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# Ultra-fast densification of highly transparent Y<sub>2</sub>O<sub>3</sub> ceramic with La<sub>2</sub>O<sub>3</sub> as sintering aid by spark plasma sintering

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Highly transparent  $Y_2O_3$  ceramics were produced using spark plasma sintering (SPS) at 1600 °C and 30 MPa for 5 min. When the SPS process was applied with various amounts of  $La_2O_3$  as dopant. The specimen doped with 3 mol%  $La_2O_3$  showed the highest density, and rapid particle growth and pore growth occurred, exhibiting that the relative density and average grain size are 99.2% and 17.2 µm, respectively. The specimen showed excellent transmittance of 79.44% in the visible light region (600 nm), resulting that  $La_2O_3$  would be a useful dopant for improving the transmittance and mechanical properties of transparent  $Y_2O_3$  ceramics produced with SPS.

Key words: Y2O3 Transparent ceramics, Spark plasma sintering, Densification, La2O3, Sintering aid.

#### Introduction

Transparent  $Y_2O_3$  ceramics are being researched extensively as a promising material for optical applications. The advantages of  $Y_2O_3$  are its high melting point (2430 °C), high corrosion resistance, thermal stability, and broad transparency [1-7].  $Y_2O_3$  is also known as the best material for infrared (IR) windows because it has a higher and wider range of transmittance than other typically used materials such as sapphire, AlON, YAG, MgAl<sub>2</sub>O<sub>4</sub>, etc. [8].

Transparent Y<sub>2</sub>O<sub>3</sub> ceramics are generally produced with various sintering methods such as hot press [9], hot isostatic pressing [10, 11], and pressure-less sintering [12-14]. However, spark plasma sintering (SPS) allows the temperature to be controlled across a wide range, from low to high temperatures above 2000 °C within a short time and accelerates neck formation between powder particles owing to the generation of spark plasma. In addition, SPS also has grain surface purification, thermal diffusion, and electric field diffusion properties. As a result, SPS has the advantage of achieving full sintering within a very short time at a low temperature compared to conventional sintering methods [15-17]. The application of SPS to sinter oxides that contain ionic bonds is known to be likely to more easily generate the oxygen vacancies because of the effect of the spark plasma and electric field [18-20]. Furthermore, the SPS process is performed in a carbon-rich environment, and carbon is generated from the graphite die used as the heating element [21]. Consequently, the sintered oxide produced with SPS contains a high number of oxygen vacancies and high carbon content, both of which detrimentally affect the optical transparency.

Meanwhile, the sintering aid in the production of transparent ceramics is the most important factor that determines the transmittance and mechanical strength as these characteristics generally dominate the microstructure, and have been used to improve the optical quality and density of transparent ceramics. The following compounds have previously been used as sintering aids: ThO<sub>2</sub> [22], ZrO<sub>2</sub> [23], La<sub>2</sub>O<sub>3</sub> [24], LiF [25], and HfO<sub>2</sub> [26]. Among them, the use of  $La_2O_3$  in  $Y_2O_3$  ceramics has the effect of increasing the grain boundary mobility [27]. Therefore, when sintering is performed under the same conditions, it induces grain growth and densification, and provides kinetics capable of eliminating micropores between grain boundaries. Furthermore, it is also suitable for the improvement of transmittance [28]. However, a large amount of sintering aid can change the stoichiometry of materials, form a second-order phase, and separate from the boundary, thereby negatively affecting the transparency [29].

The present study aims to develop a process to simply and rapidly produce  $Y_2O_3$  ceramics with high density and optical quality using  $La_2O_3$  as dopant while minimizing the number of oxygen vacancies that occur during the SPS process. We attempted to establish the optimal sintering conditions by using various amounts of  $La_2O_3$  dopant during the SPS process and investigated the effects of  $La_2O_3$  on the densification behaviour, microstructure, and mechanical and optical properties as a function of the concentration.

