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Journal of the European Ceramic Society 31 (2011) 237–240
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Technical note

Highly transparent lutetium titanium oxide produced by spark plasma sintering

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Received 25 June 2010; received in revised form 20 August 2010; accepted 6 September 2010

Abstract

Transparent $Lu_2Ti_2O_7$ pyrochlore was fabricated by reactive sintering using spark plasma sintering at 1723 K for 45 min. The sintered body exhibited 72% transmittance at a wavelength of 2000 nm and 40% transmittance at 550 nm. The average grain size was 14.5 μm with uniform microstructure.

Keywords: Pyrochlore; Transparent ceramic; $Lu_2Ti_2O_7$; Spark plasma sintering

1. Introduction

Pyrochlore rare-earth (*RE*) titanates ($RE_2Ti_2O_7$) have varied interesting applications such as ion conduction,[1] dielectrics,[2] catalytic activity,[3] radiation resistance for nuclear waste encapsulation,[4] and phosphors.[5,6] These characteristic properties result from their unique crystal structure consisting of two interpenetrating networks of corner-sharing Ti_2O_6 octahedra and RE_2O chains of distorted cubes.[7] Thus, transparent pyrochlore rare-earth titanates are promising multifunctional materials combining the optical and other properties, such as dielectric and photocatalytic properties; however, they have attracted little attention as transparent bodies because they are difficult to be fabricated by melting due to high melting point.

Lutetium titanium oxide ($Lu_2Ti_2O_7$) also has a pyrochlore structure and is particularly suitable for application in an optical imaging system due to its high refractive index and high density. Although ionic and catalytic properties of polycrystalline $Lu_2Ti_2O_7$ were reported, transparent polycrystalline $Lu_2Ti_2O_7$ body has not been synthesized so far.

Recently, spark plasma sintering (SPS) has been used to fabricate transparent ceramics because of its characteristic fast densification without significant grain growth. By controlling the sintering parameters, such as temperature, heating rate, pressure, dwell time, and atmosphere, highly transparent ceramics have been produced.[8,9] In this paper, we report the fabrication of transparent $Lu_2Ti_2O_7$ by SPS using commercially available common powders.

2. Experimental procedure

Lu_2O_3 (Shin-Etsu Rare Earth, Tokyo, Japan, 99.99%) and TiO_2 (Kanto Chemical Co. Inc., Tokyo, Japan, 99.9%, Rutile) were used as the starting materials for $Lu_2Ti_2O_7$. These powders were mixed in the stoichiometric ratio Lu:Ti = 1:1 and then ball-milled with zirconia balls in ethanol for 10 h. Then, 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). The sintering temperature was raised to 873 K in 3 min and 1373 K in 5 min, and then held at that temperature for another 5 min. The temperature was further increased to 1723 K at 0.17 K/s and maintained for 45 min. A pressure of 10 MPa was maintained up to the point that the temperature reached 1373 K, after which it was increased to 100 MPa in 1 min. After sintering, the specimen was annealed at 1023 K in air for 6 h. The specimen was mirror-polished on both sides using diamond slurry. The final thickness of the specimen was 0.8 mm.

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doi:10.1016/j.jeurceramsoc.2010.09.010

