

## TEMPLATED GRAIN GROWTH - THE ART AND SCIENCE OF PATTERNING CERAMIC MICROSTRUCTURES

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*The Templated Grain Growth (TGG) process is a relatively new process to texture ceramics. Three ferroelectric ceramic systems are used to illustrate the factors controlling texture development during TGG. TGG was utilized to fiber-texture both  $(\text{Sr}_{0.53}\text{Ba}_{0.47})\text{Nb}_2\text{O}_6$ , and  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ , in the [001] and to sheet-texture  $(\text{Sr}_{0.90}\text{La}_{0.10})_2\text{Nb}_2\text{O}_7$ . A direct correlation between crystallographic texture and properties is displayed for all three systems. An enhancement of either the piezoelectric, pyroelectric, and/or dielectric response due to the crystallographic texturing in the desired direction is evident for all systems.*

### INTRODUCTION

Traditional bulk ceramic processing has usually resulted in the formation of microstructures which exhibit physical properties governed by the  $\infty$ mm symmetry. Each grain in the polycrystalline sample has a crystallographic orientation different from the neighboring grains. This random distribution results in an averaging of properties in all directions, often leading to an isotropic appearance for even an anisotropic system which usually displays anisotropic properties in single crystal form. In contrast, textured ceramics can exhibit anisotropic physical properties which are typical of single crystals. Therefore, enhanced and anisotropic electrical, electromechanical, magnetic, optical, and structural properties can be achieved in a ceramic sample with the desired texture.

TGG offers the possibility of fabricating grain-oriented polycrystalline ceramics which exhibit single crystal-like properties in the desired crystallographic direction. It has been shown that oriented template particles can be used to develop textured microstructures by TGG in alumina<sup>1</sup>, mullite<sup>2</sup>, and  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ <sup>3</sup>. The process involves the orientation of anisotropically-shaped template particles in a dense, fine-grained matrix by shear-forming techniques. Template particles must be large and anisometric in shape, so that they can be oriented during forming and grow preferentially during heating. The driving force for the TGG process is the difference in surface free energy between the

templates and the matrix grains. The relative size of the matrix and template particles during densification plays an important role in texture development<sup>4,5</sup>. The final texture in the microstructure depends strongly on the initial number of template particles and their distribution throughout the body.

In this paper, we report on the texturing of three ferroelectric systems,  $(\text{Sr}_{0.53}\text{Ba}_{0.47})\text{Nb}_2\text{O}_6$ ,  $(\text{Sr}_{0.90}\text{La}_{0.10})_2\text{Nb}_2\text{O}_7$ , and  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{PbTiO}_3$ . We were interested in texturing the first two ceramic systems in the spontaneous polarization direction for the benefit of poling efficiency and increased properties.  $(\text{Sr}_x\text{Ba}_{1-x})\text{Nb}_2\text{O}_6$  possesses the tetragonal tungsten bronze structure for  $x=0.25$ - $0.75$ <sup>6</sup> which shows either normal or relaxor ferroelectric properties, depending on the composition<sup>7</sup>. For this system, we were interested in fiber-texturing (1-D texturing) the ceramic in the [001] utilizing acicular  $\text{KSr}_2\text{Nb}_5\text{O}_{15}$  particles.  $(\text{Sr}_{0.90}\text{La}_{0.10})_2\text{Nb}_2\text{O}_7$  is a regular ferroelectric material with a perovskite-layered structure ( $\text{Ca}_2\text{Nb}_2\text{O}_7$  structure)<sup>8</sup>. In this system, the required texturing direction is along the c-axis or [001], which was achieved by using blade-like  $\text{Sr}_2\text{Nb}_2\text{O}_7$  templates.  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{PbTiO}_3$  (PMN-PT) is different than the above systems. PMN-PT is a perovskite relaxor ferroelectric material which displays a rhombohedral (or pseudo-cubic) symmetry at a composition below the morphotropic phase boundary ( $<0.35$  mol%  $\text{PbTiO}_3$ )<sup>9</sup>. Fiber-texturing in the [001] is also required for this system even though the spontaneous polarization is in the  $<111>$ . Park *et al* showed that PMN-PT compositions just below the MPB (30-34 mol%  $\text{PbTiO}_3$ ) displayed enhanced piezoelectric response in the  $<001>$  under high field conditions due to a phase transformation from the rhombohedral to the tetragonal state. Therefore, it is desirable to fiber-texture the PMN-PT composition near the MPB in the  $<001>$ , and this was accomplished by using oriented {001}- $\text{BaTiO}_3$  tabular particles.

