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Texturing of mullite by templated grain growth with aluminum borate whiskers

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Abstract

Textured mullite was produced by templated grain growth with a mixture of mullite powder and aluminum borate ($9Al_2O_3\cdot 2B_2O_3$) whiskers. A gated doctor blade was used to align the whiskers in the *c*-axis in the mullite matrix during tape casting. When heated by themselves in air, aluminum borate whiskers formed α-Al_2O_3 at > 1400°C but were stable enough for templated mullite growth in a TiO_2-doped mullite sintered at 1500°C. Starting with 3 wt.% TiO_2 and 10 wt.% templates, an ~90% textured mullite was obtained after 6 h at 1600°C. The <001> textured mullite was 97% dense and had a FWHM of 9.6° in the [001]. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Grain growth; Mullite; Whiskers

1. Introduction

Mullite is an excellent candidate for high temperature applications such as gas filters, shrouds and heat exchangers because of its high temperature stability and relatively low thermal expansion coefficient ($\alpha = 5.3 \times 10^{-6}$ °C^{-1}).[1] In many of these applications, fibers are used to fabricate the part or used as reinforcement. Therefore, much research has focused on enhancing the creep properties and strength of mullite fibers. For example, Kriven et al. produced polycrystalline fibers of mullite by pulling them from an undercooled melt[2] and Sayir et al. produced single crystal fibers by directional solidification using a laser heated float zone method.[3] Unfortunately, such fibers are difficult to produce and are expensive. 3M Co. produces polycrystalline, mullite-based fibers using a sol-gel process. For high temperature applications, it is necessary to restrict grain growth during processing as well as for high temperature. Wilson recently reported that small concentrations of SiO_2 can be used to inhibit grain growth in Nextel 610 fibers.[4] Alternatively, a model proposed by Raj and Ashby[5] predicts that oriented grains with aspect ratios of 50 increase the creep resistance by a factor of 10^5 relative to a random, equiaxed microstructure.

Hong and Messing[6] obtained highly textured mullite by templating grain growth on oriented acicular mullite particles in a diphasic mullite precursor. Templated grain growth (TGG) is a process in which anisotropic particles oriented in a matrix, grow preferentially to obtain a textured microstructure.[7] They reported that TiO_2 enhanced anisotropic growth of the mullite templates. Using 3 wt.% TiO_2 and 10 wt.% mullite template particles, they produced ~90% textured mullite. This process is classified as reactive templated grain growth (RTGG)[6,8] because the matrix crystallizes during the process. RTGG has some important advantages for producing highly textured materials as a result of the seeding of the matrix phase transformation by the template particles. However, the large volumetric shrinkage associated with the phase transformation and the use of a sol-gel precursor makes it unsuitable for producing bulk mullite, although it may be acceptable for fiber production.

To produce textured ceramics, the TGG process relies on the use of anisometric particles because they can be oriented by shear forming processes like tape casting and extrusion. Although mullite needles are ideal templates for the TGG of mullite, there are no commercial sources for acicular mullite particles. Clearly, the process of HF digestion of a mullite ceramic containing acicular grains is inefficient, costly and unsafe since it relies on the use of HF.[6]

As shown earlier, template materials must satisfy conditions for epitaxy as well as chemical stability[9] to effect the phase transformation. Aluminum borate ($9Al_2O_3\cdot 2B_2O_3$) satisfies the conditions for epitaxy for

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mullite since it is orthorhombic and its lattice parameters ($a = 7.6874$ Å, $b = 15.0127$ Å, $c = 5.6643$ Å)[10] either closely match the *a* parameter or are twice the *b* and c parameters of mullite ($a = 7.5456$ Å, $b = 7.6898$ Å, $c = 2.8842$ Å).[11] Also, it is structurally similar to mullite and consists of AlO_6 octahedra aligned in the *c*-direction and is crosslinked by corner-shared AlO_4 tetrahedra.