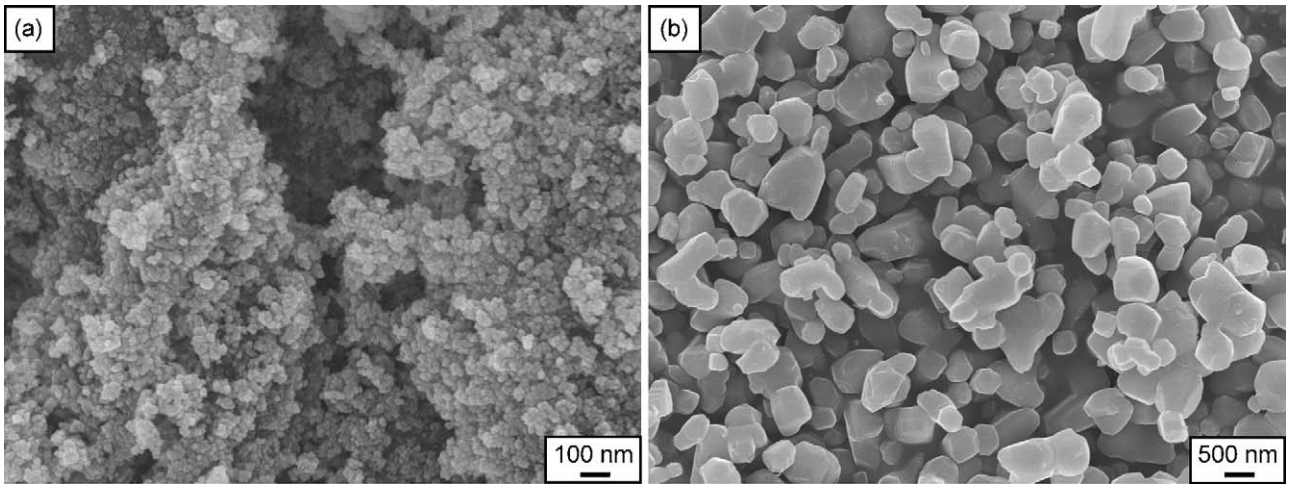

Fig. 1. FESEM of starting powders: (a) Lu_2O_3 and (b) TiO_2.

The density was measured by the Archimedes method in distilled water. The specimen had a relative density of 99.7%. The crystal phase was investigated with X-ray diffraction (XRD, RAD-2C, Rigaku, Japan). A field emission scanning electron microscope (FESEM, JSM-7500F, JEOL, Japan) was used to observe the morphology of the starting powders. The mirrored surface was thermally etched at 1623 K in air for 1 h. Micrographs of the thermally etched and fracture surfaces were recorded in a scanning electron microscope (SEM, S-3100H, Hitachi, Japan). The average grain size was determined from the linear intercept length.[10] 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 (FTIR, 460 Plus, Jasco, Japan) without an integrating sphere.

3. Results and discussion

Fig. 1a and b shows FESEM images of as-received (a) Lu_2O_3 and (b) TiO_2 powders. The Lu_2O_3 powder is spherical and slightly agglomerated with an average particle size of 30 nm. The TiO_2 powder is polyhedron and about 500 nm in size.

Fig. 2 shows the XRD patterns before (a) and after (b) annealing of the specimen sintered by SPS at 1723 K for 45 min. The patterns matched up accurately with a standard pattern of cubic $Lu_2Ti_2O_7$ pyrochlore (JCPDS card No. 23-0375). The relative intensities of the peaks were close to those of the standard card, but a slight (1 1 1) orientation was identified. No impurity peak was observed. A low-temperature phase transition of $Lu_2Ti_2O_7$ from fluorite to pyrochlore occurred at about 1073 K, and the cation disorder (antistructural defects in positions Lu–Ti) decreased from 18% to 6% as the calcined temperature increased from 1133 to 1323 K.[8] In the present work, the SPS temperature was 1723 K, high enough to result in an ordered pyrochlore without detectable cation disorder by the XRD. The calculated lattice parameters for the specimens before and after annealing were 1.00221 and 1.00231 nm, respectively, which agreed with the values on the JCPDS card (1.0019 nm) within experimental error.

Fig. 3a and b shows FESEM images of the thermal-etched and fracture surfaces of the $Lu_2Ti_2O_7$ body sintered at 1723 K for 45 min. The average grain size was about 14.5 μm, with a standard deviation of 4.3 μm. The fracture mode is mainly intergranular.

Fig. 4 is a photograph of the transparent $Lu_2Ti_2O_7$ body sintered at 1723 K for 45 min. Fig. 5a shows the in-line transmittance spectrum for wavelengths from ultraviolet to near infrared. The absorption edge is at about 340 nm, and the transmittance has a value of 40% and 72% at wavelengths of 550 nm and 2000 nm, respectively. The band gap of $Lu_2Ti_2O_7$ has been reported to be 3.0 eV, as estimated from the reflectance spectrum of the $Lu_2Ti_2O_7$ powder prepared by a polymerized complex technique.[11] We calculated the band gap to be 3.6 eV from the absorption edge. This value is in between Lu_2O_3 (5.4 eV) and TiO_2 (3.0 eV) and similar to that of cubic pyrochlore $Y_2Ti_2O_7$ and $Gd_2Ti_2O_7$ (3.5 eV).[10] The reflective loss across both surfaces of the specimen can be calculated as 32.4%, assuming

