Microstructural effects on hardness and optical transparency of birefringent aluminosilicate nanoceramics

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Abstract

Transparent nanoceramics, synthesized at extreme conditions of high pressure and temperature, are new classes of materials highly attractive for photonic applications, such as optical windows, which require additional increased hardness and toughness. In this study, mechanical properties of transparent polycrystalline nanoceramics consisting of triclinic Al2SiO5 kyanite (~91.4 vol%) and trigonal Al2O3 corundum (~8.6 vol%) fabricated at high pressure (10 GPa) and temperature (1200-1400°C) were investigated. It is already known that the optical transparency of kyanite-based nanoceramics increases with decreasing average grain size. The present study shows that the hardness of these ceramics increases with decreasing grain sizes down to ~70 nm according to the Hall-Petch strengthening. This grain size seems to mark a transition range where an inverse Hall-Petch effect is indicated due to signs of a moderate hardness decrease at a smaller grain size of ~35 nm. The observed hardness-grain size relation can fairly be described by an existing composite model, which considers the crystals to be harder than the noncrystalline grain boundaries. Within the range of average grain sizes examined, the kyanite habit changes from more equant to more columnar. This behavior is associated with the observed strong crack deflection by the columnar kyanite grains with aspect (length to diameter) ratios ranging from ~2 to 10 and may positively affect the fracture toughness.

KEYWORDS
alumina, aluminosilicates, Hall-Petch, mechanical properties, microstructure, nanomaterials
1 | INTRODUCTION

Optically transparent single crystals and glasses are widely used for photonic applications, for example, as active media in high-energy lasers or as optical lenses. Since most of these materials are fragile, there is a strong demand for mechanically durable transparent solids. Polycrystalline ceramics or composites can fulfill this demand, because their unique microstructure can enhance the mechanical properties, for example, hardness and fracture toughness. Common polycrystalline ceramics are opaque, even when composed of intrinsically transparent crystals. To obtain very high optical transparency, the microstructure must impede the presence of light scattering centers. These scattering centers arise from refractive index mismatch between constituting phases. This applies in particular for grain boundaries, pores, and other secondary phases in the polycrystalline ceramics, but also among optically anisotropic noncubic crystals themselves. Light scattering models, based on the Rayleigh-Gans-Debye scattering theory, predict that polycrystalline materials consisting of randomly orientated crystals, which are optically anisotropic (birefringent), can be transparent if the grain sizes are decreased to the sub-micrometer scale and the porosity is close to zero. Several studies demonstrate that the material hardness can simultaneously be enhanced by reducing the grain size following the Hall-Petch relation or by fabricating composite ceramics, in which the second phase is harder than the matrix.

Transparent polycrystalline noncubic alumina, which exhibits a positive correlation between decreasing grain sizes and increasing hardness as well as optical transparency, has been extensively investigated. Krell et al. fabricated transparent alumina ceramics with a high hardness (HV = 20-21 GPa) and a high optical in-line transmission (55%-65%) using hot pressing sintering. The high transparency is attributed to small grain sizes (400-600 nm), low porosity, and the low to moderate birefringence (Δn = 0.008). Nishiyama et al. synthesized even harder (HV = 25.5 GPa) transparent fully dense nanocrystalline alumina with higher in-line transmission (58%-78%) at a smaller average grain size (150 nm) using a high-pressure high-temperature (high-PT) synthesis approach.

Nanoceramics composed of triclinic kyanite crystals (Δn = 0.012-0.016) with small amounts of trigonal α-alumina (Δn = 0.008) crystals were successfully fabricated by the high-PT crystallization from glass. These composites are fully crystallized, have an isotropic microstructure with average grain sizes of several hundred to a few tens of nanometers and are highly transparent with a real in-line transmission (RIT) of 78% (at a light wavelength of 645 nm), which is close to that of cubic polycrystalline ceramics. Such a high transparency is remarkable, since kyanite single crystals are optical biaxial and birefringent in all directions (nmax = 0.012-0.016). Note that the main phase kyanite crystallizes in the low-symmetry triclinic system consisting of an array of AlO6 octahedra and SiO4 tetrahedra and has a high anisotropy. Since these samples cover a wide range of grain sizes and very narrow grain size distribution in each sample, investigations on the material hardness will provide important information about the controls of the microstructure on the transparency-hardness relationship of polycrystalline ceramics. In the present study, this relationship is investigated on triclinic kyanite-based nanoceramics.

2 | EXPERIMENTAL METHODS

The starting materials in this study were prepared according to procedures previously described in Gaida et al. In brief, synthetic aluminosilicate (Al2O3-SiO2) glasses were prepared by a container-less aerodynamic levitation method in a high-temperature furnace installed at the Institute of Industrial Science, Tokyo (Japan). The quantitative chemical composition of the starting glass was determined to be homogenous for the entire glass sphere with 57.4 ± 0.5 mol% Al2O3 and 42.6 ± 0.5 mol% SiO2. Additional details can be found elsewhere.