Importantly, aluminum borate is available in commercial quantities as acicular whiskers. However, aluminum borate has been reported to decompose to α-Al_2O when heated in air at $1440°C$[12] and that whiskers of aluminum borate also decompose at $1450°C$.[13] When heated at $2°C/min$, aluminum borate starts to decompose as low as $1200°C$.[14] Hong and Messing showed that template growth starts at $1550°C$ when starting with mullite whiskers and a diphasic mullite precursor. Thus, it is important to determine whether aluminum borate is sufficiently stable at the high temperatures required for TGG. In this paper, we first present a series of experiments to establish the stability conditions of the commercial aluminum borate whiskers. Then we discuss texture evolution in TiO_2-doped mullite by TGG starting with $9Al_2O_3 \cdot 2B_2O_3$ template particles and a crystalline mullite powder.

2. Experimental procedure

As-received aluminum borate whiskers (Shikoku Chemical Co., Marugame-shi, Japan) and mullite powder (Chichibu Cement Co., Japan) were used. The powder and template slurries were prepared separately to avoid whisker breakage during ball milling. Aluminum borate whiskers were dispersed in ethanol and sonicated for 20 min. Mullite was attrition milled for 11 h in ethanol using 5 mm yttria stabilized zirconia balls (Tosoh Ceramics, Brook, NJ). A tape casting slurry was prepared by mixing an appropriate amount of mullite with a vinyl-based binder solution (39 wt.%) (Ferro 73210, Ferro Corp., Cleveland, OH) and modifier (1 wt.%) (Ferro M111, Ferro Corp., Cleveland, OH). Then, 0–5 wt.% TiO_2 of 47 m^2/g surface area (P25, Degussa-Huls, Frankfurt-Main, Germany) was added to serve as a liquid phase former during sintering and to enhance anisotropic grain growth. The powder slurry was prepared by ball milling the powder, binder solution and modifier for 24 h in toluene using 1 mm zirconia balls. The template slurry, consisting of 1 or 10 wt.% template particles, was mixed in toluene with the same binder solution and fast stirred for 24 h for good dispersion. The powder and template slurries were then mixed and stirred for 24 h.

Tapes were cast on a glass substrate at a casting speed of 7 cm/s and a blade gap of 200 μm. A gated-doctor blade[15] with gate spacings of 200 μm was used for the uniform distribution and extension of shear for alignment of the whiskers. After drying at room temperature for 24 h, tapes were cut and laminated at 83 MPa. The binder was removed by heating to $250°C$ at $0.86°C/min$, then to $275°C$ at $0.5°C/min$ and finally to $600°C$ at $0.75°C/min$. At each step, there was an isothermal hold of 1 h. Samples were sintered between 1450 and $1600°C$ for 1 to 12 h.

Samples were characterized by XRD and SEM. Texture development was investigated by calculating relative peak heights (Lotgering factor)[16] and by X-ray pole figure analysis. The Lotgering factor is ($f = \dfrac{\frac{\Sigma I(00l)}{\Sigma I(hkl)} - \frac{\Sigma I^0(00l)}{\Sigma I^0(hkl)}}{1 - \frac{\Sigma I^0(00l)}{\Sigma I^0(hkl)}}$). XRD measurements were performed both perpendicular and parallel to the casting direction on samples mounted on a glass slide with Cu K_α radiation between 5 and 90° with a step size of 0.02 and rate of 2°/min. The pole figure was measured in steps of $\Delta\omega = 2.5°$ and $\Delta\beta = 5°$ in the ranges of $0° \leqslant \omega \leqslant 65°$ and $0° \leqslant \beta \leqslant 360°$ with a measuring time of 2 s/step. Microstructural observations were performed on as-fired and polished samples. All polished samples were thermally etched at the sintering temperature for 5 min prior to HF etching.

3. Results and discussion

The initial powder was agglomerated with an average agglomerate size of 60 μm. After attrition milling, the average particle size was 0.53 μm. An electron micrograph of the aluminum borate whiskers is shown in Fig. 1. The average length of the whiskers is 15 μm and the average thickness is 0.5 μm.