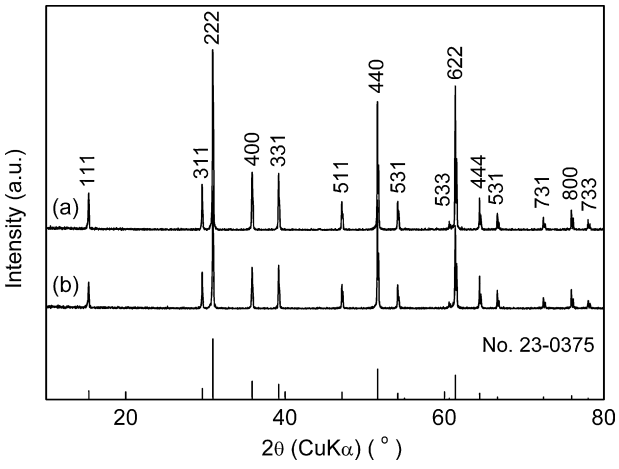

Fig. 2. XRD pattern of $Lu_2Ti_2O_7$ body sintered at 1723 K for 45 min (a) before and (b) after annealing.

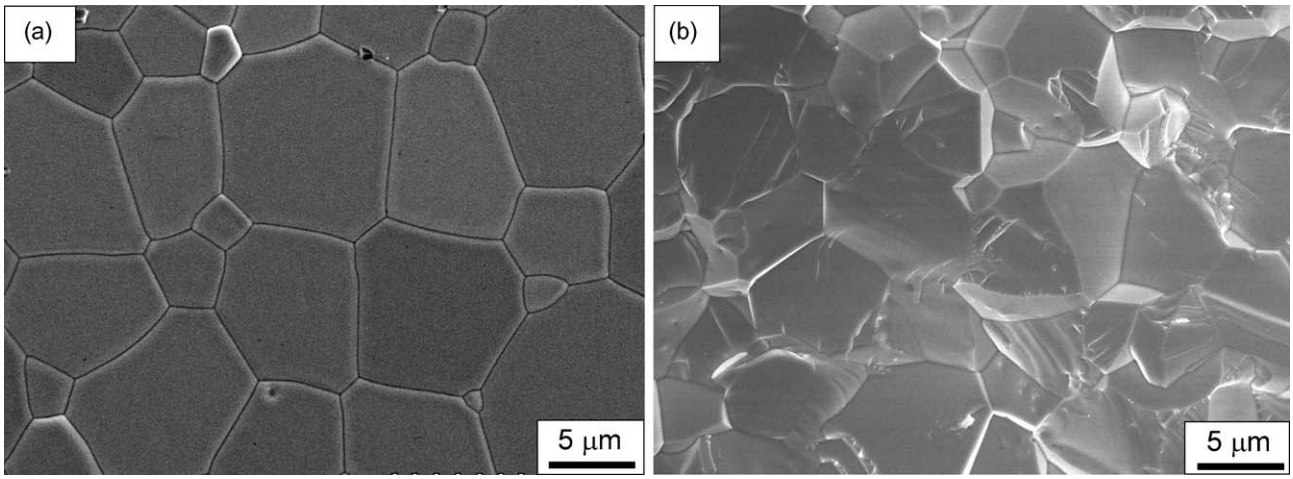

Fig. 3. The thermal-etched and fracture surfaces of $Lu_2Ti_2O_7$ sintered at 1723 K for 45 min.