This study focuses on the texturing of these three ferroelectric systems by TGG, and it shows the effect of texturing on the piezoelectric, pyroelectric, and/or dielectric properties. The properties achieved were compared and contrasted to single crystal and randomly oriented ceramic properties for the three systems.

## RESULTS AND DISCUSSION

### Fiber-Textured $(\text{Sr}_{0.53}\text{Ba}_{0.47})\text{Nb}_2\text{O}_6$

Textured  $(\text{Sr}_{0.53}\text{Ba}_{0.47})\text{Nb}_2\text{O}_6$  (SBN53) ceramics with a relative density  $>95\%$  were fabricated by TGG<sup>10</sup>.  $0.85$  mol%  $\text{V}_2\text{O}_5$  was used as a liquid former to enhance the grain growth of the SBN53 ceramic grains.  $\text{KSr}_2\text{Nb}_5\text{O}_{15}$  template particles, synthesized by a molten salt process, were aligned by tape casting in a mixture of solid-state-synthesized  $\text{SrNb}_2\text{O}_6$  and  $\text{BaNb}_2\text{O}_6$  powders. The



resulting ceramics possess strong fiber-texture along the polar axis, [001], of SBN53. Samples with 15.4 wt% templates reached a texture percentage >90% after sintering at 1200 °C for 4 h (Figures 1, 2). These samples showed a peak dielectric constant of 7550 (at 1 kHz) at the Curie temperature (145 °C), and a room temperature remanent polarization of 13.2  $\mu\text{C}/\text{cm}^2$  and saturation polarization of 21  $\mu\text{C}/\text{cm}^2$  (60-85% of single crystal)<sup>11</sup>, piezoelectric strain coefficients of 78 pC/N (70-85% of single crystal)<sup>11, 12</sup>, and pyroelectric coefficients of  $2.9 \times 10^{-2} \mu\text{C}/\text{cm}^2 \text{ } ^\circ\text{C}$  (52% of single crystal)<sup>13</sup>. These results show that TGG is a viable option for accessing single crystal properties in polycrystalline ceramics.

### Sheet-Textured $(\text{Sr}_{0.90}\text{La}_{0.10})_2\text{Nb}_2\text{O}_7$

$(\text{Sr}_{0.90}\text{La}_{0.10})_2\text{Nb}_2\text{O}_7$  (SLN) ceramics reached approximately 97% of theoretical density when sintered between 1450-1500 °C for 1-4 h<sup>14</sup>. These ceramics were sintered with a minimum amount of excess niobium (500-1000 ppm) to produce the required liquid phase, which enhanced the growth of the aligned template grains, 10 vol%  $\text{Sr}_2\text{Nb}_2\text{O}_7$  (SN) blade-like templates,

