Light scattering by residual pores in transparent zirconia ceramics

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We studied the effects of residual pores on the transparency of cubic zirconia ceramics by applying Mie scattering theory. The optical haze value H , defined as the diffuse transmission divided by the total forward transmission, was calculated as a function of the pore size (r_{pore}) and the porosity of residual pores (V_{pore}) with sample thickness (t) = 1 mm. Even a small amount of pores critically affect the transparency; $V_{\text{pore}} < 5$ ppm is required to maintain H value within 1%, when $r_{\text{pore}} = 0.05 \mu\text{m}$ is assumed. The theoretical study also revealed that the acceptable amount of residual pores for $H = 1\%$ gradually decreases with an increase in the refractive index of the materials.

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Transparent and translucent ceramics have been studied extensively since the seminal work on translucent alumina polycrystal by Coble in the 1960s.¹⁾ Subsequently, researchers have carried out many studies to develop transparent ceramics, such as MgO ,²⁾ Y_2O_3 ,³⁾ MgAl_2O_4 (spinel),⁴⁾ and $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG).⁵⁾ Various optical applications of transparent ceramics have been proposed, e.g., infrared windows,⁶⁾ Nd laser host materials,⁷⁾ armor applications,⁸⁾ and optical lenses.⁹⁾ Reference 10 gives a comprehensive review of transparent and translucent ceramics.

With its large refractive index, yttria stabilized zirconia (YSZ) single crystals are widely used as artificial gem stones. YSZ ceramics crystallize into a cubic structure and are a candidate for transparent ceramics. Thus, much effort has been dedicated to fabricate transparent cubic zirconia ceramics.^{9),11)–16)} Recently, we developed highly transparent 8 mol % Y_2O_3 -doped ZrO_2 (8Y) ceramics using a novel hot isostatic pressing procedure.¹⁷⁾ **Table 1** lists the optical and physical properties of the transparent zirconia ceramics (8Y) as compared with typical transparent materials.¹⁸⁾ High transparencies with large refractive indices and dielectric constants are unique to transparent zirconia ceramics.

For optical applications, such as laser host materials and lenses, high transparencies are required. As no birefringence exists at the grain boundary for a cubic crystal, residual pores are the primary scattering centers. Although many studies have addressed transparent ceramics, few papers report theoretical studies of residual pores and the resultant transparency.^{17),19)–21)} Thus, it is worthwhile to analyze the transparency as a function of residual pores. In the present work, we theoretically examine transparent zirconia ceramics. The effects of residual pores on the optical haze H , which is practically used for evaluating transparency, are precisely studied with the Mie scattering theory.

The transmission can be expressed by the Lambert–Beer equation:¹⁹⁾

$$T = (1 - R)^2 \exp(-C_{\text{sca}} t) \quad (1)$$

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Table 1. Optical and mechanical properties of transparent zirconia ceramics 8Y, SiO_2 , and sapphire¹⁸⁾

	Transparent zirconia ceramics 8Y	SiO_2 glass	Sapphire
In-line transmission at D65, 1 mm (%)	73	94	86
Haze value at D65, 1 mm (%)	1.5	0.3	0.5
Refractive index at 589 nm (—)	2.20	1.46	1.78
Dielectric constant at 1000 kHz (—)	28	3.8	8.5
Fracture toughness ($\text{MPa}\cdot\text{m}^{0.5}$)	1.7	0.7	3.5
Bending strength (MPa)	250–400	60–80	350–450
Hardness (H_v)	1200	700	1800

Here, R is the reflectivity [—], C_{sca} [m^{-1}] is the effective scattering coefficient, and t is the sample thickness. We assumed that both the in-line and total forward transmissions could be expressed by the Lambert–Beer equation; this assumption seems to be valid for non-multiple scattering systems.²¹⁾

