Development of highly transparent zirconia ceramics

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Highly transparent zirconia ceramics were developed and their optical and mechanical properties were comprehensively studied. A low optical haze value (H<1.0 %), defined as the diffuse transmission divided by the total forward transmission, was achieved by using high-purity powder and a novel sintering process. Theoretical in-line transmission (74 %) was observed from the ultraviolet–visible region up to the infra-red region; an absorption edge was found at 350 nm and 8 μm for the ultraviolet and infrared region, respectively. A colorless sintered body having a high refractive index (n_d = 2.23) and a high Abbe's number (ν_d = 27.8) was obtained. A remarkably large dielectric constant (ε = 32.7) with low dielectric loss (tan δ = 0.006) was found. Transparent zirconia ceramics are candidates for high-refractive index lenses, optoelectric devices and infrared windows. Transparent zirconia ceramics also possess excellent mechanical properties. Various colored transparent zirconia can be used as exterior components and for complex-shaped gemstones.

1. Introduction

Transparent and translucent ceramics have been studied extensively ever since the seminal work on translucent alumina polycrystal by Coble in the 1960s.[1] Subsequently, researchers have conducted many studies to develop transparent ceramics such as MgO,[2] Y_2O_3,[3] $MgAl_2O_4$ (spinel),[4] and $Y_3Al_5O_{12}$ (YAG).[5] Various optical applications for transparent ceramics have been proposed, e.g., infrared windows,[6] Nd laser host materials,[7] armor applications,[8] and optical lenses.[9]

One recent industrial development of transparent ceramics was the application of a lens named Lumicera for a slim digital camera developed by Tanaka.[10] The use of perovskite-based transparent ceramics having a high refractive index reduced the focal length. Reference 11 and open web information[12] give comprehensive reviews of transparent and translucent ceramics.

With their high refractive index, yttria-stabilized zirconia (YSZ) single crystals are widely used as artificial gemstones. YSZ ceramics crystallize into cubic structure and are candidates for transparent ceramics. Thus, adequate effort has been dedicated to fabricating transparent cubic zirconia ceramics.[9,13-19] Transparent zirconia ceramics using titanium oxide as a sintering additive were firstly reported by Tsukuma.[15] However, the sintered body had poor transparency and low mechanical strength. In this study, highly transparent zirconia ceramics of high strength were developed. Their optical and mechanical properties were comprehensively studied, and the effects of the microstructure on these properties were discussed.

2. Experimental

Sample preparation

High-purity 10 mol% yttria-doped zirconia powder made by hydrolysis process [20] was used as a starting powder. As a sintering additive, 10 mol% of titanium oxide with respect to zirconia was used. The starting powder was compacted into a green body, and transparent zirconia was obtained by a subsequent novel high-densification process. [21]

Optical properties

The sample material was ground to a thickness of 1 mm and thoroughly polished on both sides to eliminate surface scattering in subsequent measurements. The

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in-line transmission of the ultraviolet–visible (UV–VIS) region was measured using a double-beam spectrophotometer (V-650, JASCO Corporation, Tokyo, Japan) with a wavelength range of 200–800 nm. The infrared (IR) spectrum was measured using a Fourier transform infrared spectrometer (IR Prestige-21, Shimadzu, Japan) with a range of 3–9 μm.

As the absolute value of transmission includes the effects of surface reflections, the optical haze value H, defined as the diffuse transmission divided by the total forward transmission, is widely used to evaluate the transparency of transparent materials. The optical haze value at the D65 sources was evaluated using a haze meter (NDH 5000, Nihon Denshoku, Tokyo, Japan). The refractive index was measured using a spectroscopic ellipsometer (M-2000V, J. A. Woollam Japan, Tokyo, Japan) from 370 to 1000 nm. The refractive index was fitted to the Cauchy equation; the Abbe's number ν_d was calculated using the data at n_d (587.56 nm), n_F (486.1 nm), and n_C (656.3 nm). The dielectric constant and the dielectric loss tangent at 1 MHz were also measured by the impedance method at the room temperature.

Mechanical properties

The microstructure of the transparent zirconia was estimated by scanning electron microscopy (SEM) (JSM-5400, JEOL Corporation, Tokyo, Japan), and the grain size was estimated by the intercept method. A correction factor of 1.56 was used in the calculation. The three-point bending strength was measured in line with JIS-R-1601; a gauge length of 30 mm and a cross-head speed of 0.5 mm/min were applied. The fracture toughness and hardness were estimated by indentation following JIS-R-1607. Young's modulus and Poison's ratio were measured by the plus method in line with JIS-R-1602.