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## **Experimental**

#### Powder preparation and SPS sintering

As starting materials, commercially available highly pure Y<sub>2</sub>O<sub>3</sub> powder (99.99% pure, Cenotec, Korea) and La2O3 powder (99.9% pure, Kojundo, Japan) were used. The  $Y_2O_3$  powder was doped with 0, 1, 3, and 5 mol% La<sub>2</sub>O<sub>3</sub> and these mixtures were blended by ball milling with zirconia balls with a diameter of 1.5 mm in a weight ratio of 1:10. Then the blended powders were dried in an electric oven at 60 °C for 24 hrs. The dried powder samples were placed in a graphite die with an inner diameter of 15 mm that was wrapped with graphite foil and sintered using an SPS system (Sumitomo Coal Mining, S-515S, Japan) at 1600 °C under vacuum (10 Pa) at a, uniaxial pressure of 30 MPa. The sintering conditions were as follows: (i) the specimen was heated at a heating rate of 100 °C / min at room temperature until the final sintering temperature (1600 °C) was reached at which it was maintained for 5 min; (ii) the pressure was maintained at 30 MPa from the beginning; and (iii) after sintering, the pressure was released and the current was discontinued. The size of the sintered specimen was 15 mm in diameter and 1 mm in thickness. Subsequently, the specimen was subjected to an annealing process using a box furnace in an oxygen atmosphere at 1100 °C at a heating rate of 10 °C /min. The microstructure and optical properties were evaluated by grinding both surfaces of the specimen with a grinder, after which they were polished with a 1-µm diamond paste.

#### Characterization

X-ray diffraction analysis (XRD) was used to perform phase analysis with Cu Ka ( $\lambda = 1.548$  Å) in the range of  $2\theta = 20^{\circ}-80^{\circ}$  at 40 kV and 30 mA(Rigaku-denki, D/MAX-2500, Japan). The average grain size of the specimen was analysed using field emission-scanning electron microscopy (FE-SEM, NOVA Nano SEM 450, FEI, Czech Republic) in an acceleration voltage range of 5-15 kV. The in-line transmittance of the produced specimen was measured in the wavelength range of 300-2000 nm using a UV-Vis-NIR spectrophotometer (Lambda 950, Perkin-Elmer, America). The relative density was measured using the Archimedes method, and the average Vickers hardness was determined by 15 indentations using a digital hardness tester (FV-700e, Future-Tech Co. Ltd, Japan). The flexural strength was measured by 3-point bending with a mechanical tester (RB302, R&B Co. Ltd, Korea).

## **Results and Discussion**

Fig. 1 shows the XRD patterns of the specimens of  $Y_2O_3$  ceramics doped with various concentrations of  $La_2O_3$  and sintered in vacuum at 1600 °C for 5 min.



Fig. 1. XRD patterns of  $Y_2O_3$  ceramics doped with 0, 1, 3, 5 mol%  $La_2O_3$  at 1600 °C for 10 min.



Fig. 2. Variation of transmittance and image of as-polished  $Y_2O_3$  ceramics doped with 0, 1, 3, 5 mol% La<sub>2</sub>O<sub>3</sub> at 1600 °C for 10 min.

None of the specimens showed a La<sub>2</sub>O<sub>3</sub> phase or other impurities and the pattern coincided with the standard cubic Y<sub>2</sub>O<sub>3</sub> phase with the space group of Ia<sup>-3</sup>. This indicates that La<sub>2</sub>O<sub>3</sub> is dissolved in Y<sub>2</sub>O<sub>3</sub> in the composition range of 1-5 mol% La2O3. Fig. 2 shows the in-line transmittance and image of an Y<sub>2</sub>O<sub>3</sub> ceramic specimen, with a thickness of 1 mm, and doped with various concentrations of La2O3. As shown in this figure, every specimen clearly shows the text behind, but the un-doped specimen is less transparent than the other specimens doped with La<sub>2</sub>O<sub>3</sub>. The specimen doped with 1 mol% La<sub>2</sub>O<sub>3</sub>, showed a higher transmittance than the un-doped specimen. The specimens doped with 3 mol% or higher amounts of La<sub>2</sub>O<sub>3</sub> showed very high transmittances. The specimen doped with 3 mol% La<sub>2</sub>O<sub>3</sub>, showed an excellent transmittance of 79.44% at a wavelength of 600 nm. Thus, the specimens doped with  $La_2O_3$  have higher transmittances than pure  $Y_2O_3$ ceramics. This is because the specimens doped with La<sub>2</sub>O<sub>3</sub> have larger or a greater number of micropores and higher scattering is activated when the light passes



