FULL PAPER

Improvement in sinterability and high-temperature mechanical properties by grain boundary design for high purity mullite ceramics: Crystallization of grain-boundary glassy phase

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High-purity mullite ceramics are fabricated to improve their high-temperature mechanical properties using an intelligent eco-friendly sintering process with a transient silica-rich liquid phase formed during sintering, followed by the crystallization of the residual glassy phase of SiO₂. The fabricated ceramics possess high density and excellent high-temperature flexural strength. The sinterability of the mullite ceramics improved dramatically when silica-rich compositions were used. This can be attributed to the viscous flow of the silica-rich viscous liquid phase formed during sintering at high temperatures. To increase the high-temperature flexural strength without degrading the fracture toughness, the residual boundary phase was crystallized into cristobalite by controlling its amount and size. The crystallite size of the precipitated cristobalite obtained using suitable post-annealing conditions, i.e., at 1500 °C for 120 h or more, was suppressed; very fine crystals of size 33–38 nm were obtained. The flexural strength measured at 1400 °C for the specimens, which were post-annealed at 1500 °C for 120 h, exceeded that of the as-sintered specimen without resulting in any degradation in fracture toughness at room temperature. These results suggest that suitable grain boundary design conditions, including the composition and post-annealing conditions, can improve the sinterability and high-temperature mechanical properties of the highly pure mullite ceramics at low sintering temperatures. Such grain boundary design can lead to the development of eco-friendly processing of low-temperature sintering for high-performance structural ceramics.

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1. Introduction

Mullite ceramics obtained from high-purity raw materials have been reported in several studies from the viewpoint of their high-temperature mechanical properties.^{1)–7)} In these studies, it was clear that mullite ceramics with ideally controlled microstructures exhibit a high-temperature strength, better creep resistance, low thermal expansion, and low thermal conductivity than non-oxide ceramics, such as silicon nitride and silicon carbide ceramics.^{1),8)–10)} Therefore, mullite ceramics have attracted significant attention as potential engineering ceramics for high-temperature applications in air.^{11),12)}

We investigated the high-temperature mechanical properties of mullite ceramics fabricated from raw powders

with a stoichiometric composition of 3Al₂O₃·2SiO₂ (hereafter abbreviated as 3:2 mullite, meaning 60 mol % Al₂O₃ composition).⁴⁾ These mullite ceramics exhibited superior flexural strength up to 1400 °C. In addition, the mullite ceramics with compositions near stoichiometry exhibited totally different sintering behavior because of the difference in the amount of liquid phase formed during high-temperature sintering, depending on the homogeneity and the size of the raw powders.^{13),14)} Consequently, sinterability of mullite ceramics with silica-rich compositions is good even at lower temperatures, whereas that of 3:2 mullite and mullite ceramics with alumina-rich compositions is poor. Moreover, the silica to alumina ratio and their homogeneity had a large effect on the mechanical properties of the resulting mullite ceramics at high temperatures.⁶⁾ Mullite ceramics having silica-rich compositions usually densified at lower temperatures as compared with 3:2 mullite. Their flexural strength increased at around 1300 °C, then dramatically decreased above 1400 °C due to the stress relaxation caused by the softening of the

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glassy phase at the boundary. In contrast, the mullite ceramics having alumina-rich compositions showed poor sinterability as compared with 3:2 mullite, and their flexural strength gradually decreased from room temperature to 1400 °C.

Densification of poorly sinterable material has been investigated in typical non-oxide engineering ceramics, such as silicon nitride and silicon carbide.^{15),16)} Dense non-oxide ceramics have been successfully obtained by generating a liquid phase during sintering. Using fine α -silicon nitride powder and high-purity Y_2O_3 (99.99 wt %) additive, Tsuge et al. obtained high-density silicon nitride ceramics with good high-temperature flexural strength using hot pressing.¹⁷⁾ However, the oxidation of silicon nitride ceramics under air atmosphere accelerated at temperatures above 1200 °C. Therefore, it is difficult to use silicon nitride ceramics at high temperatures for a long time. For silica and alumina systems, silica-rich powders are more sinterable than single-phase mullite powder because of the liquid phase formed during sintering.¹³⁾ If the sintering temperature is decreased below 1600 °C, then the production cost is reduced because a special furnace with an expensive heating element is no longer required; this is in line with the Sustainable Development Goals. Therefore, the sintering of mullite ceramics with silica-rich compositions is a promising method for developing high-temperature structural ceramics through eco-friendly processing. However, in such systems the residual glassy phase usually degrades the mechanical properties of mullite ceramics at room temperature and at higher temperatures by decreasing the viscosity of the boundary phase.⁶⁾

