Transparent polycrystalline nanoceramics consisting of triclinic Al_2SiO_5 kyanite and Al_2O_3 corundum

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Abstract

Transparent polycrystalline nanoceramics consisting of triclinic Al_2SiO_5 kyanite (91.4 vol%) and Al_2O_3 corundum (8.6 vol%) were fabricated at 10 GPa and 1200 – 1400 °C. These materials were obtained by direct conversion from Al_2O_3 - SiO_2 glasses fabricated using the aerodynamic levitation technique. The materials obtained at 10 GPa and 1200 °C shows the highest optical transparency with a real in-line transmission value of 78% at a wavelength of 645 nm and a sample-thickness of 0.8 mm. This sample shows equigranular texture with an average grain size of 34 ± 13 nm determined by Transmission Electron Microscopy observations. The optical transparency increases with decreasing mean grain size of the constituent phases. The relationship between real in-line transmission and grain size is well explained by a grain-boundary scattering model based on a classical theory.

Introduction

Transparent polycrystalline ceramics are alternative materials for transparent glasses and single crystals, e.g. due to their high shaping and doping flexibility, or excellent mechanical properties¹. Numerous studies have been performed to fabricate transparent ceramics. Transparent spinel (MgAl_2O_4) ceramic² is the most popular example and other transparent ceramics with spinel structure are, e.g. γ - AlONs ³ and cubic silicon nitride⁴. Cubic crystals (e.g. spinel and garnets⁵) are advantageous to fabricating transparent polycrystalline ceramics because they are not birefringent. Commonly, polycrystalline ceramics made of birefringent crystals are opaque due to successive refractive index mismatch. This effect weakens the optical transparency⁶.

Polycrystalline alumina is the most widely studied non-cubic transparent ceramic⁷. The visible in-line transmission is higher than 80% of the theoretical maximum⁶⁻⁹ attributed to full

densification (>99.99%), small grain sizes (sub-micrometer), and small refractive index difference ($\Delta n_{\text{max}} = 0.008$) for different polarizations⁸.

Apetz and van Bruggen⁸ proposed a light-transmission model based on the Rayleigh–Gans–Debye light-scattering theory. This model is applicable to any type of polycrystalline material with low structural anisotropy⁸ and predicts the optical transparency of polycrystalline birefringent ceramics depending on the grain size, porosity and sample thickness. Following this model⁸, the polycrystalline materials with a birefringence larger than that of alumina crystals can also be transparent if the grain sizes are in the nanometer-scale and the porosity is close to zero. By direct crystallization of glass prepared by the aerodynamic levitation technique, Allix and others¹ reported fabrication of transparent polycrystalline orthorhombic BaAl_4O_7 .

In the present study, two experimental techniques were combined to obtain ceramics with grain sizes in the nm-scale: the preparation of the glass starting materials using the aerodynamic levitation technique¹, and the high-pressure glass crystallization to nanopolycrystalline material¹⁰. Transparent nanopolycrystalline kyanite (Al_2SiO_5) ceramics with a small amount of corundum (α -alumina) were obtained under high pressure and temperature (high-*PT*). Kyanite crystallizes in the triclinic system and has a birefringence ($0.012 - 0.016$)¹¹ about two times higher than alumina (0.008)⁸. The present experimental data can be well explained by the theoretical model⁸.

Experimental procedure

Aluminosilicate glasses were fabricated as starting materials using an aerodynamic levitation (ADL) furnace at the Institute of Industrial Science, University of Tokyo, Japan. The glasses were produced from a 1:1 molar mixture of alumina ($\alpha\text{-Al}_2\text{O}_3$) and silica powders (99.99% purity) with a bulk composition equal to that of Al_2SiO_5 kyanite. Further details of the glass

fabrication are shown elsewhere¹². Glasses with more than 30 mol% of Al₂O₃ are difficult to fabricate in bulk form by conventional melting processes because of their low glass-forming ability and high melting temperatures¹². The chemical composition of an aliquot of the starting glass was quantified by an electron probe microanalyzer (JEOL JXA 8200, Akishima, Japan) at the GEOMAR, Helmholtz Centre for Ocean Research Kiel, Germany. The chemical composition is homogenous for the entire glass sphere with 57.4 ± 0.5 mol% Al₂O₃ and 42.6 ± 0.5 mol% SiO₂. This result documents an excess of silica evaporated during the ADL process.

