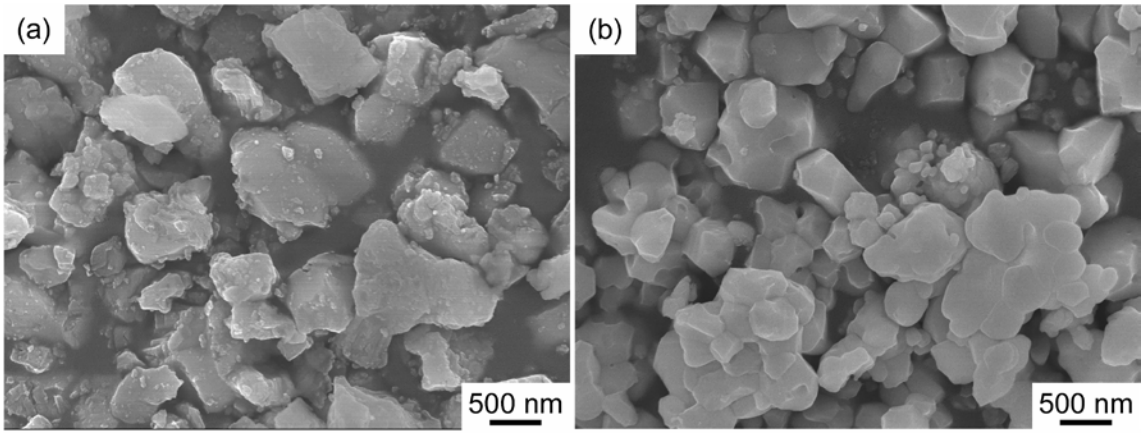

Fig. 1 Morphology of starting powders, (a) La_2O_3 and (b) ZrO_2.

Figure 2 shows XRD pattern of the $La_2Zr_2O_7$ body sintered at 1673 K for 2.7 ks. The XRD pattern can be indexed as a pyrochlore structure with a space group of *Fd*-3*m* (JCPDS card no. 73-04444). The lattice parameter was calculated as 10.8077 (0.0012), which was accordance with the JCPDS card 73-04444 (10.808) and the results reported by Harvey *et al* [14].

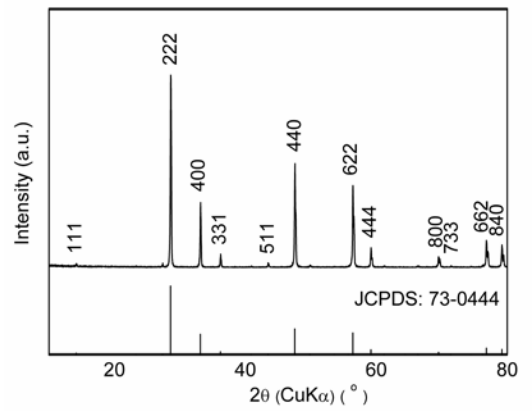

Fig. 2 XRD pattern of $La_2Zr_2O_7$ body sintered at 1673 K for 2.7 ks.

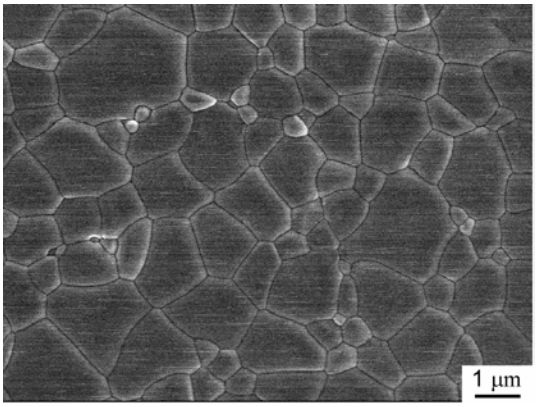

Fig. 3 FESEM of thermally etched surface of $La_2Zr_2O_7$ sintered at 1673 K for 2.7 ks.

Figure 3 shows the thermally etched surface of the $La_2Zr_2O_7$ body. The relative density was 99.5% of the theoretical value. Pores were rarely observed, indicating the high density after sintering at 1673 K. The microstructure is uniform with an average grain size of 1.5 μm. Conventional sintering such as pressureless sintering needed high sintering temperature (1873 K) to obtain less than 95% of the theoretical density [9]. Ion et al. reported $La_2Zr_2O_7$ with a relative density of 97.9% after sintering at 1673 K for 10 h [11] and Ota *et al*. reported 99.7% of 8 mol% Y_2O_3 substituted $La_2Zr_2O_7$ body sintered at 1773 K by hot isostatic pressing for 2 h [3]. However, the starting powders were synthesized by a nitrate-modified alkoxide route and a hydrazine method with specific preheating and milling. In the present study, nearly full dense $La_2Zr_2O_7$ body with fine grains was fabricated by SPS at a relatively low sintering temperature in a short time by using commercially available La_2O_3 and ZrO_2 powders.