The crystallization of the glassy phase in the grain boundary by reheating after sintering (i.e., post-annealing) is one of the typical methods used to suppress the decrease in the flexural strength of silicon nitride ceramics at high temperatures.¹⁸⁾ A successful example of this is the suppression of reduction in the bending strength in N_2 atmosphere up to 1500 °C by crystallizing the grain boundaries of the residual glassy phase in a sintered silicon carbide ceramics.^{19),20)} Additionally, silicon carbide ceramics sintered with a small amount of Y_2O_3 additive using hot pressing with a reduced amount of the liquid phase during sintering exhibited a very high bending strength of 1 GPa at 2000 °C.²¹⁾ However, it is very difficult to develop high-temperature structural oxide ceramics usable in air, even by post-annealing.

Therefore, herein we focused on the sintering behavior of mullite ceramics with silica-rich compositions to obtain dense mullite ceramics at lower temperatures by means of an eco-friendly, transient liquid-phase sintering process. In addition, we tried to crystallize the grain boundary glassy phase in the resulting mullite ceramics to design the microstructure of the post-annealed mullite ceramics to have improved high-temperature mechanical properties. The effect of the precipitated cristobalite phase, which has $\alpha \rightleftharpoons \beta$ phase transition²²⁾ with volume change and higher coefficient of thermal expansion than mullite, on the mechanical properties of the mullite ceramics was investigated.

2. Experimental procedure

Mullite precursor powders (Hokko Chemical, Tokyo, Japan), with alumina content of 60, 64, 68, and 71.8 wt %, were used as the starting raw material. These powders were calcined at 1450 °C for 1 h to crystallize amorphous powder into mullite. The aggregated rough powders were milled in methanol in an attrition mill (Model S-01S, Nippon Coke & Engineering, Japan), which consisted of a nylon resin-lined pot and silicon nitride beads of 4 mm diameter. The obtained fine powders were isostatically pressed at 200 MPa after uniaxial pressing using a metal mold. The compacted bodies were sintered from 1450 to 1690 °C for 4 h, at a heating rate of 10 °C·min⁻¹ in an electric furnace.

The sintered bodies ($\sim 40 \times 30 \times 5$ mm³) were cut into a rectangular shape, and the surfaces ground using a #600 diamond wheel and chamfered. Then, specimens with dimensions of $3 \times 4 \times 38$ mm³ were prepared for the standard JIS R1601 flexural strength test. These test specimens were placed in a platinum container for post-annealing, which was performed by annealing at 1500 °C for 48, 72, 96, 120, 240, and 360 h at a heating rate of 5 °C·min⁻¹ in air. The post-annealed specimens were cooled in the furnace.

The specific surface area of the starting raw materials was measured by the Brunauer–Emmett–Teller method using nitrogen as an absorption gas (Model Soapmatic 1800, Carlo Erba, Italy). The bulk densities of the sintered materials were estimated by Archimedes' method using distilled water as a displacement liquid based on the JISR1634 standard (Test methods for density and apparent porosity of fine ceramics). The relative density of specimens with different compositions was calculated from the measured bulk density and theoretical density. The theoretical density of mullite ceramics with different alumina contents used in this study were calculated using the rule of mixtures (mullite and silica) reported by Sato et al.²³⁾ The phase identification of the raw materials and sintered bodies was conducted using X-ray diffraction (XRD, RAD-2B, Rigaku, Japan). Alumina and silica contents of the raw powders were measured using X-ray fluorescence (Model 3070, Rigaku, Japan). The crystallite size of cristobalite in the 60 wt % alumina content specimen annealed at 1500 °C for various soaking durations was calculated using Scherrer's equation²⁴⁾ from XRD patterns.