High-*PT* runs were performed using a Kawai-type hydraulic press equipped with a Walker-type module (mavo press LPR 1000-400/50, Max Voggenreiter GmbH, Mainleus, Germany) at Deutsches Elektronen-Synchrotron (DESY, Hamburg, Germany). The second stage anvils were tungsten carbide cubes with a truncated edge length of 11 mm. A semi-sintered MgO with 5% Cr₂O₃ octahedron (edge length of 18 mm) was used as the pressure medium. The fabricated starting glasses have a diameter of 2.3 - 2.5 mm and are polished to a thickness of 1.2 mm. Further details of the high-*PT* runs are shown elsewhere¹³. Three samples were fabricated at 10 GPa and 1200, 1400, and 1600 °C, encapsulated within inert platinum.

X-Ray diffraction (XRD) measurements were performed at P02.1¹⁴, PETRA III at DESY. The X-rays (~60 keV, 0.20725 Å) were monochromatized by a diamond and a silicon crystal (111 lattice) in Laue geometry. The incident beam-size was $\sim 200 \times 200$ μm and the Debye rings of the sample were recorded by an area detector (XRD 1621; PerkinElmer, USA). The sample-to-detector distance (~1082 mm) and the detector orthogonality were calibrated using the diffraction pattern of CeO₂ powder.

Real in-line transmission (RIT) was measured using a modified spectrophotometer (Lambda 900 UV/VIS/NIR, PerkinElmer, USA) at the Institute for Material Sciences, Kiel University, Germany. The samples were polished down to 1 μm and the thickness was 0.8 mm. The incident light beam was adjusted to hit the plain centres of the samples perpendicularly. The

beam size on the sample was 0.45×0.25 mm and the slit size before the detector compartment was 1 mm. A silica glass was used as the external standard for the experimental setup.

Samples were analysed by a Transmission Electron Microscope (TEM) FEI Tecnai F30 G² STwin (FEG, 300 kV) at the Institute for Materials Science, Kiel University, Germany. The samples were prepared to ~60 nm thick foils using the focused ion beam (FIB) technique (Helios NanoLab Dualbeam, FEI, USA). The sample synthesized at 1200 °C was additionally analysed by a TEM (JEM-2010, JEOL) operating at 200 kV at Geodynamics Research Center, Ehime University, Japan. Images at lower magnifications were recorded to yield best possible statistic averages of the grain sizes. The sample synthesized at 1200 °C exhibits grain sizes below 50 nm. Grain sizes were estimated by a direct measurement of more than 80 grains that appear in black (consistent with the Bragg condition)¹⁰. Grain sizes of the samples synthesized at higher temperatures (1400 and 1600 °C) were larger and grain boundaries clearer to identify. Thus, to determine the grain sizes of these samples the intercept method was used on more than 400 intercepts per each sample synthesized at 1400 °C and 1600 °C, respectively¹⁰. Elemental mappings of the samples were performed in scanning TEM (STEM) mode using an EDX detector (Si/Li, EDAX).

Results

Figure 1a shows a photograph of the three recovered samples and a starting aluminosilicate glass. The starting glass is transparent and the contained pores disappeared during the high-*PT* synthesis. The sample synthesized at 1200 °C is highly transparent. The transparency decreases with increases in the synthesis temperature so that the sample synthesized at 1600 °C is opaque/white.

Figure 1b shows X-ray diffraction (XRD) patterns of the starting material and the recovered samples. The low and flat background intensity for all recovered samples indicates that these