The value of R was calculated using the values of the reflective index of the media (n_{med}) and air (n_{air}). Here, we calculated n_{med} using the Sellmeier formula as a function of wavelength for 8 mol % Y_2O_3 - ZrO_2 .²²⁾

$$R = \frac{(n_{\text{med}} - n_{\text{air}})^2}{(n_{\text{med}} + n_{\text{air}})^2} \quad (2)$$

In this study, only residual pores were candidates for the scattering centers because no birefringence occurred at the grain boundary. Thus, the effective scattering coefficient of the residual pores could be expressed with the porosity and pore radius as follows:¹⁹⁾

$$C_{\text{sca}} = N_{\text{pore}} \cdot G_{\text{pore}} \cdot Q_{\text{sca}} = \frac{3V_{\text{pore}}}{4r_{\text{pore}}} Q_{\text{sca}} \quad (3)$$

Here, N_{pore} is the pore density [m^{-3}], G_{pore} is the geometrical cross section of the pores [m^2], Q_{sca} is the scattering efficiency [—], V_{pore} is the porosity of residual pores [—], and r_{pore} is the radius of the residual pores [m].

Fig. 1. Calculated total forward transmission (broken line), in-line transmission (solid line), and diffuse transmission (dotted line) of transparent zirconia ceramics, assuming $V_{\text{pore}} = 13$ ppm, $r_{\text{pore}} = 0.05 \mu\text{m}$, and sample $t = 1$ mm. The theoretical limit using the Sellmeier formula²²⁾ and experimental data¹⁷⁾ for the in-line transmission are also plotted as solid and open circles, respectively.

According to Mie scattering theory, the scattering coefficient can be calculated by an integration of the amplitude functions $S_1(\theta)$ and $S_2(\theta)$, the vertical and horizontal components of the scattered light, respectively.

$$Q_{\text{sca}} = \frac{1}{G} \int_0^{2\pi} \int_{\theta_1}^{\theta_2} \frac{|S_1(\theta)|^2 + |S_2(\theta)|^2}{k^2} \sin \theta d\theta d\phi \quad (4)$$

For the in-line transmission, we integrated Eq. (4) for the region $\theta_1 = 0$ and $\theta_2 = \pi$ while the total forward transmission was the integration of the backward scattering region, i.e., $\theta_1 = \pi/2$, $\theta_2 = \pi$. All the calculations of Mie scattering were performed using an algorithm written by Bohren and Huffman,²³⁾ coded in Fortran. Details of the calculations are described elsewhere.²¹⁾

Diffuse transmission can be calculated as follows:

$$T_{\text{diffuse}} = T_{\text{total}} - T_{\text{in-line}} \quad (5)$$

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 transparency for transparent materials. The optical haze value H can be defined using the in-line and total forward transmissions.

$$H = \frac{T_{\text{diffuse}}}{T_{\text{total}}} = \frac{T_{\text{total}} - T_{\text{in-line}}}{T_{\text{total}}} \quad (6)$$

We calculated the transmissions of transparent zirconia ceramics using the Mie scattering model as a function of wavelength, neglecting effects of surface scattering. **Figure 1** shows the simulated transmissions and plots experimental data previously reported for in-line transmission.¹⁷⁾ The calculated in-line transmission was in good agreement with the experimental data when we assumed that $V_{\text{pore}} = 13$ ppm and $r_{\text{pore}} = 0.05 \mu\text{m}$. The pore size was almost the same as that of an experimentally observed pore.¹⁷⁾ Although the calculated in-line transmission agrees with the experimental value above 400 nm, a large discrepancy is observed below 400 nm. The absorption edges of YSZ and Fe impurities as previously reported must be responsible for the strong absorption in the UV region.¹⁷⁾

The theoretical transmission is almost constant above 400 nm whereas it gradually decreases with decreasing wavelength

Fig. 2. Calculated transmissions of transparent zirconia ceramics as a function of the residual porosity V_{pore} , assuming an incident wavelength 550 nm, $r_{\text{pore}} = 0.05 \mu\text{m}$, and $t = 1$ mm.

below 400 nm. We estimated the Abbe number to be 33.0 using the Sellmeier formula.²²⁾ Due to the low dispersion of the refractive index, the Abbe number is larger than those of other high refractive materials.¹⁰⁾ The calculated optical haze values H are 4.0, 2.0, 1.1, and 0.67% for 500, 600, 700, and 800 nm, respectively. The optical haze H gradually increases with decreasing wavelength. This trend must arise from the wavelength dependence of the scattering efficiency of the diffuse transmission. In the short wavelength region, light scattering in the forward region is enhanced.