The microstructures were observed using a scanning electron microscope (SEM T300, JEOL, Japan). The specimens were prepared by thermal etching of the mirror-polished surface at 1500 °C for 20 min or by chemical etching in a 1 % HF solution at 0 °C for 24 h. Furthermore, after the sintered body was thinned by ion milling, the microstructure of the sintered body was observed using a transmission electron microscope (TEM, JEM-4000FX, JEOL, Japan).

The thermal expansion coefficients of the sintered bodies were measured from room temperature to 1000 °C in air using thermal mechanical analysis equipment (Model

TMA-HT, Rigaku, Japan). Flexural strength in air was measured using a three-point bending test at a displacement rate (crosshead speed) of $0.5 \text{ mm} \cdot \text{min}^{-1}$ on a universal testing machine (DCS-2000, Shimadzu, Japan) using more than three specimens. Fracture toughness was measured at room temperature using the chevron-notched beam method and calculated by the equation given by Munz et al.²⁵⁾

3. Results and discussion

3.1 Influence of sintering and post-annealing on microstructure and crystal phase

Table 1 lists the alumina content analyzed by X-ray fluorescence, specific surface area, and the average diameter calculated from the specific surface area of the raw powders used herein. The specimen names in Table 1 depict the alumina content, e.g., 60A means the specimen with 60 wt% alumina content. The particle size of every raw powder used was $\sim 100 \text{ nm}$, irrespective of their type, indicating that they were very fine. However, the average diameter of the raw powders gradually decreased with an increase in alumina content, indicating that grain growth was enhanced with an increase in silica content in the raw powders during calcination by the viscous sintering, even at the relatively low temperature of 1450°C .

The effect of the composition on the bulk density of the specimens sintered at temperatures from 1450 to 1690°C for 4 h is shown in **Fig. 1**. The temperatures, at which the bulk density leveled off, decreased dramatically with increasing amounts of silica content. For example, from this figure, 60A and 64A were seen to be fully densified at ~ 1550 and 1600°C , respectively. Meanwhile, the temperature at which full density was obtained for 71.8A was 1650°C . The highest relative densities of the specimens were almost 100 % at 1550°C for 60A and 1600°C for

64A, and 98.0 % at 1650°C for 71.8A. Thus, the sintering behavior in the silica–alumina system improved remarkably by increasing the silica content. This densification behavior in relation to composition was in accordance with the results described in our previous reports.¹³⁾

Figure 2 shows representative microstructures observed by SEM for 60A, 64A, 68A, and 71.8A sintered at 1650°C for 4 h, chemically etched after polishing. It is seen that the size and numbers of the sharply etched grain boundaries, i.e., the chemically etched glassy grain boundaries, dramatically increased with increasing silica content in the specimen. In addition, mullite grains became elongated in the specimens with silica-rich compositions.

XRD patterns for the 60A sintered at 1650°C and post-annealed at 1500°C for different time periods from 0 to 240 h are shown in **Fig. 3**. A broad peak around $2\theta = 20^\circ$ in the as-sintered specimen, attributed to the amorphous phase, disappeared, and cristobalite was identified in all the specimens annealed for more than 48 h. The diffraction intensity of the cristobalite increased with increasing annealing time up to 120 h and then leveled off, suggesting that the boundary glassy phase was almost crystallized by

Table 1. Chemical composition and specific surface area of the milled starting powders

Symbol	Alumina content wt %	Specific surface area $\text{m}^2 \cdot \text{g}^{-1}$	Particle diameter nm
60A	60.4	19.3	103.0
64A	63.8	20.6	95.2
68A	67.9	23.5	82.1
71.8A	71.7	24.6	77.4

Fig. 1. Effect of sintering temperature for 4 h on the sinterability of the SiO_2 – Al_2O_3 compacts.

Fig. 2. Scanning electron micrographs of polished chemically etched surfaces [$\text{HF } 1\% \text{ (aq.)}$ at 0°C for 24 h] of the specimens sintered at 1650°C for 4 h.

Fig. 3. XRD patterns of the 60A specimen (sintered at 1650°C for 4 h) post-annealed at 1500°C up to 240 h.

Fig. 4. Crystallite size of the 60A specimen (sintered at 1650 °C for 4 h) post-annealed at 1500 °C for 120, 240, and 360 h, respectively.