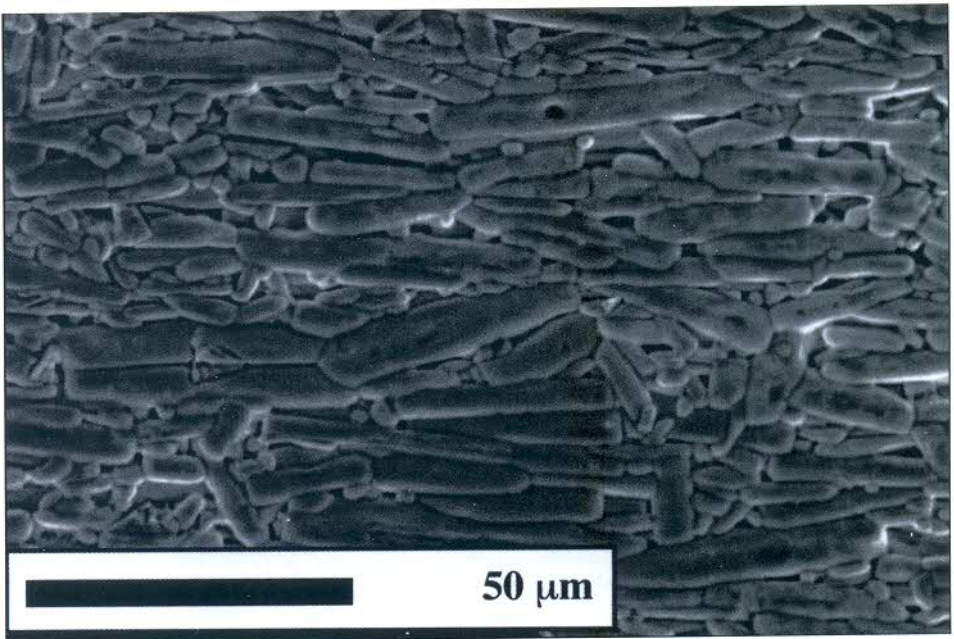


FIGURE 1 - SBN53 textured in the [001] with 15.4 wt%  $\text{KSr}_2\text{Nb}_5\text{O}_{15}$  templates + 0.85 mol%  $\text{V}_2\text{O}_5$  sintered at 1350 °C for 4 h.

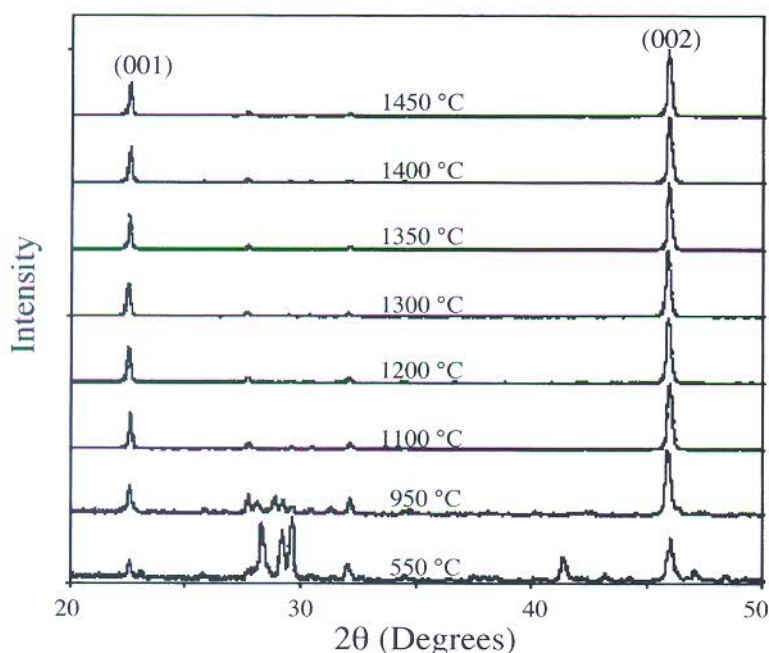


FIGURE 2 - Texture evolution of  $(\text{Sr,Ba})\text{Nb}_2\text{O}_6$  containing 15.4 wt%  $\text{K Sr}_2\text{Nb}_3\text{O}_{15}$  templates + 0.85 mol%  $\text{V}_2\text{O}_5$  sintered at 1400 °C for 4 h.

formed by molten salt synthesis in  $\text{KCl}^4$ , were initially aligned in the SLN matrix powder by tape casting through 1.0 millimeter-spaced gates located behind the doctor blade. The gates provided the required shear field to orient the length of the templates along the casting direction. This tape casting process made the b-planes of all the templates parallel to each other and the tapecast surface, and made a particular direction (a-direction) in the oriented b-plane of all templates parallel to a common direction (casting direction). By achieving this alignment of the blade-like templates, the proper initial green processing conditions for sheet-texture were satisfied, and thus, the texture was developed with further heat treatment during sintering.