High-pressure synthesis of the glasses into nanocrystalline ceramics was carried out using a previously installed Kawai-type hydraulic press equipped with a Walker-type module (mavo press LPR 1000-400/50; Max Vogenreiter GmbH) and a currently installed 6-ram large volume press (mavo press LPQ6 1500/100; Max Vogenreiter GmbH), at the P61B beamline at Deutsches Elektronen-Synchrotron (DESY). Cemented tungsten carbide (WC) second stage anvils were used with truncated edge lengths of 11 and 7 mm, respectively. These anvils compressed a pressure medium consisting of a 5% Cr2O3 doped octahedral MgO with edge length of 18 mm (and 14 mm for the 6-rams LVP) with cylindrical sample and resistive heater (LaCrO3) inside. Further details of the high-PT syntheses are described elsewhere. The sample with highest transparency was reproducible synthesized in three experiments at 10 GPa and 1200°C.

Phases were identified from synchrotron X-ray diffraction patterns of the samples measured at PETRA III (P02.1, λ = 0.2073 Å) at DESY, at the European Synchrotron Radiation Facility (ESRF) in France (ID06-LVP, λ = 0.2024 Å), and at the Aichi Synchrotron Radiation Center (BL5S1, λ = 0.7497 Å) in Japan, and by Raman spectroscopy performed at the Department of Materials Physics at Nagoya University (Japan). Transmission electron microscopy (TEM) investigations were performed with a FEI Tecnai F30 STwin (FEG, 300 kV) installed at the Institute for Materials Science at Kiel University (Germany). Details of microstructure characterization and light transmission measurement can be found in Gaida et al.

Hardness HV measurements were carried out at the DESY and at the Tokyo Institute of Technology (Japan) using a
Vickers indenter (HV-114; Mitsutoyo) at indentation loads of 2, 3, and 5 kg (19.6, 29.4, and 49.0 N, respectively) and using a microhardness indenter (HM-221; Mitsutoyo) at an indentation load of 0.2, 0.5, and 1 kg (1.9, 4.9, and 9.8 N, respectively). A hard steel standard with 900 HV was used for calibration. The top and bottom surfaces of the recovered samples were mirror-polished using diamond paste with particle size of 1 µm. Two to three indents were made depending on the indentation load. Indentations were evaluated using an optical microscope and a scanning electron microscope. HV was calculated using the following equation: 

\[ H_V = \frac{1854.4P}{d^2} \]

where \( P \) is the applied load (N) and \( d \) is the arithmetic mean of the length (in µm) of the two diagonals of a Vickers indentation trace. The fracture toughness \( K_{lc} \) was estimated from the length of the cracks caused by the indentation, where the empirical relation between crack length and applied force is described by the LEM model:17

\[ K_{lc} = \zeta \left( \frac{E}{H} \right)^{1/2} \left( \frac{P}{c^{3/2}} \right) \]

where \( E \) is the Young’s modulus (in GPa) and \( \zeta \) is a calibration constant of 0.016 determined by Anstis et al.18 The Young’s modulus of the two-phase composite was calculated from the reported elastic moduli of kyanite19 and α-alumina20 using the Hill’s approximation.21

The fracture surfaces of the recovered samples were observed on several Au or Pt coated fragments of fractured samples using two field-emission scanning electron microscopes operating at 10 kV (FESEM, Zeiss Ultra Plus and Hitachi S-4800) installed at the Institute for Materials Science at Kiel University (Germany) and the Department of Materials Physics at Nagoya University (Japan).