Fig. 3. FE-SEM image of thermally etched Y<sub>2</sub>O<sub>3</sub> ceramics surface doped with (a)0, (b)1, (c)3, (d)5 mol% La<sub>2</sub>O<sub>3</sub> at 1600 °C for 10 min.



Fig. 4. TEM images of  $Y_2O_3$  sample (a) un-doped and (b) doped with 3 mol%  $La_2O_3$  showing the presence of occluded nanopores and the straight grain boundary at the triple junction.

through the ceramics in the nanometre range, compared to the un-doped specimen [24].

Fig. 3 shows the etched surfaces of the  $Y_2O_3$ 

specimens doped with different concentrations of  $La_2O_3$ . In general, the grain size gradually increased as the amount of dopant,  $La_2O_3$ , increased. The specimens



Fig. 5. Variation of the average grain size and relative density of SPS-sintered  $Y_2O_3$  ceramics doped with 0, 1, 3, 5 mol% La<sub>2</sub>O<sub>3</sub> at 1600 °C for 10 min.

doped with 0 mol% and 1 mol% La<sub>2</sub>O<sub>3</sub> did not show significant differences in grain size, but the specimen doped with 1 mol% La<sub>2</sub>O<sub>3</sub> contained fewer micropores. The specimen doped with 3 mol% La<sub>2</sub>O<sub>3</sub> had a greater grain size than those doped with 0 mol% and 1 mol% La<sub>2</sub>O<sub>3</sub>, and showed a dense, uniform microstructure with almost no inter-granular and intra-granular pores. Moreover, grains with abnormal grain growth were not observed, which suggests that densification progressed in a thermodynamically stable manner. However, the grain size of the specimen doped with 5 mol% La<sub>2</sub>O<sub>3</sub> was less uniform compared to that doped with 3 mol% La<sub>2</sub>O<sub>3</sub>, and the presence of micropores was observed. As a result, light scattering and absorption occurred, and transmittance decreased in specimens with residual micropores. The cause of the low transmittance and light scattering of specimens may be the prevalence of micro-sized and smaller residual pores [29]. The application of SPS in the sintering of oxides with ionic bonds is likely to cause fine oxygen vacancies due to the effects of the spark plasma and electric field.

Fig. 4 shows the TEM images of an undoped specimen and a specimen doped with  $3 \text{ mol}\% \text{ La}_2\text{O}_3$  taken to analyse the effects of  $\text{La}_2\text{O}_3$ . The residual occluded nanopores at the triple junction of the specimen doped with  $0 \text{ mol}\% \text{ La}_2\text{O}_3$  are indicated by white arrows (Fig. 4(a)). The presence of occluded nanopores sized approximately 65 nm and 9.38 nm can be seen on the left and the right, respectively. In contrast, the specimen doped with 3 mol

% La<sub>2</sub>O<sub>3</sub>, exhibits clean grain boundaries with no occluded pores at the triple junction as shown in Fig. 4(b). The reason for this seems to be that in the final stage of the sintering process, the La<sup>3+</sup> ions accelerated mass transfer, which increased the diffusion of  $Y^{3+}$  ions and grain boundary mobility, thereby providing kinetics that can destroy oxygen vacancies and pores through grain growth and densification [28]. Consequently, the addition of La<sub>2</sub>O<sub>3</sub> during the sintering of Y<sub>2</sub>O<sub>3</sub> using



Fig. 6. Hardness of SPS-sintered  $Y_2O_3$  ceramics doped with 0, 1, 3, 5 mol% % La<sub>2</sub>O<sub>3</sub> at 1600 °C for 10 min.