Fig. 5. Transmission electron micrograph of the grain boundary of the 60A specimen (sintered at 1650 °C for 4 h) post-annealed at 1500 °C for 120 h.

post-annealing for 120 h or more. In addition, the peak position and the diffraction intensity of the mullite was almost the same for all the specimens. A detailed analysis of XRD patterns for 64A, 68A, and 71.8A annealed at 1500 °C for 120 h revealed that the peak intensity of cristobalite decreased with decreasing silica content. Further, cristobalite was not identified in 71.8A in spite of the presence of a small amount of glassy phase between the mullite boundaries.

Figure 4 shows the crystallite size of cristobalite precipitated in specimen 60A post-annealed at 1500 °C for 120–360 h, along with that of a high-purity commercial silica glass (99.99 wt %) annealed at 1500 °C for 120 h. The crystallite size of cristobalite was ~35 nm, regardless of the annealing time, whereas that of the high-purity commercial silica glass was ~52 nm. The cristobalite precipitated by the post-annealing was found to have fine nano-sized particles. Figure 5 shows the transmission electron micrograph of the grain boundary of the 60A specimen post-annealed at 1500 °C for 120 h. The results of the XRD pattern for 60A in Fig. 3 suggest that the glassy phase

Fig. 6. Temperature-dependence of the thermal expansion of specimen 60A (sintered at 1650 °C for 4 h): post-annealed at 1500 °C for 120 h, and as-sintered, respectively.

almost crystallized to cristobalite by post-annealing for more than 120 h. Raj et al. studied the crystallization of the amorphous phase existing in a small area in several aluminum crystals using thermodynamic analysis.²⁶⁾ They reported that crystallization of the amorphous phase existing at the grain boundaries depends on the angle between grain surfaces, and some parts resisted crystallization. Furthermore, a study on the crystallization behavior of the grain boundary glassy phase by Clark²⁷⁾ revealed the presence of the residual glassy phase. Therefore, the TEM observation in the present study and the results in previous reports^{23),26),27)} imply that the grain boundary phase could consist of two phases, namely nanosized cristobalite and glassy phase. Here, the crystallite size of the cristobalite precipitated in the resulting mullite ceramics was larger than that observed by TEM but smaller than that precipitated by annealing pure quartz glass. It is expected that the crystallite size seen in the XRD pattern would be different from that directly observed in TEM because the cristobalite precipitated in the mullite was under tensile stresses from precise measurements of lattice constants.²²⁾

3.2 Effect of thermal mismatch on the mechanical properties at room temperature

Figure 6 shows the thermal expansion behavior from room temperature to 1000 °C for specimen 60A before and after post-annealing at 1500 °C for 120 h. A slope change at ~250 °C was observed in the thermal expansion curve for the post-annealed 60A. This slope change is ascribed to the transformation of cristobalite from α to β -phase, resulting in residual compressive stress in the sintered ceramics at higher temperatures.²⁸⁾ In such a case, we can expect an improvement in the mechanical properties of the resulting ceramics at room temperature.^{29),30)}

Moreover, the fracture toughness of ceramics containing a second phase is affected by the residual stress caused by the difference between the coefficients of thermal expansion of the matrix and second phase.³¹⁾ The silica-alumina

Fig. 7. Flexural strength and fracture toughness of specimen 60A (sintered at 1650 °C for 4 h) post-annealed at 1500 °C for 120 h after a 10-cycle heat test.

ceramics in this study can be considered as a composite material of mullite and silica glass or mullite and cristobalite. In Fig. 6, the thermal expansion curve of the post-annealed 60A specimen includes the effect of the transformation of cristobalite with volume change. Such volume change will lead to residual stresses, depending on heat cycles, affecting the mechanical properties of the resultant mullite ceramics. The thermal expansion of silica glass from room temperature to 1000 °C is $5.5 \times 10^{-7}/\text{K}$, which is much smaller than that of mullite ($5.3 \times 10^{-6}/\text{K}$), whereas the thermal expansion coefficient of cristobalite is $1.9 \times 10^{-5}/\text{K}$ higher than that of mullite.²⁸⁾ Therefore, we studied the effect of the thermal cycles on the mechanical properties up to 1000 °C.