3 | RESULTS

Transparent nanoceramics were reproducibly obtained from starting aluminosilicate glass preparation using an aerodynamic levitation furnace, followed by high-PT-induced \((P = 10 \text{ GPa}, T = 1200-1400°C)\) glass crystallization to nano-polycrystalline ceramics. Synchrotron X-ray diffraction and Raman spectroscopy (Figure S1) data of the synthesized samples in this study are consistent with results from Gaida et al13 and confirm that the synthesized ceramics are mainly composed of Al₂SiO₅ kyanite with less than 10 mol% of α-alumina. The low and flat background intensity in the synchrotron XRD pattern indicates that all ceramics are fully crystallized. Figure 1A shows the indentation-load dependence of Vickers hardness \((H_V)\). The determined hardness slightly decreases with indentation-load from 2 to 5 N and became relatively stable at indentation loads from 5 to 50 N. The decrease in the hardness with increasing indentation load can be explained by the increasing ratio of plastic to elastic deformation of the sample surface through the indenter. Elastic deformation has a greater influence at the lower indentation loads, which leads to higher hardness values. Hence, consistent with previous studies,8,22 too low indentation loads lead to an over-determination of hardness values. Thus, representative \( H_V \) values of the recovered samples were determined from the arithmetic mean of the five values (measured at 4.9, 9.8, 19.6, 29.4, and 49 N), which show negligible dependence on increasing indentation load (elastic strain). The Vickers hardness increases with decreasing grain size from 14.4 ± 0.8 GPa (average grain size of 611 ± 170 nm) to 20.2 ± 0.8 GPa (average grain size of 69 ± 17 nm) following the Hall-Petch relation (Figure 1C). An inverse Hall-Petch effect is suspected to occur within the grain size interval from ~70 down to 35 nm, since \( H_V \) is again slightly lower (18.3 ± 1.1 GPa) in the ceramic with the smallest grain size of 34 ± 14 nm (the most transparent composite). However, \( H_V \) of these polycrystalline ceramics is still enhanced compared with the overall kyanite single crystal \((H_V \sim 10.7 ± 1.6 \text{ GPa})\) for the perfect cleavage plane (100) and \( H_V \sim 18.0 ± 2.9 \text{ GPa} \) for the (010) plane.19 Observations of the fracture surface reveal that equant gains dominate for the two samples with an average grain size below 100 nm (Figure 2A,B), whereas the sample with the largest grain size is characterized by an increasing occurrence of columnar kyanite crystals with aspect ratios of 2-10 and accompanied

**FIGURE 1** A. Indentation load dependence of Vickers hardness for the ceramics with an average grain size of 34 ± 14 nm (blue dots, 10 GPa and 1200°C), 69 ± 17 nm (green dots, 10 GPa and 1400°C), and 611 ± 170 nm (red dots, 10 GPa and 1600°C). B. Grain size dependence of Vickers Hardness. The inset in (B) demonstrates an indentation
enhanced crack deflection (Figure 2C,D). The latter may enhance the fracture toughness of this sample as indicated by the evaluation of the indentation crack lengths, that is, indentation fracture resistance\(^23\) (Figure S2).

4 | DISCUSSION

Only few data are available on the mechanical properties of polycrystalline ceramics fabricated with average grain sizes below 100 nm, in particular due to the challenges in the synthesis process.\(^9\) The presence of both Hall-Petch strengthening and an inverse softening significantly differs in previous studies depending on the respective ceramic and even on the sinter processing of ceramics with the same composition, as reported for spinel (\(\text{MgAl}_2\text{O}_4\)).\(^24\) A Hall-Petch breakdown has not been detected for nanocrystalline \(\text{Si}_3\text{N}_4,\text{ZnAl}_2\text{O}_4\), or \(\text{MgAl}_2\text{O}_4.\)\(^26\) The latter was fabricated by using deformable punch plasma sintering (DP-SPS).\(^24,26\) In contrast, hardening and softening according to the Hall-Petch and inverse Hall-Petch relation were observed for spinel prepared by high-pressure spark plasma sintering and high-pressure high-temperature synthesis,\(^27,28\) nanocrystalline magnesium oxide (\(\text{MgO}\)),\(^29\) and alumina/silica composite ceramics.\(^8\) These ceramics indicate that the inverse Hall-Petch effect, where the Vickers hardness starts to decrease with decreasing grain size, mainly occurs below a range of average grain size between 30 and 100 nm. Based on the nanocrystalline \(\text{MgO}\)\(^29\) and alumina/silica composite\(^8\) ceramics, a model was developed describing the grain size dependence of the hardness of a statistically homogenous dense polycrystalline ceramics.\(^29,30\) This so-called “percolative composite model” considers the crystals to be harder than the non-crystalline grain boundaries\(^30\) and was applied to the kyanite-based ceramics of this study. Some data necessary to calculate the hardness-grain size relationship by this composite model are not directly available, in particular the grain boundary properties (i.e., volume and hardness), and need to be assessed from the results of this study as described next.

Hall-Petch strengthening does not consider grain boundaries and can be described by the hardness of the crystalline grain interior \(H_c\) and the grain size:

\[
H_c = H_0 + \frac{k}{\sqrt{G}},
\]

where \(H_0\) is the intrinsic hardness of the grain, \(k\) is a strengthening constant depending on the material, and \(G\) is the average grain diameter. In contrast, the inflection at a specific grain size, where a hardness maximum of polycrystalline dense material is attained, depends on the intercrystalline grain boundary hardness with \(H_b = hH_0\) and its volume fraction. Taking the mainly equant grains and equigranular texture at that small grain sizes most likely relevant for inverse Hall-Petch into account, the grain shape is a close approximation of a Tetrakaidecahedron (truncated octahedron).\(^30-32\) From such geometric shape volume fractions of both crystalline and intercrystalline material can be calculated as a function of...
grain boundary thickness and grain size. Experimental observations \(^{33-35}\) and theoretical calculations \(^{36-38}\) point toward that the grain boundary thickness \(\delta\) of polycrystalline material varies between 0.4 and 2 nm. The resulting grain size-dependent crystalline and intercrystalline volume fractions in the bulk polycrystalline material with equant grain size, equigranular texture, and a realistic grain boundary thickness of 1.8 nm (see below) are shown in Figure 3.