3.1. Thermal stability of aluminum borate whiskers

The thermal stability of the aluminum borate whiskers was evaluated by heating them in air for 6 h from 1400 to 1600°C. The aluminum borate whisker morphology is
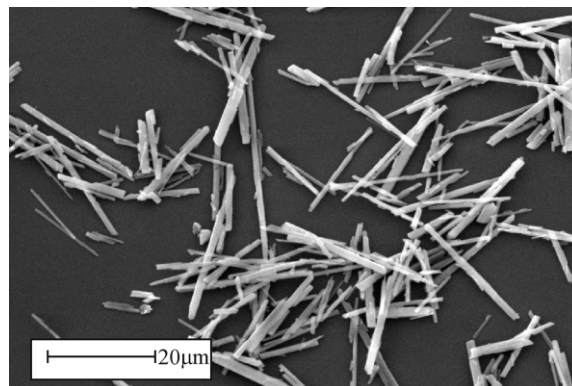

Fig. 1. SEM micrograph of aluminum borate whiskers.

seen to be stable at 1400°C and the whiskers to be aluminum borate as determined by X-ray diffraction (Fig. 3). At 1500°C the whiskers decompose to α-Al_2O_3 after 6 h (Figs. 2 and 3). The whiskers retain a whisker morphology at 1500°C but are really α-Al_2O_3 fragments of the original whiskers. At 1600°C the whisker morphology is completely lost and only 5 μm nodular α-Al_2O_3 remains.

Samples consisting of 10 wt.% whiskers and either 3 or 5 wt.% TiO_2 were sintered in air at 1450 to 1600°C for 6 h. For comparison, samples with no templates and 3 wt.% TiO_2 were sintered. As seen in Fig. 4 the samples either with or without templates and 3 wt.% TiO_2 sintered to ~88% density at 1450°C. When doped with 5 wt.% TiO_2, samples with 10% templates sintered to ~95% density. These results indicate that the template particles do not hinder densification. This is probably a result of liquid phase formation and the decreased viscosity of the liquid as a result of the TiO_2 dopant[17] which also explains why better densification occurs with 5 wt.% TiO_2. When sintered for 6 h at 1500°C, all samples densified to 98% density. Samples sintered at 1600°C decreased to ~97% density. Hong and Messing observed a similar decrease in density in mullite composed of either random anisotropic or oriented grains.[18]

It was not possible to uniquely observe aluminum borate in the sintered mullite samples by XRD because all of the major X-ray peaks of mullite and aluminum borate overlap. Interestingly, weak α-Al_2O_3 peaks were observed in samples heated to 1600°C for 6 h. As discussed below the whiskers serve as templates for mullite growth, which indicates that they do not decompose into α-Al_2O_3 before densification. Thus, we believe that the aluminum borate whiskers were encapsulated in the mullite matrix during sintering and α-Al_2O_3 forms after growth. Although we tried to observe the aluminum borate whiskers at the core of mullite grains by energy dispersive spectroscopy we could not detect them. It is believed that the whiskers form a solid solution with the mullite and that excess aluminum oxide is precipitated in the mullite microstructure. Unfortunately, a complete phase diagram is not available for this system. The white spots seen in Figs. 5 and 6 were observed by SEM and EDS to be α-Al_2O_3. Studies are underway to determine how α-Al_2O_3 forms in this system.

3.2. Microstructure and texture evolution

The microstructures of samples sintered at 1450 and 1500°C show that the templates initiate growth at
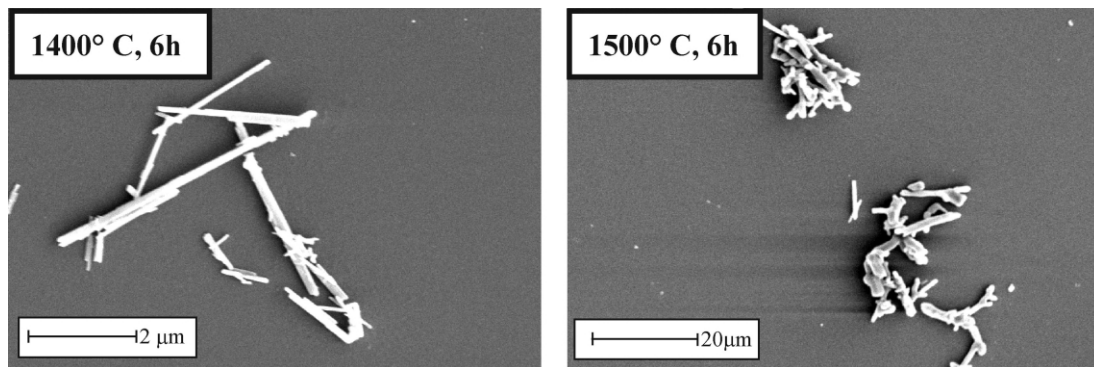