Figure 7 shows the strength and the fracture toughness at room temperature after 10 heat cycles from room temperature to 500 or 1000 °C for the 60A specimen post-annealed at 1500 °C for 120 h. Although residual stress was expected to have a large effect on the mechanical properties, the effects of the thermal history on the flexural strength and fracture toughness of the post-annealed 60A specimen were not significant at room temperature in this result. In order to discuss the effect of the residual stresses on the mechanical properties after heat treatment, Fig. 8 shows the linear thermal expansion/shrinkage behavior for the post-annealed 60A test piece, together with those of pure mullite and cristobalite on cooling from 1500 °C to room temperature using the data calculated by Sato et al.²²⁾

The volume change in the post-annealed 60A specimen accompanied by the transformation of the grain boundary cristobalite on heating would be a volume shrinkage of about 5.6 %, ²²⁾ but the residual stress is expected to become zero due to stress relaxation in the remaining glassy phase during higher-temperature annealing. In the cooling process from 1500 °C to room temperature, the compressive stresses on the cristobalite will arise in cristobalite up to the temperature (~ 250 °C) at which the phase transformation from a high-temperature phase to a low-temperature phase is observed. The phase transformation of the cristobalite

Fig. 8. Change in thermal behavior of pure mullite and cristobalite during cooling from 1500 °C to room temperature (RT) calculated from their thermal expansion coefficients, compared with that measured for the post-annealed specimen 60A from RT to 1000 °C.

causes it to shrink rapidly, relaxing the residual stress on the mullite phase and finally slightly changing the residual stress from tensile to compressive. However, the residual stress present in the specimen did not induce cracks of the size that affect the mechanical properties of the specimen, and the fracture toughness value was not significantly affected. The fracture toughness, at room temperature, of the post-annealed specimen was almost the same as mullite ceramics with 64–74 wt % alumina content measured by the chevron-notched beam method.³²⁾ In other words, the effect of thermal history on the mechanical properties of the specimens subjected to reheating and cooling was insignificant. This result can be explained by the following reasons: Firstly, the size of the cristobalite is as fine as a few tens of nanometers.³³⁾ Furthermore, the specimens used in the experiments were small, with a cross-sectional area of $3 \times 4 \text{ mm}^2$, so the shape effect of the thermal mismatch is also expected to be small.

In the case of the mullite-silicon carbide composite reported by Nakao et al., the 100–200 μm cracks produced by the Vickers indenter were able to heal at above 1000 °C in air.³⁴⁾ It was found that the healing activator recovered the cracks generated on the surface of the ceramics at a low temperature and in a short time. From these results, the effect of thermal mismatch on mechanical strength and fracture toughness of the mullite-cristobalite ceramics at room temperature can be explained by the crack healing shown by the residual glassy phase. Therefore, it was concluded that the mullite ceramics containing very fine cristobalite prepared in this study can act as excellent structural ceramics even under thermal cycles.

3.3 Effect of crystallization of the grain boundary phase on high-temperature strength

Plots of three-point flexural strength as a function of temperature for the as-sintered and post-annealed 60A

Fig. 9. Variation of the flexural strength of the 60A specimens (sintered at 1650 °C for 4 h) post-annealed at 1500 °C for 120 h and the as-sintered specimens as a function of temperature.

Fig. 10. Flexural strength evaluated at 1400 °C in the air for the specimens post-annealed at 1500 °C for 120 h and the as-sintered specimens (sintered at 1650 °C for 4 h) as a function of alumina content.

specimens at 1500 °C for 120 h are shown in **Fig. 9**. The strength of the as-sintered 60A specimen showed a strong temperature dependence, and it reached 600 MPa at 1300 °C, which was approximately twice the strength at room temperature. However, the flexural strength of the as-sintered 60A measured at 1400 °C decreased drastically below the strength at room temperature. Meanwhile, the strength of the post-annealed 60A showed a higher flexural strength at 1300 °C than that at room temperature, and maintained its high value even at 1400 °C.

These results demonstrate the effect of crystallization of the grain boundary glassy phase on the mechanical properties of the mullite ceramics with silica-rich compositions. **Figure 10** shows the relationship between alumina content and flexural strength at 1400 °C. The flexural strength of the as-sintered specimens at 1400 °C tended to increase with an increasing alumina content, whereas the

Fig. 11. Scanning electron micrographs of the fracture surface evaluated at room temperature and 1400 °C of the 60A specimens as-sintered at 1650 °C for 4 h and post-annealed at 1500 °C for 120 h.

high-temperature strength of the post-annealed specimens gradually decreased with an increasing alumina content. However, the flexural strength of the post-annealed 60A was higher than that of 71.8A, indicating the usefulness of the grain boundary design by suitable post-annealing in developing better high-temperature structural ceramics.