In principle, the volume fraction of the intercrystalline component (including grain boundaries, triple junctions, and quadruple nodes) dominates, when the grain sizes are below 10-15 nm and are still significant (~5-15 vol%) for the range of grain sizes where a maximum hardness is indicated.

The corresponding Vickers hardness \((H_{\text{calc}})\) of the ceramic is calculated by the Hill’s approximation \(^{21}\):\[
H_{\text{calc}} = \frac{1}{2} \left( f_c H_c + f_{ic} H_{ic} \right) + \left( \frac{f_c}{H_c} + \frac{f_{ic}}{H_{ic}} \right)^{-1} \]

with \(f_c\) and \(f_{ic}\) as the volume fraction of the grain interior and the grain boundary with a Vickers hardness \(H_c\) and \(H_{ic}\), respectively. By inserting \(H_{c}, H_{ic}, f_c, \text{ and } f_{ic}\) into the equation for \(H_{\text{calc}}\), the hardness can be calculated as a function of the grain diameter \((G)\). The calculated hardness values are within the error range of the measured ones by using \(\delta = 1.4-2.2\) nm and \(h = 0.7-0.8\). The normal Hall-Petch relationship indicated by the measured values of the samples is fairly reproduced within the error limits of the model (Figure 4A). Signs of softening when grain sizes decrease from ~70 to ~35 nm are suggested by the present data but needs further statistical confirmation to prove inverse Hall-Petch behavior. The differences between the calculated and measured relationship between grain size and hardness shown in Figure 4A may result most obviously from variations and deviations in the true grain boundary thickness and the conformity and size of grains. The latter is in particular apparent at the largest obtained grain size (~610 nm) since the grain habitus becomes more and more strongly prismatic with increasing grain size. Nonetheless, this model explains the Hall-Petch breakdown by excessive volume increase in the

\[H_{\text{calc}} = \frac{1}{2} \left( f_c H_c + f_{ic} H_{ic} \right) + \left( \frac{f_c}{H_c} + \frac{f_{ic}}{H_{ic}} \right)^{-1} \]
softer grain boundary fractions and does not consider the role of dislocations, grain boundary mediated mechanisms, such as grain boundary rotation or sliding, and nanocracks in the intercrystalline compounds, which are proposed to dominate in nano-sized ceramics.

However, the nanoceramics are substantially harder than kyanite single crystals or glasses and highly optical transparent although consisting of triclinic, optical biaxial crystals (Figure 4B,C). The prismatic kyanite crystals observed for the sample with the largest grain size seem to reinforce the toughness most obviously due to the observed crack deflection and its encountering effect on crack propagation.

5 | CONCLUSION

The hardness of low to highly transparent nanocrystalline composites of birefringent triclinic Al2SiO5 kyanite (~91.4 vol%) and trigonal Al2O3 α-alumina (~8.6 vol%) fabricated by temperature-induced nano-crystallization at high pressure from aluminosilicate glass was investigated. Together with the optical transparency, the Vickers hardness increases with decreasing grain sizes down to 50-70 nm following the Hall-Petch strengthening. An inverse Hall-Petch relation with an opposite correlation between hardness and grain size is suggested to occur below this range of grain size. At grain sizes close to the signified Hall-Petch-inverse Hall-Petch transition, this nanocrystalline kyanite-based composite is highly optical transparent and still significantly harder than the corresponding kyanite single crystals. A composite model that explains the hardening by dislocation and plastic flow in the less ordered intercrystalline material fairly reproduces the observed correlation between grain size and hardness. To date, only few studies have been published reporting the physical properties of bulk nanoceramics, with the main reason being the challenges in the fabrication process. This study and a few more showed that temperature-induced crystallization from glass at high pressure facilitates high nucleation rates and rapid nucleation followed by slow crystal growth making it applicable for the synthesis of dense nanoceramics with homogenous grain size. However, it has to be mentioned that recent studies demonstrated that also pressure-less high-temperature crystallization from glass, high-pressure spark plasma sintering (HP-SPS), and deformable punch spark plasma sintering (DP-SPS) are applicable for the synthesis of nanoceramics, although only shown for a few compositions so far. The applied synthesis method of temperature-induced crystallization from glass at high pressure allows fabricating nanoceramics with reinforced physical properties. In particular, the reproducibility and low grain size variation of these ceramics readily provide an excellent opportunity to draw comparison of theoretical predictions with experimental data and, thus, to advance the knowledge on the influence of nanostructures, including intercrystalline components, on material reinforcement.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.