are fully crystalline. The XRD patterns show the presence of kyanite in all samples. The formation of kyanite at these conditions (1200 – 1600 °C and 10 GPa) is consistent with previously reported phase relations of Al_2SiO_5 ¹⁵. The samples synthesized at higher temperature (1400 and 1600 °C) show sharp reflections of α -alumina. The XRD reflections of the sample synthesized at 1200 °C are much broader and especially the reflections of α -alumina are weaker that only the 113 reflection of α -alumina can be clearly observed. Other α -alumina reflections (104, 110) are present but are partly overlapped by reflections from kyanite because of the broadening. XRD profile-fitting for all samples using kyanite and α -alumina as the constituting phases allows to explain the patterns. The presence of α -alumina is consistent with the chemical composition of the starting glass with an excess of Al_2O_3 . Using these XRD patterns, unit cell parameters of kyanite and, from the more intense pattern of the samples obtained from 1400 and 1600 °C, of α -alumina were calculated (Table 1). The values are consistent with those of pure compositions^{16,17} (Al_2SiO_5 and Al_2O_3), suggesting that the recovered sample consists of Al_2SiO_5 kyanite and α - Al_2O_3 alumina. Since the chemical composition of the starting glass was quantitatively measured, a mass-balance calculation was used to determine the volume fractions of these two phases in the samples resulting in 91.4 vol% of kyanite and 8.6 vol% of α -alumina. The bulk density was measured by the Archimedes method to be 3.68 ± 0.02 , 3.70 ± 0.04 and 3.71 ± 0.03 g/cm³ for the samples synthesized at 1200, 1400 and 1600 °C, respectively. These values are consistent with the calculated density (3.70 g/cm³) of a composite material with the same composition.

Figure 1c shows the determined RIT values as a function of wavelength. The RIT values of the samples synthesized at 1200 and 1400 °C sharply increase with the wavelength below the bandgap energy of kyanite¹⁸ (5.8 eV = 214 nm). The sample synthesized at 1200 °C shows the highest optical transparency and the RIT value at a wavelength of 645 nm is 78%. This value is higher than those of randomly-oriented transparent alumina ceramics⁶⁻⁸ with sub-micrometer

grain sizes and as high as that of transparent grain-oriented alumina ceramic⁹. The sample synthesized at 1600 °C is opaque for visible light.

High Angle Annular Dark Field-Scanning TEM (HAADF-STEM) observations were performed to determine the grain sizes of the recovered samples (Figure 2). All the samples show equigranular texture and the grain size increases with the synthesis temperature from 34 ± 13 nm at 1200 °C-sample; 69 ± 17 nm at 1400 °C to 611 ± 170 nm at 1600 °C. For the STEM image of the sample synthesized at 1200 °C, some grain boundaries cannot be distinguished precisely due to overlapping of grains which are smaller than the thickness of the FIB lamella (~60 nm). For characterization of the porosity, further bright-field TEM (BF-TEM) images were evaluated, in which no residual porosity could be detected. Elemental mapping of silicon and aluminum using the STEM mode reveal the presence of randomly distributed aluminum-enriched domains which appear congruent to some grains in all the samples. These observations are consistent with the results of the XRD patterns (Figure 1b) showing the presence of kyanite with α -alumina.

Discussion

The present results show that the RIT of polycrystalline aggregates of kyanite (91.4 vol%) and α -alumina (8.6 vol%) increases with decreasing grain size (Figure 1c and Figure 2). To interpret these experimental data, a light scattering model from Apetz and van Bruggen⁸ was employed. This model is based on the Rayleigh-Gans-Debye light-scattering theory and predicts the RIT of birefringent, non-porous polycrystalline materials as follows: $RIT = (1 - R_S) \exp(-3\pi^2 r \Delta n^2 d / \lambda_0^2)$, where R_S describes the reflection loss at the two sample surfaces at normal incidence (calculated using the refractive index n), $2r$ is the grain size, Δn is the mean birefringence, d is the sample thickness, and λ_0 is the wavelength of light. In the present study, the RIT was calculated using $d = 0.8$ mm and $\lambda_0 = 645$ nm which are the same values as those employed by Apetz and van Bruggen for alumina⁸. This model was verified on the optical uniaxial α -alumina with a statistical approximation of the mean birefringence to be 2/3 of the maximum birefringence ($\Delta n_{\max} = 0.008$). The authors showed an excellent agreement between the modelled and experimental data for polycrystalline alumina⁸. For optical biaxial crystals, which are birefringent in all directions, like kyanite ($\Delta n_{\max} = 0.012 - 0.016$)¹¹, this approximation tends to underestimate the mean birefringence. Applied to the kyanite-based ceramics a mean birefringence Δn of 0.013 results in good agreement of the measured and modelled RIT values (Figure 3). That the refractive index mismatch between kyanite and α -alumina enhanced the mean birefringence of these composites was not detected. The sharp decrease of RIT with increasing grain size can be well explained by the model. The theoretical models for garnet (cubic) and alumina (trigonal) are also shown for comparison. The RIT of polycrystalline non-birefringent cubic crystals is independent of grain size and only depends on the properties of the single crystal. The RIT value of polycrystalline alumina⁸ at a grain size of 300 nm is 71%, while that of polycrystalline kyanite-alumina is calculated to be 20%. Highly

transparent kyanite-based ceramics with an RIT above 70% can only be obtained when the grain size is less than 60 nm and the porosity is close to zero.