TGG samples of SLN containing 10 vol% blade-like SN templates sintered at 1450 °C for 4 h displayed distinct sheet-texture (3-D texturing) when characterized by XRD (Figure 3, 4). Along the tape casting direction (a-direction), the (200) was the most prevalent plane, while in the polarization direction (c-direction) and the tape face direction (b-direction) displayed the (002) and (080), respectively. The dielectric behavior of the sheet-textured TGG samples was measured in the temperature range of -150 °C to 450 °C at 1 MHz for all orthogonal directions. The room temperature dielectric behavior for the a-,

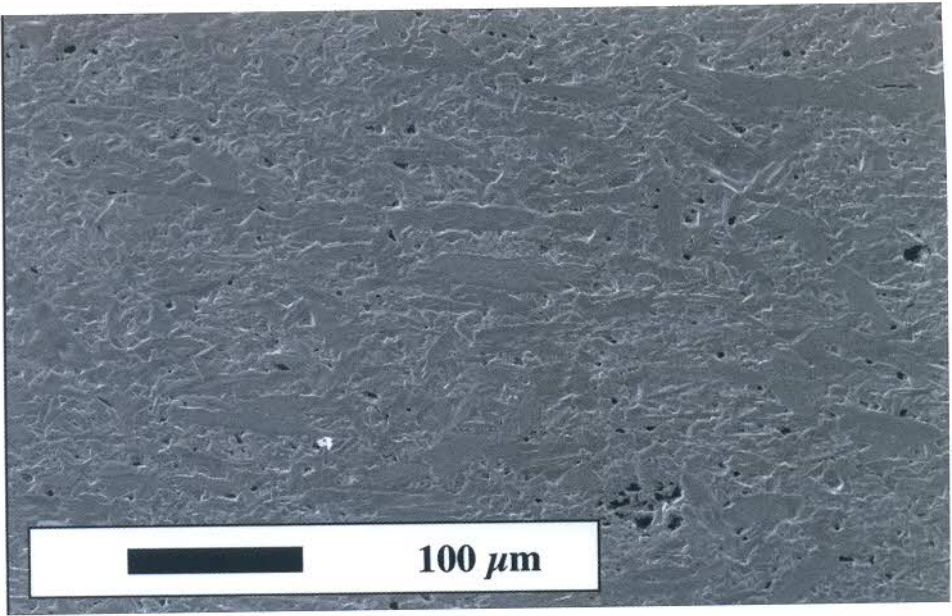


FIGURE 3 -  $(\text{Sr},\text{La})_2\text{Nb}_2\text{O}_7$  textured in the  $[001]$  with 10 vol%  $\text{Sr}_2\text{Nb}_2\text{O}_7$  templates sintered at  $1450^\circ\text{C}$  for 1 h.

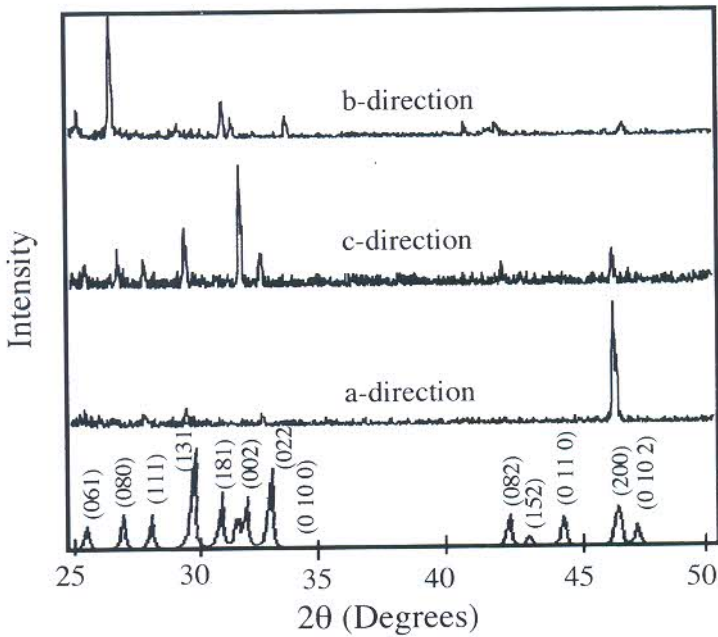


FIGURE 4 - Directional dependence of  $(\text{Sr},\text{La})_2\text{Nb}_2\text{O}_7$  textured with 10 vol%  $\text{Sr}_2\text{Nb}_2\text{O}_7$  templates sintered at  $1450^\circ\text{C}$  for 1 h.