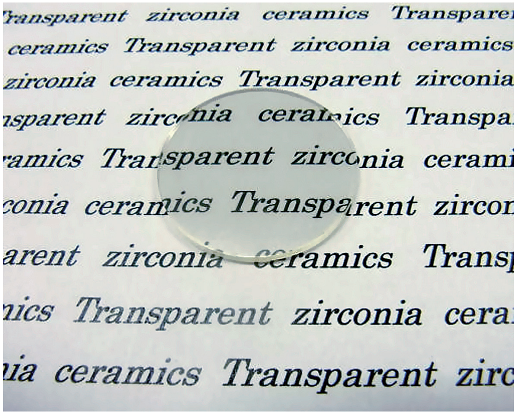

Fig. 1 Transparent zirconia ceramics (20 mm in diameter and 1 mm in thickness).

Table1 Mechanical and optical properties of transparent zirconia ceramics

Density	5.83 g/cm^3
Three-point bending strength	250-300 MPa
Hardness [Hv10]	1200
Young's modulus	200 GPa
Poisson's ratio	0.32
Fracture toughness	1.8 MPa·m$^{0.5}$
Dielectric constant [1 MHz]	32.7
Dielectric loss [1 MHz]	0.006
In-line transmission [1 mmt, D65]	74 %
Optical haze value [1 mmt, D65]	<1 %
Refractive index [n_d]	2.23
Abbe's number [ν_d]	27.8

3. Results and discussion

Figure 1 shows the appearances of the transparent zirconia ceramics obtained. The sample size is 20 mm in diameter and 1 mm in thickness. Although a slightly yellowish color has been reported for titania-doped transparent zirconia,[15] a highly transparent and colorless sintered body was obtained in our experiment. The optical and mechanical properties of the transparent zirconia ceramics are tabulated in **Table 1**. The final sintered body crystallizes into a single cubic phase with a fluoride structure (*Fm3m*). The lattice parameter as determined by the Rietveld analysis is a = 0.51216 (1) nm. Because of the smaller Ti ionic radii, the lattice parameter of transparent zirconia is 0.5 % shorter than that of 10 mol% of yttria-doped zirconia (a = 0.51447 (2) nm).

Density of the sintered body is 5.83 g/cm^3 as ascertained by the Archimedean method. Hardness, Young modulus, Poisson's ratio, and fracture toughness were determined to be Hv = 1200, 200 GPa, 0.32, and 1.8 M·Pa m$^{0.5}$, respectively. This set of values is comparable to that of YSZ ceramics such as 8Y ceramics.[22] The three-point bending strength varies between 250 and 300 MPa as a function of its microstructure that will be discussed later.

High in-line transmission with low optical haze was observed in the transparent zirconia ceramics. **Figure 2** shows the wavelength dependence of in-

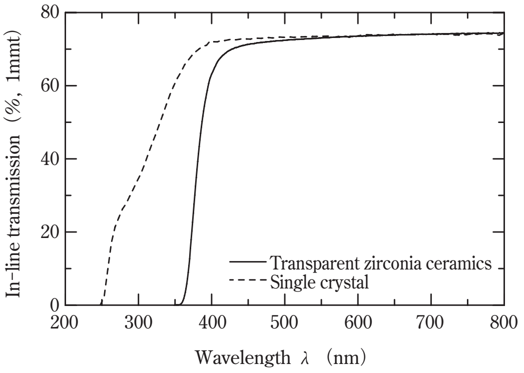

Fig. 2 In-line transmission of transparent zirconia ceramics and YSZ single crystal. The solid line represents transparent zirconia, the dashed line represents YSZ single crystal.

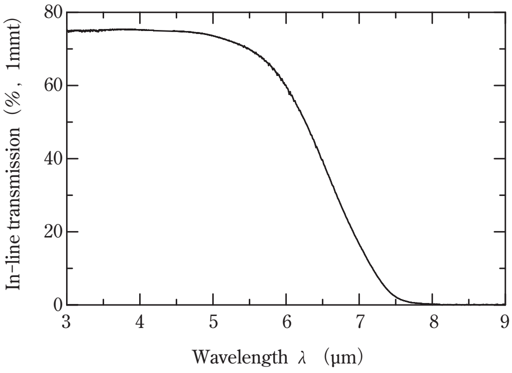

Fig. 3 Infrared transmission of transparent zirconia ceramics.

line transmission of transparent ceramics and 10 mol% yttria-stabilized zirconia single crystal with a thickness of 1 mm. The transmission of transparent ceramics is comparable to that of a single crystal in the visible region. A large reflection loss ($\cong$ 26 %) resulting from a high refractive index was observed for both the single crystal and the ceramics. Theoretical in-line transmission (74 %) was achieved for the transparent zirconia ceramics, with the optical haze value estimated to be $H < 1.0$ % at the D65 sources. No remarkable change with respect to wavelength, which causes a color hue in ceramics, was observed in the visible region.