Fig. 7. Variation in the flexural strength of the SPS-sintered  $Y_2O_3$  ceramics doped with 0, 1, 3, 5 mol% La<sub>2</sub>O<sub>3</sub> at 1600 °C for 10 min.

SPS decreases the extent of light scattering and absorption to improve the in-line transmittance of ceramics.

Fig. 6 shows the hardness (GPa) of Y<sub>2</sub>O<sub>3</sub> ceramics as a function of different concentrations of La<sub>2</sub>O<sub>3</sub> dopant. The increasing porosity and decreasing hardness of Y<sub>2</sub>O<sub>3</sub> ceramics have been reported by various researchers [29-31].  $Y_2O_3$  ceramics doped with La<sub>2</sub>O<sub>3</sub> have higher hardness values than pure specimens with no La<sub>2</sub>O<sub>3</sub>. As the concentration of La<sub>2</sub>O<sub>3</sub> increased from 0 mol% to 3 mol%, the hardness increased from 8.09 GPa to 8.45 GPa. The hardness of ceramics generally increases when the particle size is reduced, but in this study, the hardness value is relatively high even though the particle size increased by the addition of La<sub>2</sub>O<sub>3</sub>. This is attributed the mechanical properties of the undoped specimen, which has a greater number of pores and lower relative density than the specimens doped with  $La_2O_3$ . On the other hand, at the concentration of  $La_2O_3$  of 5 mol%, the number of nanopores increased and the

density decreased to 98.9%, and as a result, the hardness decreased to 8.22 GPa.

A comparison of Fig. 5 and Fig. 7 shows that the trend exhibited by the flexural strength is almost identical to that of the relative density. In general, the strength of ceramics depends on their porosity and an increase in the porosity is known to increase the stress concentration [32]. Consequently, the decrease in strength is accompanied by a concomitant increase in the stress concentration of the sample. As the added amount of sintering aid increased, the flexural strength increased from 98.9 MPa to the maximum strength of 120 MPa at 3 mol% La<sub>2</sub>O<sub>3</sub>. The strength of the specimen doped with 5 mol% La<sub>2</sub>O<sub>3</sub> showed a decreasing trend to 104 MPa as the particle size increased and the density decreased.

## Conclusions

Transparent Y<sub>2</sub>O<sub>3</sub> ceramics were successfully produced using SPS at 1600 °C and 30 MPa for 10 min using commercially available Y<sub>2</sub>O<sub>3</sub> powder. The addition of La2O3 during SPS process had a significant effect on the production of transparent Y<sub>2</sub>O<sub>3</sub> ceramics. The addition of La<sub>2</sub>O<sub>3</sub> greatly decreased the number of micropores and vacancies because of grain growth and densification, and generated a dense microstructure. The evaluation results showed that the optimal concentration of La<sub>2</sub>O<sub>3</sub> doping was 3 mol% and the 1 mm-thick specimen showed high transmittance of 79.44% at a wavelength of 600 nm. The average grain size in this case was 17.2 µm and the specimen showed a high relative density of 99.2%. As this specimen had higher relative density and lower porosity than the specimen produced with no sintering aid, its mechanical properties, i.e. its hardness and flexural strength, improved to 8.45 GPa and 120 MPa, respectively.

### References

- J.R. Lu, K. Takaichi, T. Uematsu, A. Shirakawa, M. Musha, K. Ueda, Jpn. J. Appl. Phys. Part 2-Letters 41 (2002) L1373.
- M. Ivanov, Y. Kopylov, V. Kravchenko, L. Jiang, A. Medvedev, PAN Yubai, J. Rare. Earths 32 (2014) 254.
- W.J. Tropf, M.E. Thomas, R.K. Frazer, SPIE 5078 (2003) 80-89.
- 4. S.F. Wang, J. Zhang, D.W. Luo, et al., Prog. Solid State

Chem. 41 [1-2] (2013) 20-54.

