

Dielectric and Electromechanical Properties of Barium Titanate Single Crystals Grown by Templated Grain Growth

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Abstract—Single crystals of BaTiO₃ were grown by templated grain growth (TGG). TGG involves contacting a single crystal “template” to a sintered polycrystalline matrix, then heating the assemblage to a temperature that promotes the migration of the single crystal boundary through the matrix. In this investigation the properties of millimeter-sized, plate-shaped and bar-shaped, single crystals of BaTiO₃ grown by TGG were examined in order to compare the results to single crystals grown by conventional methods. A dielectric constant, $\frac{\epsilon_{33}^T}{\epsilon_0}$, of 260, polarizations of $P_R \sim 16 \mu\text{C}/\text{cm}^2$ and $P_{\text{sat}} \sim 21.5 \mu\text{C}/\text{cm}^2$, electromechanical coupling coefficients of $k_{33} \sim 0.51$ and $k_{31} \sim 0.18$, and a piezoelectric coefficient of $d_{33} \sim 140 \text{ pC}/\text{N}$ were achieved. Entrapped porosity in the crystals made fully poling the crystals difficult.

I. INTRODUCTION

THE PROPERTIES of BaTiO₃ single crystals have been studied since soon after its discovery in 1943. Early studies were conducted on flux-grown crystals produced by the Remeika technique [1]. More recently, other crystal growth techniques such as the floating-zone method and top-seeded solution growth (TSSG) provided larger and higher quality crystals with fewer residual impurities and defects [2]–[5]. In recent years there has been increasing research to develop alternative routes to growing single crystals that would reduce both the cost and time-consuming nature of current techniques.

One of the techniques that has been applied to the BaTiO₃ system is templated grain growth (TGG) [6]–[10]. Single crystals of BaTiO₃ on the order of a few millimeters in size have been produced this way [10].

As observed before, the properties of crystals grown by different flux or melt techniques can differ appreciably [11]. Impurities can shift the Curie temperature, and porosity can decrease the dielectric constant, electromechanical coupling coefficients, and the transverse piezoelectric coefficient [11]–[13]. Of particular concern in the current work is that, to date, TGG BaTiO₃ single crystals incorporate some of the original matrix porosity. Therefore, it was the purpose of this research to determine the effect of included

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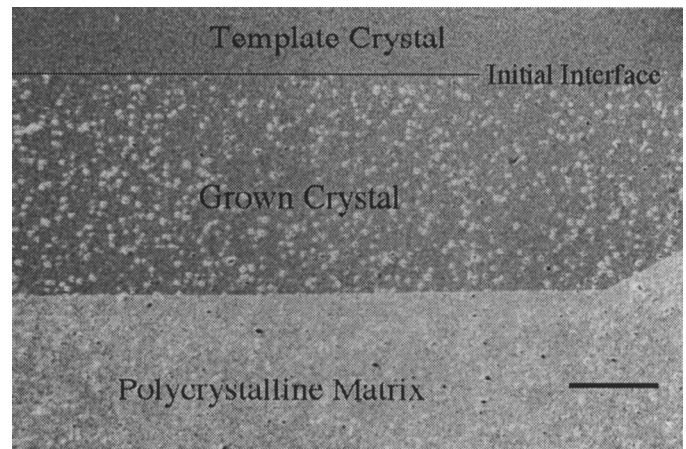


Fig. 1. Scanning electron micrograph of a BaTiO₃ crystal grown into a Ti-rich polycrystalline matrix after 2 h at 1350°C from a (100) oriented template (Bar = 0.2 mm).

porosity on the dielectric and electromechanical properties of single crystals of BaTiO₃ grown by TGG.