The in-line transmission reached that of a single crystal in the visible region, whereas a large discrepancy was observed in the UV region. The absorption edge of a single crystal was estimated to be 250 nm, which is almost comparable with the wavelength as calculated from a band gap of 4.2 eV (295 nm).[23] On the other hand, a shift in the absorption edge toward a longer wavelength was detected in the zirconia ceramics. Titania (rutile) has a narrow band gap of 3.2 eV as compared with that of zirconia. By substituting Ti atoms into Zr, the Y cation site, the electronic band structure is changed.

The in-line transmission of the IR region is shown in **Fig. 3**. Transmission gradually decreases with an increase in the wavelength, and an absorption edge is observed near 8 μm. The absorption edges of typical transparent materials are 2.7 μm, 3.5 μm, and 6 μm for soda-lime glass, quartz, and sapphire, respectively. It is noteworthy that transparent zirconia is highly transparent up to the IR region. As the absorption edge of the IR region is created by lattice vibration, the shift toward a higher wavelength might be attributed to the massive effect of heavy Zr, Y atoms.

A large dielectric constant ($\varepsilon = 32.7$) with low dielectric loss ($\tan\delta = 0.006$) was found at 1 MHz. No significant change was observed for the dielectric constant and dielectric loss up to 60 MHz. **Figure 4** shows the dielectric constant of typical transparent inorganic materials at 1 MHz. It was found that transparent zirconia ceramics have a large dielectric constant as compared with other transparent materials. The dielectric constant of electron polarization can be expressed by the square of its refractive index (n^2). As the observed dielectric constant is much larger than the estimated ($n^2 = 4.79$), another polarization mechanism is suspected in transparent zirconia ceramics. It is well known that zirconia is a typical ionic crystal. Therefore, ionic polarization may be responsible for the large dielectric constant.

The refractive index as estimated by ellipsometry can be fitted to a Cauchy equation as follows.

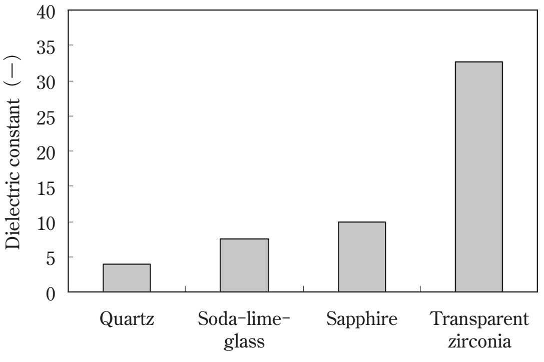

Fig. 4 Dielectric constant of typical transparent inorganic materials at 1 MHz.

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (\lambda = 0.370 - 1.000\ \mu\mathrm{m}) \qquad (1)$$

, where A = 2.165, B = 0.01859, and C = 0.00070606.

Abbe's number ν_d is defined using the refractive index of the d-line (587.56 nm), F-line (486.1 nm), and C-line (656.3 nm).

$$\nu_d = \frac{n_d - 1}{n_F - n_C} \qquad (2)$$

The Abbe's number represents the dispersion of light – the larger the Abbe's number, the smaller the dispersion. Generally, a higher refractive index reduces the Abbe's number. A larger Abbe's number causes an aberration of the optical system. Thus, a higher refractive index with a low Abbe's number is required for optical lenses.

Figure 5 shows variations in the refractive index and the Abbe's number of optical glass and transparent zirconia ceramics. Commercial transparent ceramics (Lumicera, Murata Co., Japan) and glass (K-PSFn173, Sumita Optical Glass Inc., Japan) with a high refractive index were also plotted. Transparent zirconia ceramics show an excellent relation of the refractive index with respect to the Abbe's number, i.e., a high refractive index with a low Abbe's number.