Fig. 2. SEM micrographs of aluminum borate whiskers heated for 6 h at 1400 and 1500°C in air.
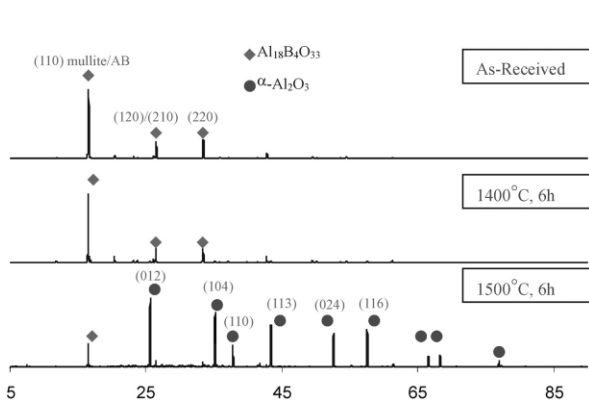

Fig. 3. X-ray diffraction of aluminum borate (AB) whiskers before and after heating at 1400 and 1500°C for 6 h in air.
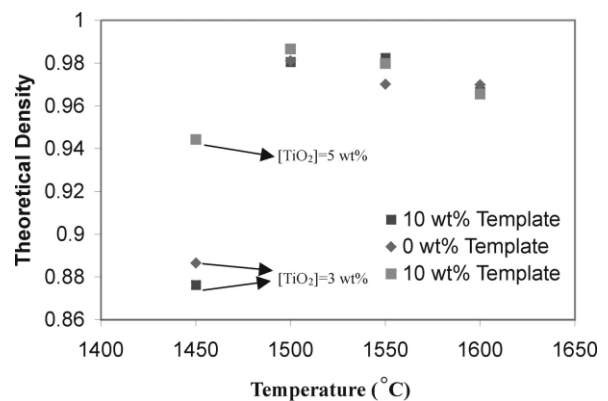

Fig. 4. Densification of mullite containing 10 wt.% aluminum borate whiskers and TiO_2 dopant after heating for 6 h.

1500°C (Fig. 5). This indicates that $9Al_2O_3 \cdot 2B_2O_3$ is stable at 1500°C and thus the aluminum borate is stable in the densified mullite. Growth at 1500°C is consistent with earlier reports that template growth does not occur until the matrix densifies to >92%.[19] Fig. 6 shows template growth as a function of TiO_2 concentration for samples heated at 1600°C for 6 h. As expected, template growth was significantly increased when 3 wt.% TiO_2 was added but there was no significant difference when 5 wt.% TiO_2 was added. The large voids are observed only when aluminum borate was added and thus may be a result of B_2O_3 volatilization at higher temperature and may explain the slight decrease in density seen in Fig. 4. Fig. 7 shows that mullite matrix grains and template grains sintered at 1600°C from 1 to 6 h significantly grew from 25 to 60 µm.

Texture evolution was measured by XRD perpendicular to the casting direction for samples containing 10 wt.% templates and sintered between 1450 and 1600°C for 6 h (Fig. 8). The Lotgering factor is seen to increase
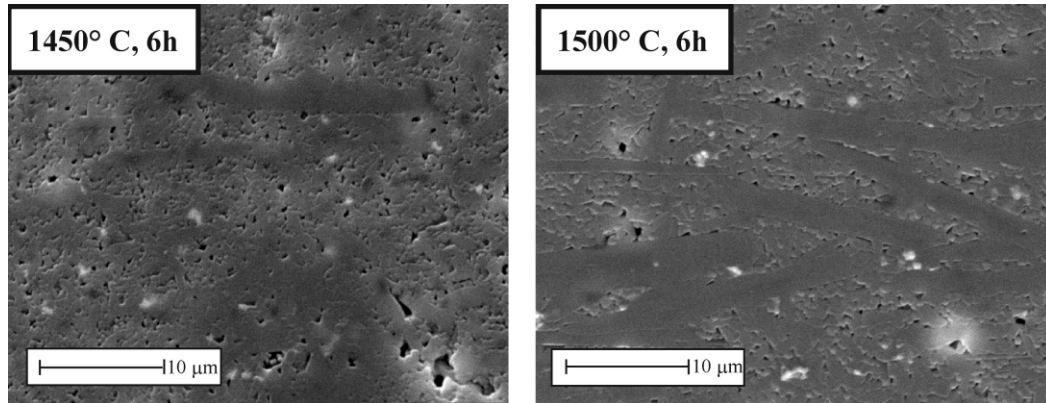