II. EXPERIMENTAL PROCEDURE

The method used to obtain BaTiO₃ crystals in this work, TGG, involves contacting a single crystal “template” to a sintered polycrystalline matrix, then heating the assemblage to a temperature that promotes the migration of the single crystal boundary into the matrix. Millimeter-sized single crystals of BaTiO₃ were produced by heating a 97% dense polycrystalline matrix with a Ba/Ti ratio < 1.00 at temperatures above the eutectic temperature of 1332°C. Details of the procedure are described elsewhere [10]. A common characteristic of TGG is that matrix porosity is included in the crystals, resulting in approximately 3 vol% porosity (measured by Archimedes and stereography of scanning electron micrographs). Fig. 1 shows a SEM of a BaTiO₃ crystal grown into a Ti-rich polycrystalline matrix after 2 h at 1350°C from a (001) oriented template. The included porosity can be clearly seen as white dots within the grown crystal. The crystals used for property measurements were grown from (001) templates by heating in air to 1350°C for 10 h. Grown crystals were sectioned from the template and polycrystalline matrix so that property measurements were performed on the grown crystals alone (i.e., none of the original BaTiO₃

crystal remained). The faces of grown crystals were oriented along (001) via X-ray Laue techniques and polished with a 1 μm diamond paste, followed by gold-sputtering to form electrodes. Two sample geometries were prepared: $\sim 1 \times \sim 4 \times 0.3\text{--}0.5$ mm plates (rectangular shaped for dielectric, piezoelectric, and k_{31} measurements) and $0.5\text{--}0.75 \times 0.5\text{--}0.75 \times 3\text{--}4$ mm bars (for k_{33} measurements). The rectangular plates had their faces electroded, which the measurement apparatus could directly contact. The bar-shaped samples were electroded on the ends, then wire leads were attached using silver epoxy, then were soldered during the measurement to the measurement apparatus. A multifrequency LCR meter (HP 4284A) was used in conjunction with a computer-controlled temperature chamber (Delta Design Inc., Model MK 9023) to measure the dielectric constant as a function of temperature on cooling (175°C to -100°C , $2^\circ\text{C}/\text{min}$) at frequencies between 100 Hz and 100 kHz. An HP 4140B picoammeter was used in conjunction with a computer-controlled temperature chamber (Delta Design Inc., Model MK 2300) to measure the pyroelectric current from room temperature to 135°C (Byer-Roundy technique). The sample was poled by field cooling (10 kV/cm, 150°C) in air; then, just prior to pyroelectric current measurement, the field was removed. The polarization seemed stable enough to last the duration of the measurement. The saturation polarization was calculated by integrating the pyroelectric current as a function of temperature.

High-field measurements (1–50 kV/cm) on (001) oriented crystals included simultaneous polarization (P) and strain (S) hysteresis curves obtained using a computer-controlled modified Sawyer-Tower system and a linear, variable-displacement transducer (LVDT, Lucas Schaeffert, Inc., Model 050-HR) sensor driven by a lock-in amplifier (Stanford Research Systems, Model SR830). The voltage was supplied using either a Trek 609C-6 high voltage DC amplifier or a Kepco BOP 1000M amplifier. The same system was used to measure unipolar strain curves on poled (001) oriented crystals. The value for d_{33} was estimated from the slope of the saturated part of the unipolar strain vs. electric field (E) curve. Electromechanical coupling coefficients were measured using the IEEE resonance technique (ANSI/IEEE Std. 176-1987) [14].

III. RESULTS AND DISCUSSION

A. Dielectric Properties

Fig. 2 shows the dielectric constant (a) and dielectric loss (b) as functions of temperature and frequency on cooling for an unpoled TGG crystal. The crystal exhibited very little dispersion in the dielectric constant over the measured temperature range. The transition temperatures occur at $T_{\text{O-T}}$ (orthorhombic-tetragonal) = 9°C and T_{C} (Curie temperature) = 131°C . These are in good agreement with the literature for stoichiometric single crystals of BaTiO_3 grown by TSSG [11], [15]. The 1 kHz room