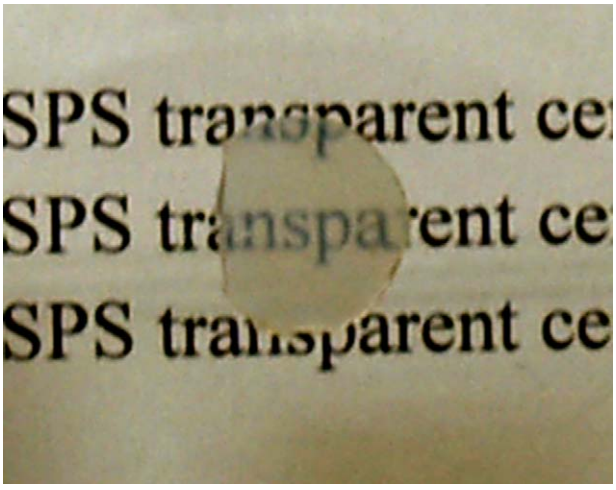

Fig. 4. Photograph of transparent $Lu_2Ti_2O_7$ sintered at 1723 K for 45 min. The specimen was placed 30 mm above the texts.

a refractive index of 2.57 at 632.8 nm.[12] Therefore, at the wavelengths 632.8 nm and 2000 nm, respectively, 70% and an almost 100% of the theoretical value were achieved. Although $Lu_2Ti_2O_7$ crystals have been studied previously, no transmittance data have been reported.[13] The present data provide the first report of a transparent $Lu_2Ti_2O_7$ sintered body.

Fig. 5b shows the transmittance for wavelengths from 2.5 to 8.5 μm. The transmittance was almost constant with a value of 72% from 2.5 to 4.6 μm and then decreased gradually to zero at 7.9 μm. The strong absorption peak at 4.24 μm might be due to gaseous CO_2.[14] The weak absorption peaks located at 2.68 and 6.37 μm might be due to O–H and C–O band stretching, respectively.[15] This kind of FTIR absorption peaks have been reported to be observed in the SPSed ceramics.[16,17] Since SPS uses a graphite die, the sintering atmosphere could contain CO and CO_2 gases. These gases might have been trapped in the specimen due to rapid sintering process of SPS. The peak related to O–H might come from adsorbed moisture on the surfaces of the specimen in air.

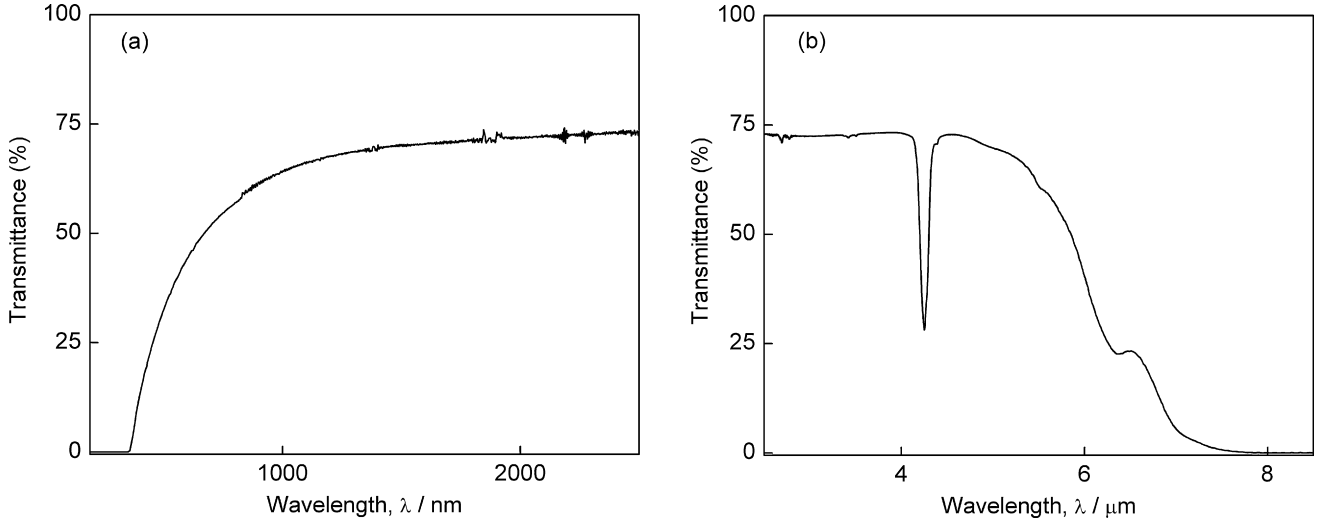

Fig. 5. Transmittance spectra of $Lu_2Ti_2O_7$ sintered at 1723 K for 45 min in the ranges (a) 190–2500 nm and (b) 2.5–8.5 μm.