In **Fig. 2**, we show the calculated in-line, total forward, and diffuse transmissions as functions of the porosity, assuming $r_{\text{pore}} = 0.05 \mu\text{m}$. As the porosity increases, the values of the total forward and in-line transmissions decrease. On the other hand, the diffuse transmission increases with increasing porosity; a broad hump appears at 300 ppm. Finally, the diffuse transmission coincides with the total forward transmission; i.e., the in-line transmission reaches zero around $V_{\text{pore}} = 1000$ ppm.

The optical haze values H are estimated to be 0.02, 0.22, 2.19, and 19.9% for 0.1, 1, 10, and 100 ppm, respectively. The H values linearly increase with increasing porosity. V_{pore} values smaller than 5 ppm are required to maintain the H value within 1%, when we assume $r_{\text{pore}} = 0.05 \mu\text{m}$.

Figure 3 shows the relationship between the haze value H with $t = 1$ mm and the porosity as a function of the pore radius at 550 nm. We calculated the haze value H from 0.01 to 0.1 μm in 0.01 μm intervals. As seen in Fig. 3, the H values strongly depend on both the porosity and the pore radius. For the same pore radius, the H value simply increases with increasing porosity, while it decreases with decreasing pore radius, assuming the same porosity. This trend is due to the pore size dependence of the effective scattering coefficient C_{sca} . The effective scattering coefficient C_{sca} is a function of the pore density N_{pore} , the geometrical cross section G_{pore} , and the scattering efficiency Q_{sca} . Although N_{pore} increases with decreasing pore size, Q_{sca} decreases because less Mie scattering occurs in a small pore.¹⁷⁾ A recent study using the spark plasma sintering method also showed that a fine-sized pore gives less effect as compared with pores with sizes comparable to wavelength.¹⁴⁾ Therefore, both miniaturization of the residual pores and their elimination are favorable for promoting transparency.

In order to compare difficulty in being transparent, we systematically calculated the effects of the refractive indices of

Fig. 3. Relationship between the optical haze H and the porosity V_{pore} as a function of the pore radius r_{pore} at 550 nm, assuming $t = 1$ mm. The haze value H is plotted from 0.01 to 0.1 μm at 0.01 μm intervals.

Fig. 4. The required porosities for $H = 1\%$ as a function of the refractive index of the medium; the refractive indices of SiO₂, MgAl₂O₄ (spinel), MgO, Y₃Al₅O₁₂ (YAG), Y₂O₃, and 8Y-ZrO₂ are also shown as open circles. For the calculation, we assumed $r_{\text{pore}} = 0.05 \mu\text{m}$, wavelength = 550 nm, and $t = 1$ mm.

the media on the optical haze H with $t = 1$ mm at 550 nm. **Figure 4** depicts the results, plotting the required porosities for $H = 1\%$ against the refractive indices of the media. Results of typical transparent materials are also plotted as open circles. Since the absolute value of transmissions includes the reflection loss, it is difficult to directly compare the transparencies of different materials. Thus, the optical haze shown in Fig. 4 corresponds to the net difficulty in being transparent. The required porosity decreases with increasing refractive index of the media; the required porosities are $V_{\text{pore}} = 24.9, 10.5, 10.2, 8.1, 6.8,$ and 4.6 ppm for SiO₂, spinel, MgO, YAG, Y₂O₃, and 8Y-ZrO₂, respectively. This trend is due to the difference in the scattering efficiencies Q_{sca} . Q_{sca} increased with the refractive index of the material. The porosity values necessary to make these compounds transparent with $H = 1\%$ are almost half of those of typical transparent ceramics, such as spinel and MgO. Although there have been many attempts to prepare highly

transparent zirconia 8Y, they have not been successful. The difficulty in fabricating highly transparent zirconia ceramics may be attributed to the strong scattering effect due to high refractive indices.