Figure 6 shows the microstructure of transparent ceramics. A uniform grain structure can be observed, and no abnormal grain growth was detected. It was found that the three-point bending strength(σ_f) strongly depends on the grain size (d). The bending strength increases with a decrease in the grain size. Figure 7 shows the relation between the bending strength and grain size. The bending strength obeys empirical $1/d^{0.5}$ rules [24] as follows:

$$\sigma_f = \sigma_0 + \frac{k}{\sqrt{d}} \qquad (3)$$

Here, σ_f and d are the bending strength and grain size, whereas k and σ_0 are constant. A similar relation was reported for translucent alumina ceramics.[24] Being similar to Grifith's expression, flaws having a similar grain size may be responsible for the fracture origin.

The relation between optical haze value H and grain size is shown in **Fig. 8**. Transparency strongly depends on grain size, and transparency degrades as the grain size decreases. Translucent ceramics having a non-cubic structure, such as alumina (hexagonal structure), show similar behavior with respect to grain size. In-line transmission increases with a decrease in grain size, which is due to the effect of birefringence at the grain boundary.[25, 26] As transparent zirconia ceramics crystallize into a cubic structure, an absence of birefringence at the grain boundary must be considered. However, **Fig. 8** implies another candidate for scattering origin at the grain boundary.

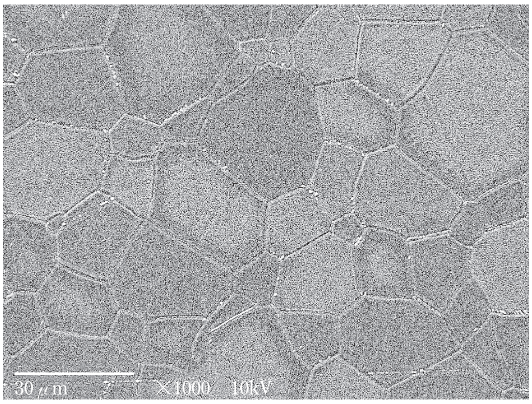

Fig. 6 Typical microstructure of transparent zirconia ceramics.

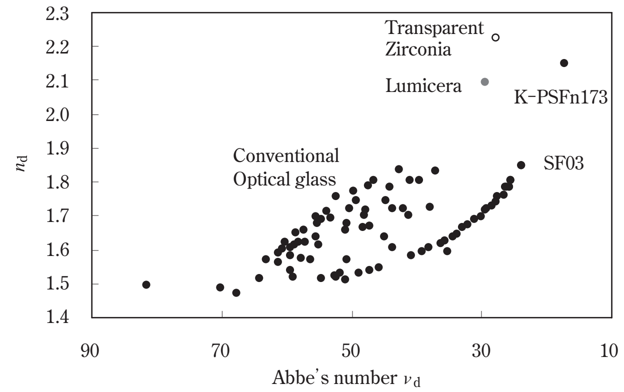

Fig. 5 Relation between refractive index (n_d) and Abbe's number (ν_d) of optical glass and transparent ceramics.

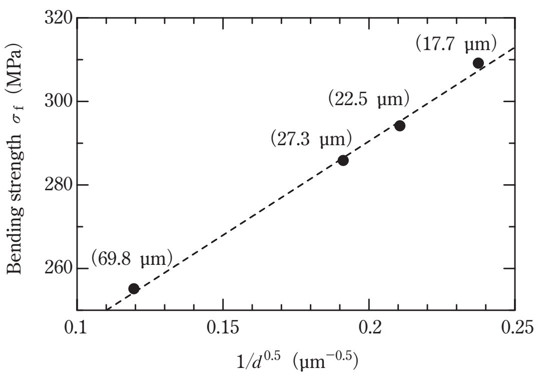

Fig. 7 Effect of the grain size (d) on the bending strength (σ_f) of transparent zirconia ceramics. Numerical values in parenthesis represent the grain size.

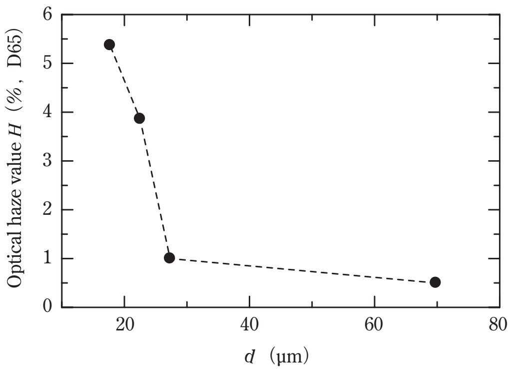

Fig. 8 Effect of the grain size (*d*) on the optical haze value (*H*) of transparent zirconia ceramics.