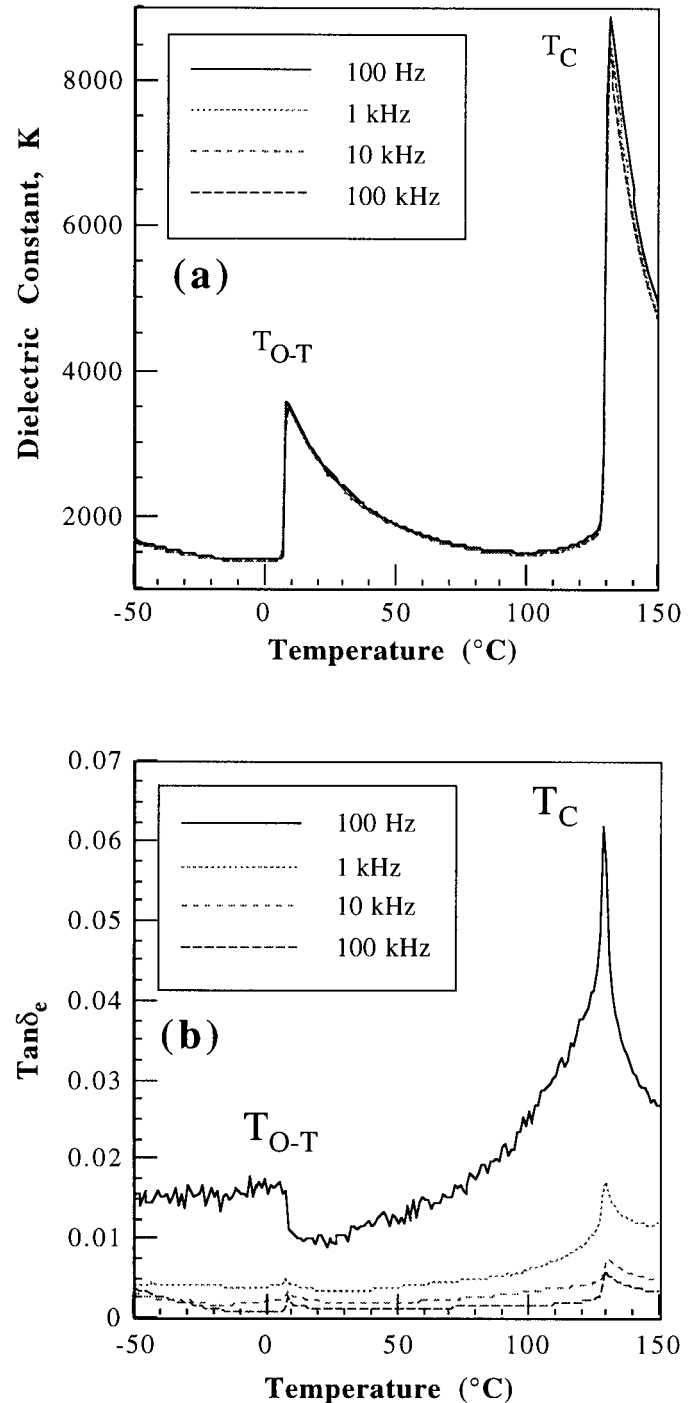


Fig. 2. Dielectric constant, K (a) and dielectric loss, $\text{tan } \delta_e$ (b) as a function of temperature and frequency on cooling (175°C to -100°C , $2^\circ\text{C}/\text{min}$) for TGG grown BaTiO_3 single crystal measured in one of the pseudocubic (100) directions. ($T_{\text{R-O}}$ = rhombohedral to orthorhombic transition, $T_{\text{O-T}}$ = orthorhombic to tetragonal transition, T_{C} = Curie temperature.)