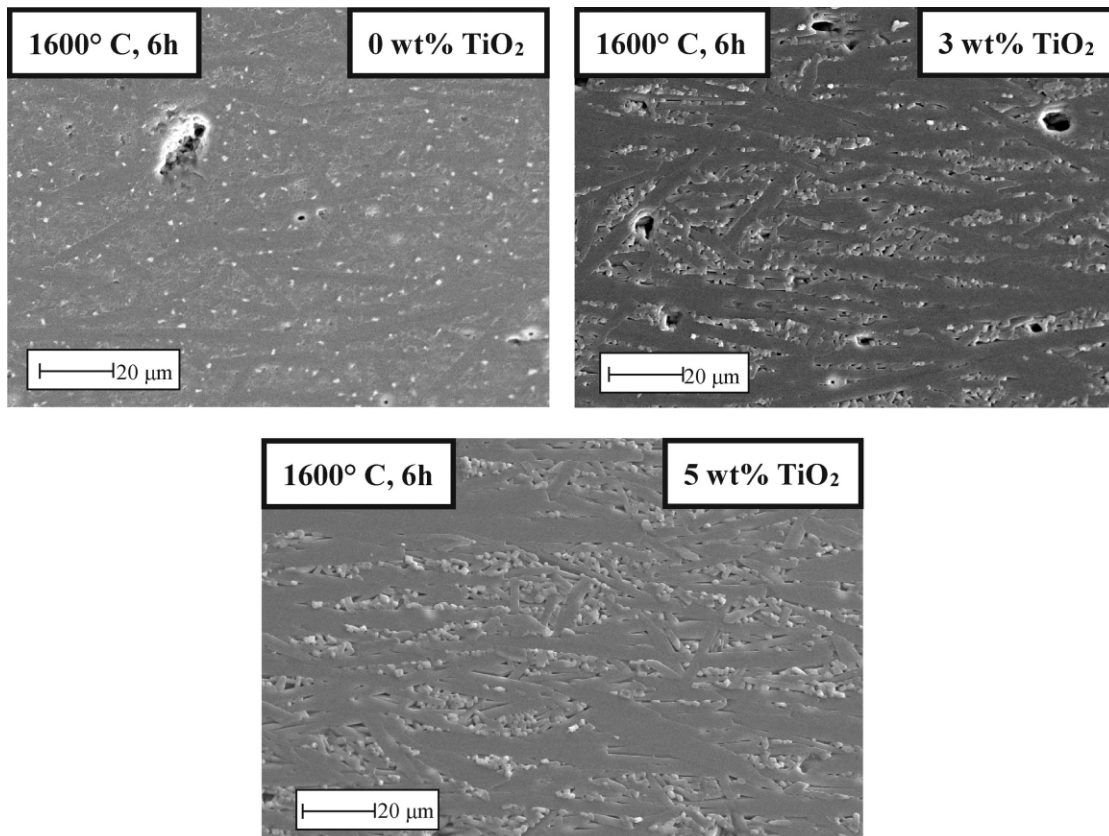Fig. 5. SEM micrographs of textured mullite (10 wt.% templates and 3 wt.% TiO_2) sintered at 1450 and 1500°C for 6 h.