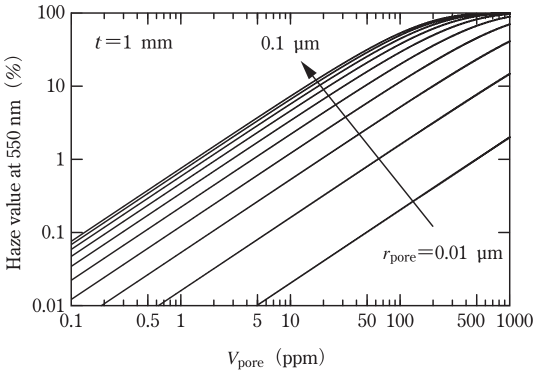

Fig.10 Relation between optical haze H and porosity V_{pore} as a function of the pore radius r_{pore} at 550 nm, assuming t = 1 mm[28]. Haze value H is plotted from 0.01 μm to 0.1 μm at 0.01 μm intervals.

Figure 9 shows a TEM micrograph of the grain boundary of a transparent zirconia ceramics. Residual pores selectively migrate at the grain boundaries. The pore size is estimated to be < 100 nm. Pores located at the grain boundary can be easily eliminated during densification through grain growth. On the other hand, pores entrapped in grains are not expected to be removed-even by pressure-assisted sintering.[27] Localized residual pores on the grain boundary imply well-controlled densification of transparent zirconia ceramics.

The effect of residual pores on transparency is shown in **Fig. 10.** [28] Optical haze H is theoretically calculated using a Mie scattering problem. According to the findings of this study,[28] porosity with optical haze H = 1 % is estimated to be V_{pore} < 10 ppm when d_{pore}=100 nm is assumed, where V_{pore}, d_{pore} are porosity and pore size, respectively. Many small pores of size d_{pore} <10 nm were detected on the grain boundary. However, the effect of scattering must be negligible because scattering efficiency Q_{sca} reaches zero for visible light.[18] Thus, the elimination of pores with a visible wavelength scale is essential for transparency.

Figure 11 shows various transparent zirconia ceramics including colored zirconia ceramics. High transparency with various colors can be obtained by the addition of pigments, such as lanthanoid oxide. The hue can be changed by using a suitable set of pigments, thereby changing the concentration of the pigment, and the size of the sintered body. As transparent zirconia can be molded using a ceramic injection molding (CIM) technique, a complex-shaped body is available. Exterior parts and complex-shaped gem are suitable applications for transparent zirconia ceramics.

Conclusion

Highly transparent zirconia ceramics were

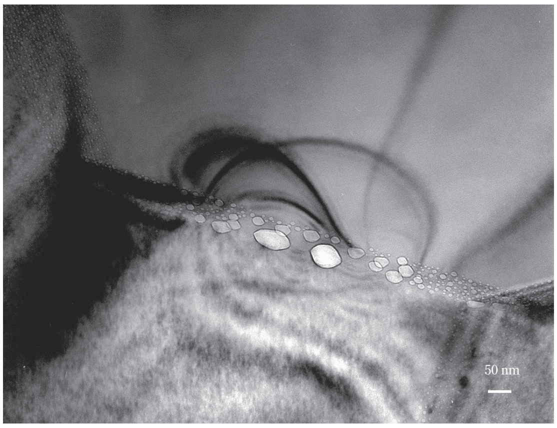

Fig. 9 TEM micrograph of residual pores at grain boundary in transparent zirconia ceramics.

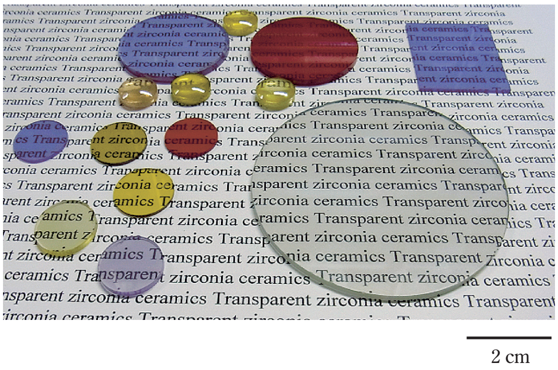

Fig.11 Various transparent zirconia ceramics. The small convex-shaped ceramics were made by a ceramic -injection-molding technique. The others were fabricated by mechanical-pressing methods.