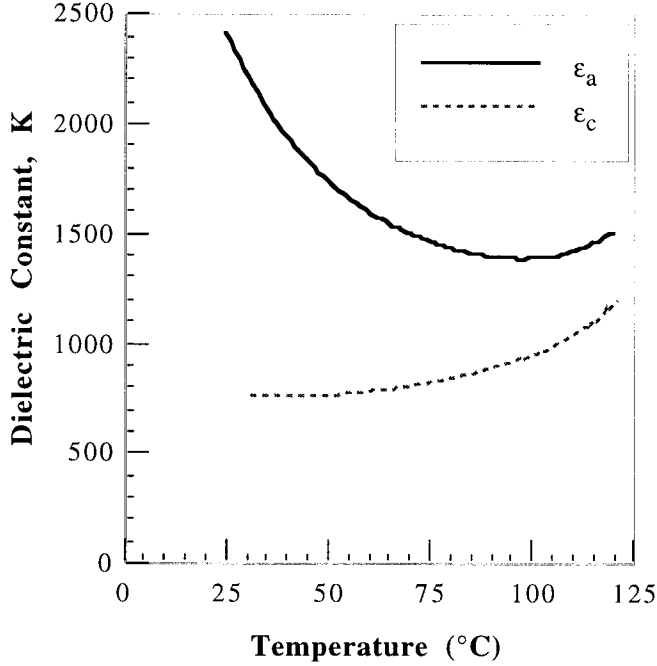


Fig. 3. Dielectric constant, K (1 kHz) along the a (ϵ_a/ϵ_0) and c (ϵ_c/ϵ_0) axes in the tetragonal phase as a function of temperature for TGG grown BaTiO_3 single crystal.

temperature dielectric constant and loss tangent for the unpoled crystal are approximately 2570 and 0.003, respectively, reasonable for an unpoled crystal. The trapped porosity, as mentioned earlier, also will lower the dielectric constant based on mixing rules [16]. If we assume discrete spherical pores, the system is similar to a 0-3 composite [17]. Logarithmic mixing rules can be used to calculate the effect of porosity on the dielectric properties using the following equation:

$$\log_{10}(K) = \sum_n V_n \log_{10}(K_n) \quad (1)$$

where K is the relative dielectric constant, n is the number of phases, and V is the volume fraction. Fig. 3 shows the temperature dependence of the dielectric constant along the a (ϵ_a/ϵ_0) and c (ϵ_c/ϵ_0) axes in the tetragonal phase measured at 1 kHz on poled samples. The room temperature values of ϵ_a/ϵ_0 and ϵ_c/ϵ_0 are 2430 and 770, respectively. Although the trends shown in Fig. 3 are the same as reported in the literature [11], the values for ϵ_a/ϵ_0 and ϵ_c/ϵ_0 are lower and higher than for a fully poled crystal, respectively, as shown in Table I. If the a -axis dielectric constant is calculated using the mixing laws and the single domain value of $\epsilon_a/\epsilon_0 = 3600$, a value of approximately 2800 would correspond to 3 vol% porosity. The experimental value of 2430 observed is lower and can be accounted for by errors in the porosity measurement (3 vol%), as well as to the partial depoling of the TGG crystals upon removal of the electric field. The 1 kHz room temperature dielectric loss tangents measured along the a -axis and c -axis were 0.005 and 0.009, respectively. If one considers that one of the major contributions to dielectric loss at

TABLE I
SUMMARY AND COMPARISON OF DIELECTRIC PROPERTIES OF (001) TGG SINGLE CRYSTAL OF BaTiO_3 AND SINGLE CRYSTALS PREPARED BY TOP-SEEDED SOLUTION GROWTH AS REPORTED IN THE LITERATURE.

Property (RT, 1 kHz)	Reported value (single domain) [11], [15]	TGG Crystal
ϵ_a/ϵ_0	3600	2430
$\text{Tan } \delta_e$ (a -axis)	< 0.01	0.005
ϵ_c/ϵ_0	150	770
$\text{Tan } \delta_e$ (c -axis)	< 0.01	0.009
$\epsilon_{33}^T/\epsilon_0$	150	263 (DC bias, 20 kV/cm)
$\text{Tan } \delta$	< 0.01	0.003
T_C ($^{\circ}\text{C}$)	135	132
C ($^{\circ}\text{C}$)	1.8×10^5	1.8×10^5
T_0 ($^{\circ}\text{C}$)	112	112

TABLE II
SUMMARY OF POLARIZATION PROPERTIES OF (001) TGG AND TSSG SINGLE CRYSTALS OF BaTiO_3 .

