● Highly translucent, high strength La-doped zirconia ceramics.

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1. Introduction

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, Y_2O_3, $MgAl_2O_4$ (spinel), and $Y_3Al_5O_{12}$ (YAG).[2] Improving light transmittance of zirconia has also been attracting much attention because of its industrial importance.[3-5] For example, fully stabilized zirconia (FSZ) is extensively studied since cubic crystal structure can be transparent. Although highly transparent ceramics with transmittance value that reaches that of single crystal was developed for cubic zirconia ceramics[5], its mechanical properties are poor because transformation toughening mechanism does not work. Its bending strength is about 300 MPa; fracture toughness is about 1.8 MPa·m$^{0.5}$. On the other hand, tetragonal zirconia polycrystal (TZP), such as 3Y, is well known as high-strength and high-toughness ceramics. However, with poor transmission, its typical total forward transmission at D65 is 36 % at 1mmt thickness. We have developed novel translucent zirconia ceramics with both high-translucency and high-strength. This is the first report regarding our novel translucent zirconia ceramics. In this technical report, optical and mechanical properties are briefly introduced.

2. La-doped translucent zirconia ceramics.

Highly translucent zirconia ceramics with high strength was developed using lanthanum (La) as a novel stabilizer. The sintering process of the translucent zirconia is similar to that of transparent zirconia ceramics.[5] The ceramics was sintered using hot isostatic pressing (HIP); high temperature sintering (1750 ℃) is also required.

Figure 1 shows the developed translucent zirconia ceramics. Colorless translucent ceramics is obtained. The sample size is 1 mm thick with a diameter of 16 mm. The optical and mechanical properties are tabulated in **Table 1** Density of the sintered body is 6.08 g/cm^3, calculated by the Archimedean method; its density is almost same as that of 3Y-TZP. The total forward transmission of translucent zirconia at D65 is >60 % (thickness 1mmt), and the internal transmission (without reflection loss) reaches 80 %. This translucency overwhelms that of 3Y-TZP, and the translucency is comparable with that of translucent alumina ceramics.[6] The bending strength is estimated to be about 800-1000 MPa, much higher than that of cubic structure

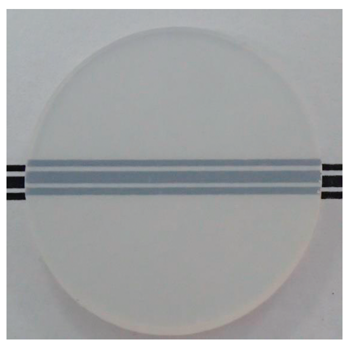


Figure 1 La-doped translucent zirconia ceramics (∅16 mm in diameter and 1 mmt in thickness)

Table 1 Optical and mechanical properties of La-doped translucent zirconia ceramics sintered at 1750 ℃.

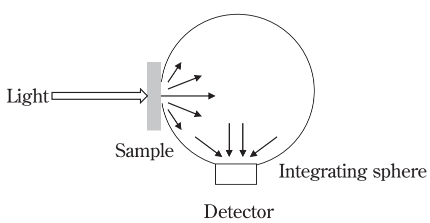
Density	6.08 g / cm^3
Total forward transmission [1mmt, D65]	60 %
Internal transmission [1mmt, D65]	80 %
Three-point bending strength	850 MPa
Biaxial strength	1000 MPa
Fracture toughness	3.3 MPa·m$^{0.5}$
Hardness [Hv10]	1200
Thermal conductivity	1.8 W / m·K

transparent zirconia. [5]

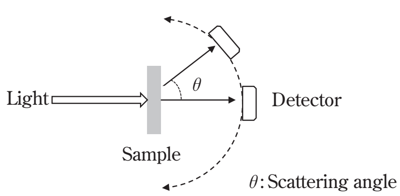
3. Optical properties

Detailed transmission properties were measured using spectrophotometer and photogoniometer. Schematic figure of the optical system is shown in **Figure 2** The sample was ground to a thickness of 1 mm and thoroughly polished on both sides to eliminate surface scattering for the subsequent measurements. The total forward transmission of ultraviolet-visible (UV-VIS) region was measured using a double-beam spectrophotometer (V-650, JASCO Corporation) with a wavelength range of 200-800 nm. **Figure 3** shows wavelength dependence of total forward transmission of the ceramics. High total forward transmission in visible light region was observed; the transmission at 600 nm is about 65 %. In the 700-800 nm region, the transmission nearly reaches a theoretical value estimated from reflection loss (≅ 26 %). The absorption edge of the ceramics is estimated to be 250 nm, which is almost same as that of YSZ single crystal. The total forward transmission of La-doped zirconia ceramics is comparable to that of translucent alumina ceramics.

Scattered light profile of the transmitted light was also evaluated using photogoniometer (GP-200, Murakami Color Research Laboratory) . Halogen lamp was used as light source for the photogoniometer. **Figure 4** shows normalized amplitude of scattered light. Scattered light mainly focuses on direct transmission region (θ =0), displaying good transparency. Thus, developed La-doped zirconia ceramics owns excellent visible-light transmission properties.



(a) Total forward transmission.



(b) Photogoniometer.