b-, and c- directions for the TGG samples were 68, 45, and 49, respectively. These values are in good agreement with the values seen for single crystals ( $K_a = 75$ ,  $K_b = 43$ ,  $K_c = 46$  at 1 MHz)<sup>15</sup>. This result strongly underscores the effect of texture on physical properties like that of the dielectric constant.

### Fiber-Textured $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{PbTiO}_3$

0.7 $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -0.3 $\text{PbTiO}_3$  (PMN-30PT) matrix powder was tapecast containing approximately 2.5 vol% Remeika formed  $\text{BaTiO}_3$  tabular templates<sup>16</sup> with the dimensions of approximately 100  $\mu\text{m}$  in diameter and 50  $\mu\text{m}$  thick. The templates were aligned in the  $\langle 001 \rangle$  during tape casting through a blade thickness of 400  $\mu\text{m}$ . The samples were cut, laminated, and burned out to a sample thickness of approximately 350  $\mu\text{m}$ . These samples were then hot-pressed in argon at 900 °C for 30 min at 40 MPa. The samples attained approximately 95-97% of theoretical density in the presence of 3.0 wt% excess  $\text{PbO}$ . The hot-pressed samples were then annealed in air at 1150 °C for 0-60 min to drive the TGG process (Figure 5). XRD of the surface of the tape, which is perpendicular to the tapecasting direction, showed the progression of texturing with further annealing time. With further annealing of 15, 30, and 60 min, the volume percentage of texture evolved from 30 to 80% (determined by Lotgering Factor) in the  $\langle 001 \rangle$ . The 80% textured sample was then poled in the texture direction at 30 kV/cm at room temperature for 15 min. The unipolar measurement (at 0.2 Hz) of the 80% textured sample displayed an elevated piezoelectric response ( $d_{33} = 750$  pC/N at 5 kV/cm,  $d_{33} = 220$  pC/N at 40 kV/cm) compared the random ceramic sample ( $d_{33} = 650$  pC/N at 5 kV/cm,  $d_{33} = 150$  pC/N at 40 kV/cm).

The excess  $\text{PbO}$  used to enhance the grain growth of PMN-PT is known to have a negative effect on the dielectric and piezoelectric properties of this system. Therefore, an approach was needed to assist in the nucleation and growth of the PMN-PT composition from the oriented  $\text{BaTiO}_3$  template without the use of the parasitic  $\text{PbO}$ -based phase. The Reactive Templated Grain Growth (RTGG)<sup>17</sup> approach was used to accomplish this desired requirement. By using a reactive precursor consisting of basic  $\text{PbCO}_3$ ,  $\text{MgNb}_2\text{O}_6$ , and fumed- $\text{TiO}_2$  instead of pure phase PMN-PT during the TGG process, the samples were fired to >99% density without the use of excess  $\text{PbO}$ . This reactive precursor composition (producing a final composition of PMN-32PT), with the addition of 5 vol%  $\{001\}$ - $\text{BaTiO}_3$  templates, was green processed and hot-pressed in the same manner as the samples described above. This precursor composition produced a sample displaying 60% texturing in the  $\langle 001 \rangle$  after annealing at 1150 °C for 10 h in oxygen. The preliminary unipolar measurements (at 0.2 Hz) of the textured sample showed a large improvement in the piezoelectric response. The ~60% textured sample showed a piezoelectric