4. Conclusion

We have successfully fabricated transparent $Lu_2Ti_2O_7$ by reactive sintering using SPS with commercially available common powders. The specimen, sintered at 1723 K for 45 min with post-annealing at 1023 K in air for 6 h, showed a theoretical transmittance of almost 100% at a wavelength of 2000 nm.

Acknowledgments

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. Shlyakhtina AV, Ukshe AE, Shcherbakova LG. Ionic conduction of a high-temperature modification of $Lu_2Ti_2O_7$. *Russ J Electrochem* 2005;**41**:265–9.
2. Erickson EE, Gray D, Taylor K, Macaluso RT, LeTard LA, Lee GS, Chan JY. Synthesis, structure and dielectric characterization of $Ln_2Ti_{2-2x}M_{2x}O_7$ (Ln = Gd, Er; M = Zr, SnSi). *Mater Res Bull* 2002;**37**: 2077–83.
3. Abe R, Higashi M, Sayama K, Abe Y, Sugihara H. Photocatalytic activity of R_3MO_7 and $R_2Ti_2O_7$ (R = Y, Gd, La; M = Nb, Ta) for water splitting into H_2 and O_2. *J Phys Chem B* 2006;**110**:2219–26.
4. Digeos AA, Valsez JA, Sickafus KE, Atiq S, Grimes RW, Boccaccini AR. Glass matrix/pyrochlore phase composites for nuclear wastes encapsulation. *J Mater Sci* 2003;**38**:1597–604.
5. Martos M, Julián-López B, Cordoncillo E, Escribano P. Structural and spectroscopic study of a novel erbium titanate pink pigment prepared by sol–gel methodology. *J Phys Chem B* 2008;**112**:2319–25.
6. Fujihara S, Tokumo K. Multiband orange-red luminescence of Eu^{3+} ions based on the pyrochlore-structured host crystal. *Chem Mater* 2005;**17**:5587–93.
7. Subramanian MA, Aramudan G, Subba GV, Rao. Oxide pyrochlores—A review. *Prog Solid State Chem* 1983;**15**:55–143.
8. Chaim R, Shen Z, Nygren M. Transparent nanocrystalline MgO by rapid and low temperature spark plasma sintering. *J Mater Res* 2004;**19**:2527–31.
9. Anselmi-Tamburini U, Woolman JN, Munir Z. Transparent nanometric cubic and tetragonal zirconia obtained by high-pressure pulsed electric current sintering. *Adv Funct Mater* 2007;**17**:3267–73.
10. Mendelson MI. Average grain size in polycrystalline ceramics. *J Am Ceram Soc* 1969;**52**:443–6.
11. Abe R, Higashi M, Zou ZG, Sayama K, Abe Y. Photocatalytic water splitting into H_2 and O_2 over $R_2Ti_2O_7$ (R = Y, rare earth) with pyrochlore structure. *Chem Lett* 2004;**33**:954–5.
12. Weber MJ. *Handbook of optical materials*. New York, USA: CRC Press; 2003. p. 78.
13. Helean KB, Ushakov SV, Brown CE, Navrotsky A, Lian J, Ewing RC, Farmer JM, Boatner LA. Formation enthalpies of rare earth titanate pyrochlores. *J Solid State Chem* 2004;**177**:1858–66.
14. Wenig RW, Schrader GL. In situ FTIR spectroscopy of 1-butene and 1 3-butadiene selective oxidation to maleic anhydride on V-P-0 catalysts. *J Phys Chem* 1987;**91**:1911–8.
15. Chen QW, Shi Y, An LQ, Chen JY, Shi JL. Fabrication and photoluminescence characteristics of Eu^{3+}-doped Lu_2O_3 transparent ceramics. *J Am Ceram Soc* 2006;**89**:2038–42.
16. Liu J, Shen ZJ, Yao WL, Zhao YH, Mukherjee AK. Visible and infrared transparency in lead-free bulk BaTiO3 and SrTiO3 nanoceramics. *Nanotechnology* 2010;**21**:075706–11.
17. Jiang DT, Amiya K, Mukherjee. Spark plasma sintering of an infrared-transparent Y2O3–MgO nanocomposite. *J Am Ceram Soc* 2010;**93**:769–73.