Property	TSSG Crystal	TGG Crystal
P_r ($\mu\text{C}/\text{cm}^2$)	21	16
P_{sat} ($\mu\text{C}/\text{cm}^2$)	25	21.5
P_{sat} (pyro) ($\mu\text{C}/\text{cm}^2$)	26 [15]	19
E_c (kV/cm)	~ 1 [16]	3
d_{33} (pC/N)	125	140

room temperature is domain wall motion, the low values suggest that the porosity in TGG crystals impedes domain wall motion. Also, these low values of loss tangents indicate that, although porous, the TGG crystals are of reasonable quality.

Above T_C the Curie-Weiss law is obeyed with Curie constants and Curie-Weiss temperatures in the range of $C = 1.5\text{--}2.0 \times 10^5$ $^{\circ}\text{C}$ and $T_0 = 107\text{--}116$ $^{\circ}\text{C}$, respectively, i.e., $\epsilon_R \cong 1.8 \times 10^5$ $^{\circ}\text{C}/(T - 112$ $^{\circ}\text{C})$ (averaged values). The observed value for the Curie constant is in the range expected for BaTiO_3 single crystals (on the order of 10^5 $^{\circ}\text{C}$), and is in very good agreement with Wemple [15] who reported a value of $C = 1.8 \times 10^5$ $^{\circ}\text{C}$. The Curie-Weiss temperature is also in good agreement with a reported value of 112 $^{\circ}\text{C}$ [15].

Fig. 4 shows the small signal dielectric constant as a function of DC bias along the c -axis. Although the sample was poled by field cooling prior to the room temperature capacitance measurement, the sample exhibited a dielectric constant higher than expected, indicating that the sample partially depoled. The measurement was taken with the application of a DC bias along the c -axis in an attempt to pole the sample as fully as possible and, therefore, approach the true $\epsilon_{33}^T/\epsilon_0$ ($T =$ stress-free state) value. This led to a room temperature $\epsilon_{33}^T/\epsilon_0 = 260 \pm 10$ at 18 kV/cm, a maximum field limited by both the sample geometry and the experimental setup. As shown in Fig. 4,

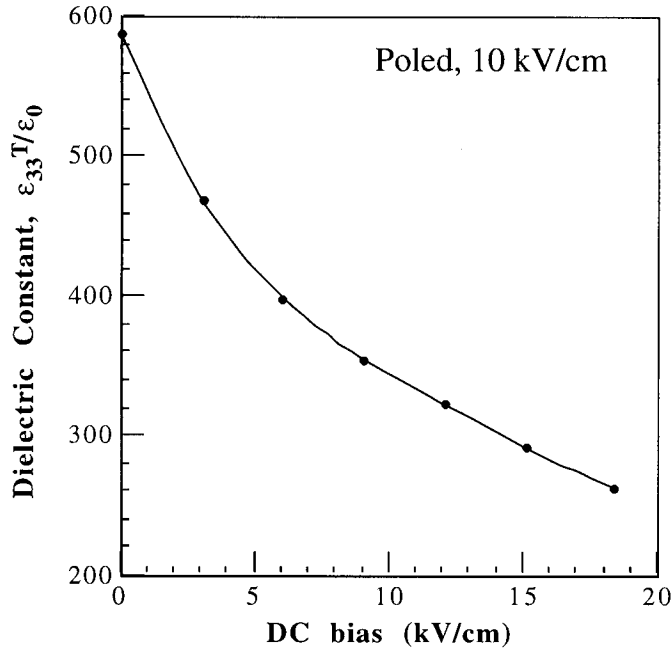


Fig. 4. Dielectric constant, $\epsilon_{33}^T/\epsilon_0$, as a function of DC bias along the c -axis for TGG grown BaTiO_3 single crystal.

the value has not reached saturation at 18 kV/cm. This suggests that, at these field levels, not all domains were aligned with the applied field and that higher fields are necessary to achieve more complete polarization. Other authors [11] report that a fully poled, single-domain state was achieved in dense crystals with values of dielectric constant saturating to 150 if mechanical in addition to electrical poling was applied. This difficulty in poling the TGG crystals is probably due to pinning of some domains by the defects in the crystal, namely, the entrapped pores. Although some domains remain switchable, the pores—which may be considered as macro-sized defects where the local electric field is distorted—and localized strain effects pin some of the domain walls, resulting in a distribution of pinned domains. Table I compares the dielectric properties of TGG crystals with values for high quality crystals from the literature.