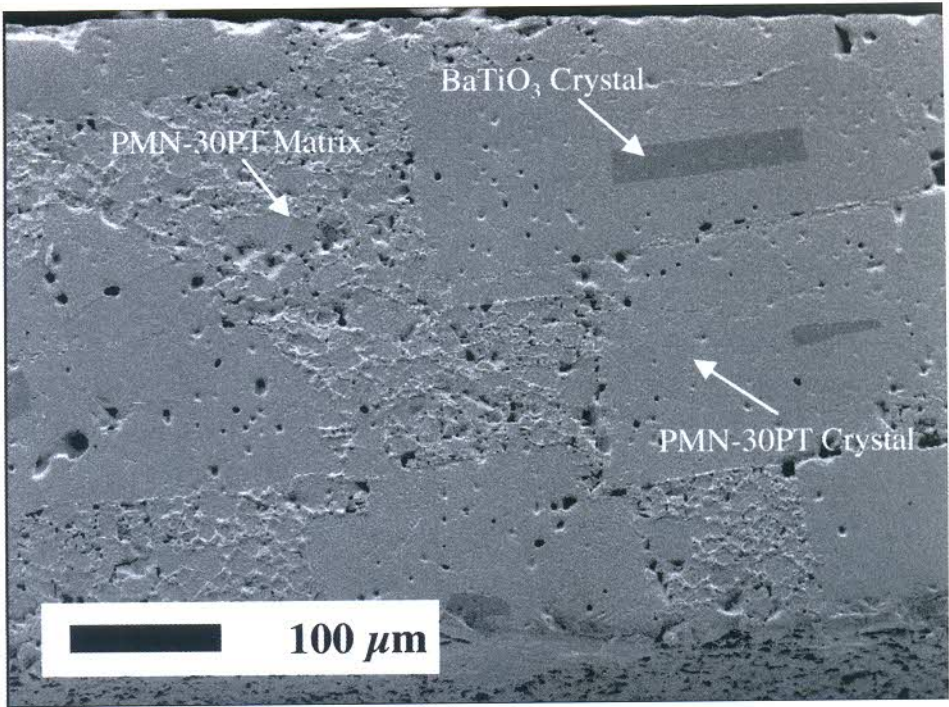


FIGURE 5 - PMN-30PT textured in the  $\langle 001 \rangle$  with 2.5 vol%  $\text{BaTiO}_3$  templates + 3 wt% excess  $\text{PbO}$  at  $1150^\circ\text{C}$  for 1 h.

coefficient ( $d_{33} = 1100 \text{ pC/N}$  at  $5 \text{ kV/cm}$ ,  $d_{33} = 300 \text{ pC/N}$  at  $40 \text{ kV/cm}$ ) about twice that of its random oriented counterpart.

## SUMMARY

TGG was utilized to fiber-texture both  $(\text{Sr}_{0.53}\text{Ba}_{0.47})\text{Nb}_2\text{O}_6$ , and  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ , and sheet-texture  $(\text{Sr}_{0.90}\text{La}_{0.10})\text{Nb}_2\text{O}_7$ . The dielectric, piezoelectric, and pyroelectric response of textured  $(\text{Sr}_{0.53}\text{Ba}_{0.47})\text{Nb}_2\text{O}_6$  displayed a directional dependence, similar to that seen in single crystals, due to the resulting crystallographic texturing of the sample. The directional dependence of the electrical properties was further emphasized by the distinct contrast of the dielectric constants in the three orthogonal directions for the sheet-textured  $(\text{Sr}_{0.90}\text{La}_{0.10})\text{Nb}_2\text{O}_7$ . The texturing of PMN-30PT using  $\text{BaTiO}_3$  templates showed that TGG may also be applied to crystal systems which show a greater isotropic symmetry, unlike the anisotropic systems typically textured by TGG and other processing methods. By texturing the PMN-PT ceramic in the  $\langle 001 \rangle$ , the piezoelectric response of the ceramic was enhanced beyond that shown by the randomly oriented PMN-PT ceramics.



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## Discussion

**P. Sajgalik:** Did you observe any residual stress in the aligned microstructures?

**G.L. Messing:** We did not any measurements of residual stress. However, investigations by others on textured alumina formed by TGG indicate there is a residual stress. Interestingly, we have never seen any textured samples crack as a result of residual stresses or as a result of thermal expansion anisotropy.