Figure 4 shows the transmittance spectra of the $La_2Zr_2O_7$ body with a thickness of 1 mm in the wavelength range of 0.2–10 μm. The transmittance increased with increasing wavelength and reached 68% at 4–6 μm. An absorption peak located at 7.03 μm might be related to stretching of CO group [15]. The absorption edge in the infrared range was 8.5 μm. Although fully dense $La_2Zr_2O_7$ bodies have been prepared by pressureless and hot isostatic pressing sintering [3,11], we first prepared transparent $La_2Zr_2O_7$ body by SPS using commercial powders.

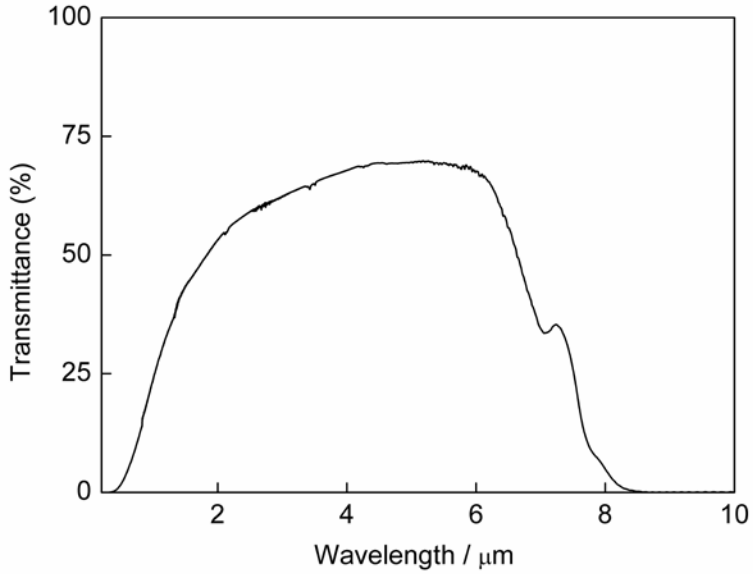

Fig. 4 Transmittance spectra of $La_2Zr_2O_7$ sintered at 1673 K for 2.7 ks.

Conclusions

Transparent $La_2Zr_2O_7$ with cubic pyrochlore structure was first fabricated by reactive spark plasma sintering at 1673 K for 2.7 ks using commercially available powders. The $La_2Zr_2O_7$ body exhibited a uniform microstructure with the average grain size of 1.5 μm. A transmittance in the wavelength range of 4-6 μm was 68%.

Acknowledgements

This research was supported in part by the Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists. This research was also supported in part by the Global COE Program of Materials Integration, Tohoku University.

References

[1] B. Liu, J.Y. Wang, Y.C. Zhou, T. Liao and F.Z. Li: Acta Mater. Vol. 55 (2007), p. 2949

[2] J. Wang, S.X. Bai, H. Zhang and C.R. Zhang: J. Alloys Compd. Vol. 476 (2009), p. 89

[3] A. Ota, Y. Matsumura, M. Yoshinaka, K. Hirota, and O. Yamaguchi: J. Mater. Sci. Lett. Vol. 17 (1998), p. 199

[4] Y. Matsumura, M. Yoshinaka, K. Hirota and O .Yamaguchi: Solid State Commun. Vol. 104. (1997), p. 341

[5] S.J. Korf, H.J.A. Koopmans, B.C. Lippens, A.J. Burggrasst and P.J. Gellings: J. Chem. Soc. Faraday Trans. Vol. 83 (1987), p. 1485

[6] Y.P. Tong, Y.P. Wang, Z.X. Yu, X. Wang, X.J. Yang and L.D. Lu: Mater. Lett. Vol. 62 (2008), p. 889

[7] R. A. McCauley and F. A. Hummel: J. Lumin. Vol. 6 (1972), p. 105

[8] F.W. Poulsen and N. Puil: Solid State Ionics Vol. 53–56 (1992), p. 777

[9] J.A. Labrincha, J.R. Frade and F.M.B. Marques: J. Mater. Sci. Vol. 28 (1993), p. 3809

[10] J. Nair, P. Nair, E.B.M. Doesburg, J.G. Van Ommen, J.R.H. Ross, A.J. Burggraaf and F. Mizukami: J. Mater. Sci. Vol. 33 (1998), p. 4517

[11] E.D. Ion, B. Malic and M Kosec: J. Sol-Gel Sci. Technol. Vol. 44 (2007), p. 203

[12] L.Q. An, A. Ito and T. Goto: J. Eur. Ceram. Soc. Vol. 31 (2011), p. 237

[13] M. I. Mendelson: J. Am. Ceram. Soc. Vol. 52 (1969), p. 443

[14] E.J. Harvey, K.R. Whittle and G.R. Lumpkin: J. Solid State. Chem. Vol. 178 (2005), p. 800

[15] D. Zhou, Y. Shi, J. Xie, Y. Ren and P. Yun, J. Am. Ceram. Soc. Vol. 92 (2009), p. 2182