In summary, we studied the effects of residual pores on the transparencies of cubic zirconia ceramics by applying Mie scattering theory. The transmissions calculated from the model are in good agreement with experimental data. Even a small amount of pores critically affect the transparency; $V_{\text{pore}} < 5$ ppm is required to maintain the H value within 1%, assuming $r_{\text{pore}} = 0.05 \mu\text{m}$. Both miniaturization and elimination of the residual pores are favorable for transparency. The theoretical study also showed that the acceptable porosities for transparency decreases with increasing refractive indices of the materials. Acceptable porosity for $H = 1\%$ is almost half compared with typical transparent ceramics, such as spinel and MgO.

References

- 1) R. L. Coble, U.S. Pat. 3026210 (1962).
- 2) M. W. Benecke, N. Olson and J. A. Pask, *J. Am. Ceram. Soc.*, **50**, 365–368 (1967).
- 3) S. K. Dutta and G. E. Gazza, *Mater. Res. Bull.*, **4**, 791–796 (1969).
- 4) R. J. Bratton, *J. Am. Ceram. Soc.*, **57**, 283–286 (1974).
- 5) A. Ikesue, I. Furusato and K. Kamata, *J. Am. Ceram. Soc.*, **78**, 225–228 (1995).
- 6) I. W. Donald and P. W. McMillan, *J. Mater. Sci.*, **13**, 1151–1176 (1978).
- 7) A. Ikesue, T. Kinoshita, K. Kamata and K. Yoshida, *J. Am. Ceram. Soc.*, **78**, 1033–1040 (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**, 283–291 (2009).
- 10) A. Krell, T. Hutzler and J. Klimke, *J. Eur. Ceram. Soc.*, **29**, 207–221 (2009).
- 11) F. W. Vahldiek, *J. Less-Common Met.*, **13**, 530–540 (1967).
- 12) K. S. Mazdiyasn, C. T. Lynch and J. S. Smith, II, *J. Am. Ceram. Soc.*, **50**, 532–537 (1967).
- 13) K. Tsukuma, *J. Mater. Sci. Lett.*, **5**, 1143–1144 (1986).
- 14) U. Anselmi-Tamburini, J. N. Woolman and Z. A. Munir, *Adv. Funct. Mater.*, **17**, 3267–3273 (2007).
- 15) S. R. Casolco, J. Xu and J. E. Garay, *Scr. Mater.*, **58**, 516–519 (2008).
- 16) J. E. Alaniz, F. G. Perez-Gutierrez, G. Aguilar and J. E. Garay, *Opt. Mater.*, **32**, 62–68 (2009).
- 17) K. Tsukuma, I. Yamashita and T. Kusunose, *J. Am. Ceram. Soc.*, **91**, 813–818 (2008).
- 18) H. Nagayama, M. Kudoh, N. Shinozaki, I. Yamashita and K. Tsukuma, “Development of Colored Zirconia Ceramics,” *TOSOH Research & Technology Review*, **53**, 53–56 (2009) [in Japanese].
- 19) J. G. J. Peelen and R. Metselaar, *J. Appl. Phys.*, **45**, 216–220 (1974).
- 20) R. Apetz and M. P. B. van Bruggen, *J. Am. Ceram. Soc.*, **86**, 480–486 (2003).
- 21) I. Yamashita, H. Nagayama and K. Tsukuma, *J. Am. Ceram. Soc.*, **91**, 2611–2616 (2008).
- 22) D. L. Wood, K. Nassau and T. Y. Kometani, *Appl. Opt.*, **29**, 2485–2488 (1990).
- 23) C. F. Bohren and D. R. Huffman, “Absorption and Scattering of Light by Small Particle,” Wiley, New York (1983).