Figure 11 shows typical fracture surfaces after mechanical tests at room temperature and 1400 °C for the as-sintered and post-annealed 60A silica-rich mullite ceramics. In the fracture surface at room temperature, a little influence of crystallization of the glassy phase was observed. Specimens with cristobalite at the grain boundaries had smaller irregular fracture surfaces. Moreover, the fracture surface at 1400 °C was greatly affected by the post-annealing, and the pull-out of the elongated mullite grains was observed in the post-annealed 60A, which contains a small amount of glassy phase and very fine cristobalite crystals. In contrast, no obvious mullite grain pull-out was observed in the as-sintered 60A.

To investigate the effect of post-annealing on flexural strength, **Fig. 12** compares the stress–strain curves measured at 1400 °C for glass-containing specimens 60A and 68A before and after post-annealing. For 60A, the glass-containing specimen fractured with a large plastic deformation before post-annealing, whereas the post-annealed 60A showed a typical stress–strain curve of the high-temperature structural ceramics with a higher stress value. The as-sintered and post-annealed 68A specimens showed almost the same strength as shown in **Fig. 10**, but creep resistance was expected to be lower in the as-sintered specimens because they fractured with plastic deformation whereas brittle fracture was observed in the post-annealed specimens.

Thus, it was demonstrated that the grain boundary design or the crystallization of the grain boundary glassy phase by the post-annealing of the silica-rich mullite ceramics containing glass at the grain boundary had a sig-

Fig. 12. Typical stress-strain curves for the 60A and 68A post-annealed specimens at 1500 °C for 120 h and the as-sintered specimens (sintered at 1650 °C for 4 h) evaluated at 1400 °C in air.

nificant effect on the high-temperature flexural strength. We have previously reported that the high-temperature strength of the mullite ceramics containing glass dramatically changed depending on the amount of the grain boundary glassy phase.⁶⁾ The flexural strength of the mullite ceramics, such as 60A, containing glass measured at 1400 °C decreased to below room temperature strength with plastic deformation due to a decrease in the viscosity of the grain boundary glassy phase, as shown in Fig. 12. Crystallizing the grain boundary glassy phase into cristobalite suppressed its plastic deformation in the mullite ceramics at high temperatures and improved its strength.

Also, Fig. 12 suggests that if the grain boundary is appropriately designed using silica-rich composition mullite ceramics, the crystallization of the grain boundary phase can improve static fracture characteristics such as creep. In particular, this study demonstrates that the degree of softening and plastic deformation of the mullite grain boundary phase is affected by the amount of residual glassy phase. Thus, the optimization of the amount of grain boundary glassy phase and/or grain boundary design is essential for improving the strength of mullite ceramics at higher temperatures. The microstructure of the fine precipitated cristobalite located within the mullite grain boundary may affect its high-temperature mechanical properties; however, further investigation (e.g., by creep deformation analysis and microstructure observation) is required to confirm this assumption.

4. Conclusions

In this study, we used post-annealing to design the grain boundary in mullite ceramics with silica-rich compositions and/or good sinterability to improve their mechanical properties. The important conclusions of the study are:

- (1) Full densification of the mullite ceramics at low temperatures was possible using silica-rich raw powders under optimized conditions.
- (2) Most of the glassy phase existing in the mullite grain boundaries after densification crystallized from amorphous to cristobalite by annealing at 1500 °C. The precipitated cristobalite particles were very fine.
- (3) The precipitated cristobalite crystals did not significantly influence the mechanical properties at room temperature.
- (4) The flexural strength of the silica-rich mullite ceramics at high temperatures was improved by the crystallization of the glassy phase in the grain boundaries. In other words, crystallization of the glassy phase in the grain boundaries suppressed the degradation of flexural strength until 1400 °C.

These results demonstrate that the crystallization of the grain boundaries of the high-temperature structural ceramics by suitable processing is a powerful tool for developing high-performance structural ceramics using a cost-effective and eco-friendly sintering process.

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