Fig. 6. SEM micrographs of 0–5 wt.% TiO_2-doped textured mullite (10 wt.% templates) heated at 1600°C for 6 h.
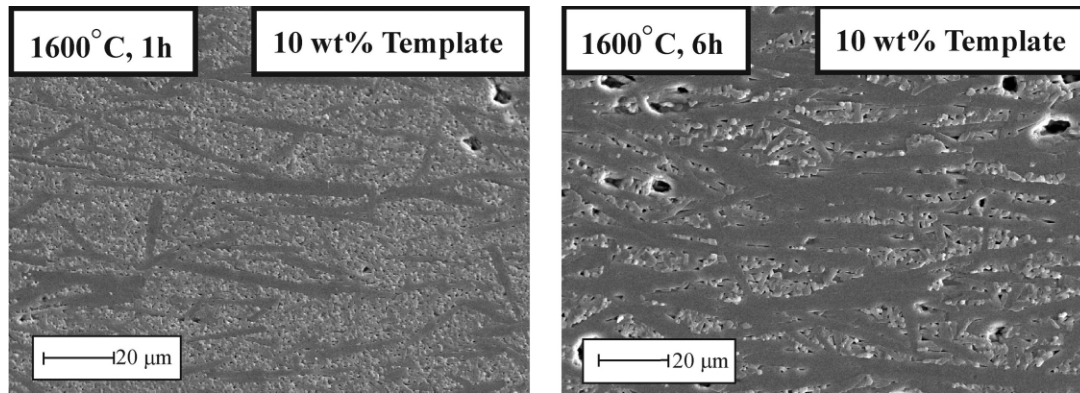
Fig. 7. SEM micrographs of textured mullite (10 wt.% templates and 3 wt.% TiO_2) heated at 1600°C for 1 and 6 h.
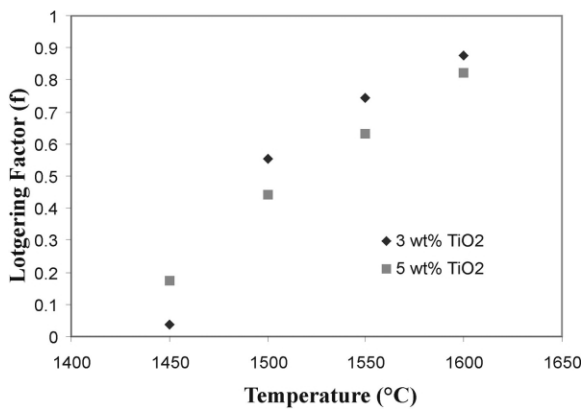

Fig. 8. Texture fraction as a function of temperature and TiO_2 dopant concentration for samples heated for 6 h.
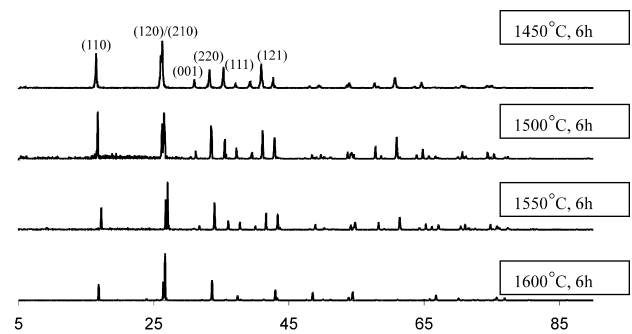

Fig. 9. X-ray diffraction perpendicular to the [001] axis of textured mullite.
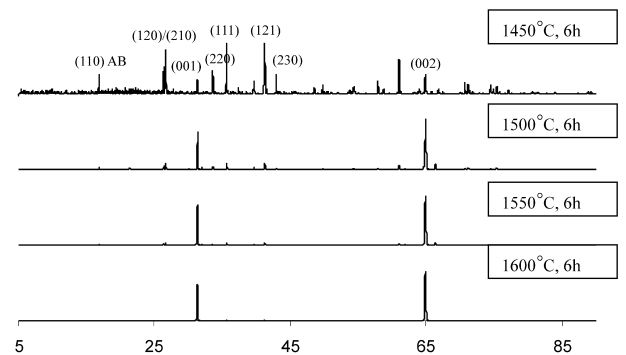

Fig. 10. X-ray diffraction parallel to the [001] axis of textured mullite produced at different temperatures. AB = aluminum borate.

from 0.03 to 0.87. Although the growth of the anisotropic mullite grains is initially greater for samples with 5 wt.% TiO_2, the Lotgering factor was 0.1 less at higher temperatures compared to the samples with 3 wt.% TiO_2. The decreased growth may be a result of increased diffusion distance associated with more liquid phase or decreased driving force for template growth because of the increased mullite matrix grain size. As seen in Fig. 6 the matrix grain size at 1600°C is 60 μm for the sample with 3 wt.% TiO_2 and 80 μm for the sample with 5-wt.% TiO_2. The decreased size difference between the size of the rapid growth surface [i.e. (001)] relative to the matrix grain size was previously shown to be a critical thermodynamic factor for template growth.[19]