Figure 2 Optical system of (a) total forward transmission and (b) photogoniometer

4. Mechanical properties

Three-point bending strength was measured following JIS-R-1601 with a gauge length of 30 mm and a cross-head speed of 0.5 mm/min. The fracture toughness was estimated using the single-edge precracked beam (SEPB) method following JIS-R-1607. The typical bending strength and fracture toughness of the ceramics are estimated to be about 850 MPa and 3.30 MPa·$m^{0.5}$, respectively. Biaxial flexure strength following ISO/DIS6872 is about 1000 MPa. Small discrepancy between three-bending strength and biaxial strength was found. This may attribute to difference of effective volume tested and surface flaws due to machining process. Vickers hardness following JIS R1610 is 1200, almost same as that of 3Y-TZP. Thermal conductivity following JIS R1611 is estimated to be 1.8 W/m·K, slightly lower than as that of 3Y-TZP (2.4 W/

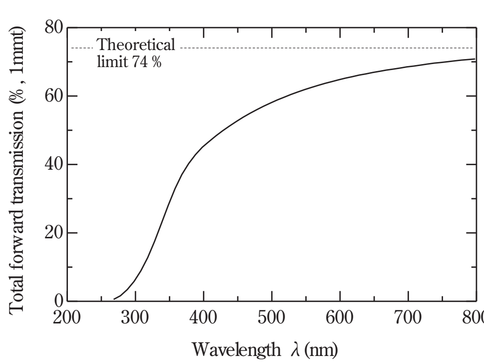


Figure 3 Total forward transmission (sample thickness 1mm) of La-doped zirconia ceramics

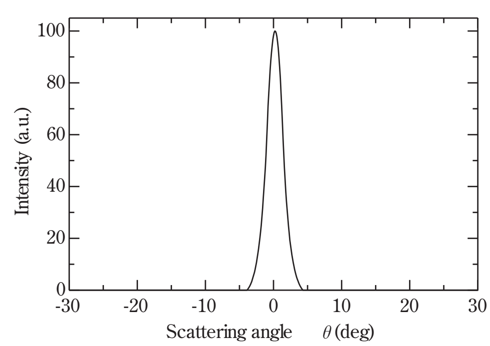


Figure 4 Scattered light profile of the transmitted light at D65 (sample thickness 1mm)

m·K).

Bending strength and fracture toughness of developed zirconia are much higher than that of transparent zirconia. It excels that of translucent alumina in bending strength.[7] We can conclude that developed novel translucent zirconia ceramics shows excellent mechanical properties as compared to previous transparent/translucent ceramics.

4. Structural properties

In order to clarify a mechanism of its translucent and strengthened nature, precise structural study has been conducted by means of high-resolution transmission electron microscopy (HR-TEM) and Raman spectrometric methods. **Figure 5** shows high resolution TEM-EDS mapping of lanthanum (La). The nano-sized tetragonal and cubic domain (<50 nm) were observed. Detailed structural studies show the novel zirconia ceramics was crystallized into fluorite structure, and tetragonal ($P4_2/nmc$) and cubic ($Fm3m$) phase were detected. The lanthanum was detected in cubic phase, but not in tetragonal phase. The phase separation size is much smaller than that of visible light wavelength. According to light scattering theory, there is no scattering in nano-size scattering origin. The effect of the scattering must be negligible because scattering efficiency Q_{sca} reaches zero.[4] Thus, a reduction of the size of heterogeneous structure reduces effect of light scattering; it can be attributed to the high translucency.

Figure 6 shows Raman spectra of fractured and polished surface. Additional peak due to monoclinic phase was clearly found on fracture surface while cubic and tetragonal phases were observed for polished surface. Raman spectra of the fracture surface clearly shows that the tetragonal phase underwent transformation into monoclinic phase under tensile stress. Therefore transformation toughening mechanism is responsible for high-strength and toughness of the La-doped translucent zirconia.

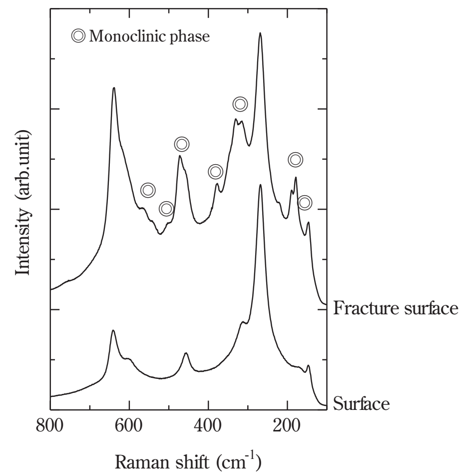


Figure 6 Raman spectra of fractured surface and polished surface. Peak of monoclinic phase indicates as double circle

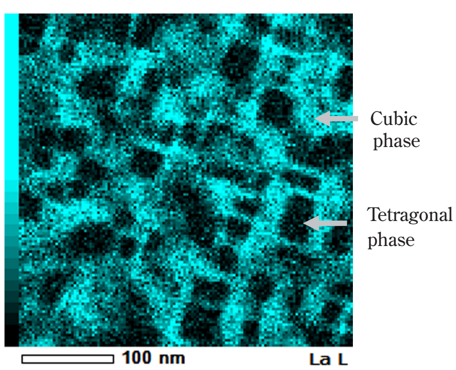


Figure 5 High resolution EDS mapping of La-atom. Blue area represents cubic phase including La, while black areas is tetragonal phase

Conclusion

We have pioneered highly translucent zirconia ceramics with high strength using lanthanum (La) as a novel stabilizer. Its bending strength is much higher than that of cubic structure transparent zirconia, and

Figure 7 Translucent La-doped zirconia made by ceramics injection molding (CIM) technique (30 mm×25 mm and 1 mmt in thickness)

its translucency also overwhelms that of 3Y-TZP. The translucent zirconia can be molded using ceramic injection molding (CIM) technique (**Figure 7**) to make complex shaped bodies. The La-doped translucent zirconia can be used as light transmittance material where high mechanical properties are required.

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