- P. Hogan, T. Stefanil, C. Willingham, R. Gentilman, 10th DoD Electromagnetic Windows Symposium (2004).
- L. An, A. Ito, T. Goto, J. Eur. Ceram. Soc. 32 (2012) 1035-1040.
- 7. K. Serivalsatit, B. Kokuoz, B. Yazgan-Kokuoz, M. Kennedy, J. Ballatow, J. Am. Ceram. Soc. 93 (2010) 1320.
- 8. C.B. Willingham et al., SPIE Proc. 5078 (2003) 179.
- S.R. Podowitz, R. Gaumé, R.S. Feigelson, J. Am. Ceram. Soc. 93 (2010) 82-88.
- J. Wang, J. Ma, J. Zhang, P. Liu, D. Luo, D. Yin, D. Tang, L.B. Kong, Opt. Mater. 71 (2017) 117-120.
- J. Mouzon, A. Maitre, L. Frisk, N. Lehto, M. Odén, J. Eur. Ceram. Soc. 29 (2009) 311-316.
- T. Ikegami, J.G. Ji, T. Mori, Y. Moriyoshi, J. Am. Ceram. Soc. 85 (2002) 1725-1729.
- L.L. Jin, G.H. Zhou, S. Shimai, J. Zhang, S.W. Wang, J. Eur. Ceram. Soc. 30 (2010) 2139-2143.
- 14. Y.H. Huang, D.L. Jiang, J.X. Zhang, Q.L. Lin, J. Am. Ceram. Soc. 92 (2009) 2883-7.
- 15. K.H. Kim, J.H. Chae, J.S. Park, J.P. Ahna, K.B. Shim, J. Ceram. Proc. Res. 10 (2009) 716-720.
- 16. K.H. Kim, K.B. Shim, Mater. Charact. 50 (2003) 31-37.
- S.H. Shim, J.W. Yoon, K.B. Shim, J. Matsushita, B. S. Hyun, S.G. Kang, J. Alloy. Compd. 413 (2006) 188-192.
- J.R. Groza, A. Zavaliangos, Mater. Sci. Eng. A287 (2000) 171-177.
- M. Omori, T. Isobe, T. Hirai, J. Am. Ceram. Soc. 83 (2000) 2878-2880.
- L. Gao, Z. Shen, H. Miyamoto, M. Nygren, J. Am. Ceram. Soc. 82 (1999) 1061.
- 21. C.W. Park, J.H. Lee, S.H. Kang, J.H. Park, H.M. Kim, H.S. Kang, H.A. Lee, J.H. Lee, K.B. Shim, J. Ceram. Proc. Res. 18 (2017) 183-187.
- 22. C. Greskovich, K.N. Woods, J. Am. Ceram. Soc. Bull. 52 (1973) 473.
- 23. X.R. Hou, S.M. Zhou, Y.K. Li, W.J. Li, Opt. Mater. 32 (2010) 920-923.
- 24. K. Majima, N. Niimi, M. Watanabe, S. Katsuyama, H. Nagai, J. Jpn. Inst. Met. 57 (1993) 1221-1226.
- 25. Ikesue, K. Kamata, K. Yoshida, J. Am. Ceram. Soc. 79 (1996) 359-364.
- 26. X. Li, X. Mao, M. Feng, S. Qi, B. Jiang, L. Zhang, J. Eur. Ceram. Soc. 36 (2016) 2549-2553.
- 27. Q. Yi, S. Zhou, H. Teng, H. Lin, X. Hou, T. Ji, J. Eur. Ceram. Soc. 32 (2012) 381-388.
- L. Zhang, Z. Huang, W. Pan, J. Am. Ceram. Soc. 98 (2015) 824-828.
- 29. R.W. Rice, J. Mater. Sci. 31 (1996) 1969-1983.
- 30. F.P. Knudsen, J. Am. Ceram. Soc. 42 (1959) 367-387.
- 31. R.W. Rice, J. Mater. Sci. 28 (1993) 2187-2190.
- B. Ahmadi, S.R. Reza, M.A. Vadeqani, M. Barekat, Ceram. Int. 42 (2016) 17081-17088.