There is significantly more growth of the templates in this study compared with mullite whisker templated growth in a sol gel mullite precursor system.[6] This difference is probably a result of the boria introduced by the aluminum borate templates. Boria was shown earlier to significantly enhance mullite grain growth.[18,20]

X-ray diffraction both perpendicular and parallel to the *c*-axis of the aluminum borate and mullite grains in textured mullite is seen in Figs. 9 and 10. For X-ray diffraction of samples perpendicular to the *c*-axis, the intensity of peaks with l≠0 decreased as the sintering temperature increased. Likewise, the peak intensity of l≠0 peaks increased for samples parallel to the *c*-axis and (hk0) planes of mullite disappeared with increasing temperature. These data clearly show that the templated mullite grains are oriented with the *c*-axis parallel to the tape casting direction. Fig. 11 is a (001) pole figure of a sample with 87% texture which was obtained by starting with 10 wt.% aluminum borate templates and doping with 3 wt.% TiO_2 and then heating at 1600°C for 6 h. The FWHM for the sample was 9.6°. There were no processing efforts to further narrow the width of the orientation distribution function.
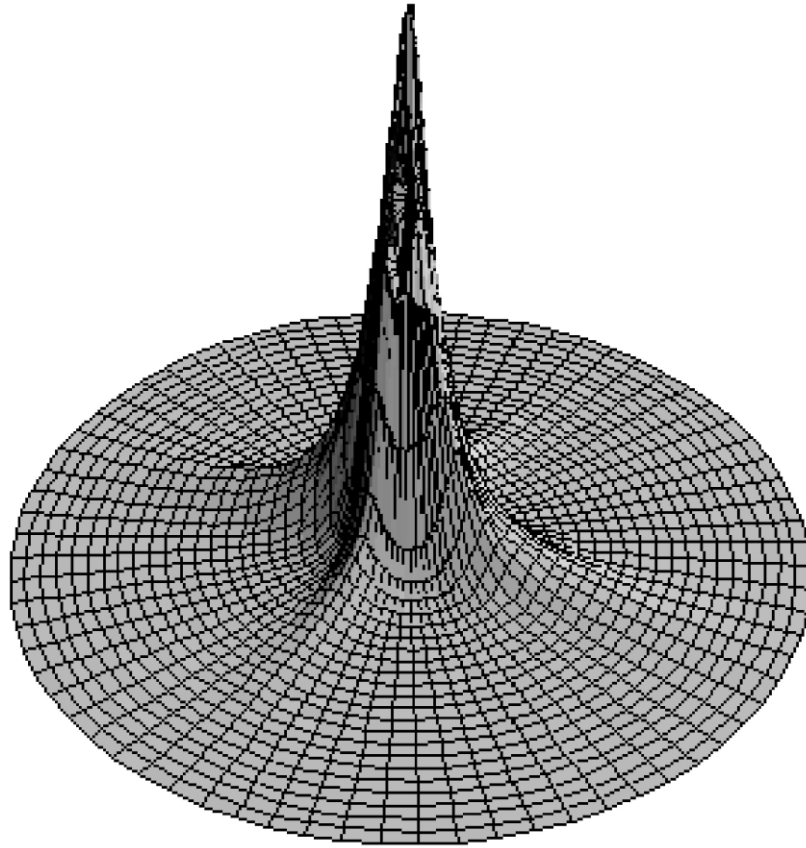
Fig. 11. Three dimensional pole figure of the (001) surface of textured mullite doped with 3 wt.% TiO_2 and 10 wt.% templates and heated at 1600°C for 6 h.

4. Summary

Highly textured mullite was produced by orienting aluminum borate template grains in a mullite matrix containing TiO_2 to enhance anisotropic growth. Aluminum borate, which decomposes by itself at temperatures above 1400°C, was stable in the mullite powder and served as a growth site (i.e. template) for mullite growth. TiO_2 served as a liquid phase former and resulted in densification to > 92% at 1500°C. Texture development started at ~92% and resulted in ~90% texture for samples doped with 3 wt.% TiO_2 and 10 wt.% template, sintered at 1600°C for 6 h. The FWHM in the [001] was determined from a pole figure analysis to be 9.6°.

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