Conclusions

Within this study, a transparent polycrystalline aggregate of Al_2SiO_5 kyanite (91.4 vol%) and Al_2O_3 corundum (8.6 vol%) was fabricated at 10 GPa and 1200 °C from aluminosilicate glass prepared with an aerodynamic levitation (ADL) furnace. This study demonstrated the excellent transparency of polycrystalline non-cubic crystals (even triclinic, optically biaxial crystals), which are more anisotropic than alumina at grain sizes less than 100 nm. A combination of bulk glass preparation using an ADL furnace and high-*PT* treatment can provide a potential platform for fabrication of transparent ceramic components. The ADL technique enables us to fabricate a variety of glasses with different compositions, even those with low glass-forming ability¹² and the high-*PT* conversion is beneficial to producing bulk nanoceramics¹⁰. Various transparent nanoceramics with enhanced properties (e.g. high hardness^{10,19}) may be produced on this platform.

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Figure captions

Figure 1 (a) A photograph of a starting glass and the recovered samples. The distance between the samples and the printed letters (“Al₂SiO₅”) is 1 mm. (b) X-ray diffraction patterns of the starting glass (grey line) and of the samples fabricated at 10 GPa and 1200 °C (blue line), 1400 °C (green line), and 1600 °C (red line). (c) Real In-line transmission of the recovered

samples: 1200 °C (blue); 1400 °C (green); 1600 °C (red), and silica glass as an external reference material (black).

Figure 2 HAADF-STEM images of the recovered samples fabricated at 10 GPa and 1200 °C, 1400 °C and 1600 °C. The grain size increases with the synthesis temperature. The sample from the lowest synthesis temperature of 1200 °C has an average grain size of $\sim 34 \pm 13$ nm. This sample shows a very high transparency. The sample synthesized at 1400 °C exhibits nano-sized grains of $\sim 69 \pm 17$ nm and the sample synthesized at 1600 °C has the highest average grain size of $\sim 611 \pm 170$ nm. The insets show EDS elemental mapping analysis for silicon (yellow) of the corresponding samples. Back areas with no silicon concentration correspond to α -alumina.

Figure 3 RIT values of the composites of kyanite and α -alumina. A theoretical model⁸ of a polycrystalline kyanite-alumina ceramic was adapted with a birefringence (Δn) of 0.013 (blue line). In this model, the reflection loss was calculated with the mean birefringence of the composite $n = 1.72$ and the thickness was set to be 0.8 mm. Theoretical models of α -alumina⁸ ($\Delta n = 0.005$, orange line) and of non-birefringent garnet (violet dashed line) are also shown for comparison.

Table 1. Unit cell parameters of the kyanite and α -alumina in the recovered samples

	T (°C)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)
H117 ky	1200	7.125(8)	7.855(6)	5.565(13)	89.7(3)	100.9(3)	106.1(1)	293.4(7)
H185 ky	1400	7.118(4)	7.846(3)	5.579(7)	90.1(2)	101.3(2)	105.9(1)	293.3(4)
H165 ky	1600	7.116(4)	7.844(3)	5.577(6)	90.1(2)	101.3(2)	105.9(1)	293.1(4)
Al ₂ SiO ₅ ky (ref. 16)		7.126(1)	7.852(1)	5.572(1)	89.22(2)	101.11(2)	106.03(1)	293.60(9)
H117 α -alumina	1200	-	-	-	-	-	-	-
H185 α -alumina	1400	4.769(1)	-	13.00(1)	-	-	-	256.0(3)
H165 α -alumina	1600	4.766(1)	-	13.00(1)	-	-	-	255.9(2)
α -Al ₂ O ₃ (ref. 17)		4.7657(9)	-	13.010(14)	-	-	-	255.89(2)

ky = kyanite; T = synthesis temperature at 10 GPa. Errors in the last decimal place are in parentheses.