developed and their optical and mechanical properties were comprehensively studied. Theoretical in-line transmission (74 %) was achieved from UV–VIS up to the IR region, and an absorption edge was found at 350 nm for the ultraviolet region, and 8 μm for the infrared region. A high Abbe's number with a high refractive index and large permittivity are superior characteristics compared with other transparent materials. Thus, transparent zirconia ceramics are candidates for high-refractive index lenses, optoelectric devices and infrared windows. Transparent zirconia ceramics also possess excellent mechanical properties. Various colored transparent zirconia can be used as exterior components and for complex-shaped gemstones.

1）R. L. Coble, *U.S. Pat*. 3026210 (1962).

2）M. W. Benecke, N. Olson and J. A. Pask, *J. Am. Ceram. Soc.*, 50, 365–8 (1967).

3）S. K. Dutta and G. E. Gazza, *Mater. Res. Bull.*, 4, 791–6 (1969).

4）R. J. Bratton, *J. Am. Ceram. Soc*., 57, 283–6 (1974).

5）A. Ikesue, I. Furusato and K. Kamata, *J. Am. Ceram. Soc.,* 78, 225–8 (1995).

6）I. W. Donald and P. W. McMillan, *J. Mater. Sci*., 13, 1151–76 (1978).

7）A. Ikesue, T. Kinoshita, K. Kamata and K. Yoshida, *J. Am. Ceram. Soc*., 78, 1033–40 (1995).

8）P. J. Patel, G. A. Gilde, P. G. Dehmer and J. W. McCauley, *AMPTIAC Newsletter.,* 4, 1–5 (2000).

9）U. Peuchert, Y. Okano, Y. Menke, S. Reichel and A. Ikesue, *J. Eur. Ceram. Soc.,* 29, 283–91 (2009).

10）T. Tanaka, *Ceramics*, 41, 687–690, (2006) (in Japanese).

11）A. Krell, T. Hutzler and J. Klimke, *J. Eur. Ceram. Soc*., 29, 207–21 (2009).

12）Wikipedia, "Transparent ceramics," 5 July, 2012 http://en.wikipedia.org/wiki/Transparent_Ceramics

13）F. W. Vahldiek, *J. Less-Common Metals,* 13, 530–40 (1967).

14）K. S. Mazdiyasni, C. T. Lynch and J. S. Smith II, *J. Am. Ceram. Soc.*, 50, 532–37 (1967).

15）K. Tsukuma, *J. Mat. Sci. Lett.*, 5, 1143–4 (1986).

16）U. Anselmi-Tamburini, J. N. Woolman and Z. A. Munir, *Adv. Funct. Mater.* 17, 3267–73 (2007).

17）S. R. Casolco, J. Xu and J. E. Garay, *Scripta Mater.*, 58, 516–9 (2008).

18）K. Tsukuma, I. Yamashita and T. Kusunose, *J. Am. Ceram. Soc.*, 91, 813–8 (2008).

19）H. Zhang, B. N. Kim, K. Morita, H. Yoshida, J. -H. LIM and K. Hiraga, *J. Am. Ceram. Soc*., 94, 2981–2986 (2011).

20）T. Tsukidate and K. Tsukuma, *Ceram. Jpn*., 17, 816–822 (1982).

21）Japanese Patent (Jpn Koukai Tokkyo Kouhou), JP 2011–11970 (in Japanese).

22）Tosoh Corporation, "Powders TZ series," in Zirconia Catalog, Tokyo, Japan, (2003).

23）D. W. McComb, *Phys. Rev. B* 54, 7094–7102 (1996).

24）K. Hayashi, O. Kobayashi, S. Toyoda and K. Morinaga, *Mater. Trans. JIM*, 32, 1024–1029 (1991).

25）R. Apetz and M. P. B. van Bruggen, *J. Am. Ceram. Soc.*,86, 480–6 (2003).

26）I. Yamashita, H. Nagayama and K. Tsukuma, *J. Am. Ceram. Soc.*, 91, 2611–2616 (2008).

27）S. -T. Kwon, D. -Y., Kim, T. -K. Kang and D. N. Yoon, *J. Am. Ceram. Soc*., 70, C69–70 (1987).

28）I. Yamashita and K. Tsukuma, *J. Ceram. Soc. Jpn,* 119, 133–135 (2011).