Pyroelectric measurements of the saturation polarization confirmed that the Curie transition of TGG grown BaTiO_3 crystals is of the first order and occurs at approximately 133°C. The measured room temperature P_{sat} was approximately $19 \mu\text{C}/\text{cm}^2$. That this value is lower than the value for single domain BaTiO_3 single crystals ($26 \mu\text{C}/\text{cm}^2$) [15], [16], [18] indicates that not all the domains were aligned by application of an electric field, and results from the same origins as previously mentioned.

B. Effect of Electric Field

Fig. 5 shows the bipolar polarization along (001) as a function of electric field at 10 Hz. The first aspect to notice is that the polarization loop is not as square as expected for a single crystal. The remanent polarization, $P_R \sim 12 \mu\text{C}/\text{cm}^2$ (versus $26 \mu\text{C}/\text{cm}^2$ for single crystals

TABLE III
SUMMARY OF PIEZOELECTRIC, ELECTROMECHANICAL, AND ELASTIC COMPLIANCE PROPERTIES OF (001) TGG AND TSSG SINGLE CRYSTAL OF BaTiO_3 .

Property	Reported values [16] TSSG Crystal	TGG crystal (DC bias)
k_{33}	0.56	0.51 (2 kV/cm)
S_{33}^D ($10^{-12} \text{ m}^2/\text{N}$)	10.8	13.2
S_{33}^E ($10^{-12} \text{ m}^2/\text{N}$)	15.7	17.8
d_{33} (pC/N)	125*	135
g_{33} ($10^{-3} \text{ Vm}/\text{N}$)	57.5	30.6
k_{31}	0.315	0.18 (18 kV/cm)
S_{11}^D ($10^{-12} \text{ m}^2/\text{N}$)	7.25	8.1
S_{11}^E ($10^{-12} \text{ m}^2/\text{N}$)	8.05	8.4
d_{31} (pC/N)	-34.5	-26
g_{31} ($10^{-3} \text{ Vm}/\text{N}$)	-23.0	-9.8

of BaTiO_3 grown by TSSG) [16], [18], and the coercive field, $E_C \sim 3 \text{ kV}/\text{cm}$, were lower and higher than BaTiO_3 crystals grown by TSSG, respectively. It is well-known that structural defects such as pores in the material tend to impede the motion of domain walls and, therefore, increase the electric field necessary to orient affected domains as described above. This leads to the higher coercive field. These same defects also may influence the remanent polarization characteristics, due to localized strain effects pinning domain walls. Again, the values for P_R and E_C are intermediate between those of other single crystals and ceramics of similar composition.

Fig. 6 shows the unipolar polarization and strain behavior along (001) direction as a function of electric field for TGG and TSSG crystals. In an attempt to observe fully saturated polarization and strain behavior of the TGG crystal, an electric field was applied until breakdown of the sample occurred. The sample had a breakdown strength of 105 kV/cm, and the data just prior to breakdown are shown in Fig. 6 (top), where the starting polarization value was normalized to the bipolar data at lower electric fields. As shown, a nonhysteretic and saturated curve at $E > 80 \text{ kV}/\text{cm}$ represents the best poling that can be achieved. However, for TSSG crystals, the curve is saturated at $E < 25 \text{ kV}/\text{cm}$. As shown in Fig. 6 (top), the TGG and TSSG crystals show remanent polarizations of approximately 21 and $16 \mu\text{C}/\text{cm}^2$, respectively. By extrapolating the linear portion of the curve back to zero field, under these conditions the TGG crystal has a saturation polarization, P_{sat} , of approximately $21.5 \mu\text{C}/\text{cm}^2$. This value is lower than for the TSSG crystal ($25 \mu\text{C}/\text{cm}^2$) due to the included porosity. As a first approximation, logarithmic (1) and linear mixing laws were used to calculate P_s , assuming a single domain value of $25 \mu\text{C}/\text{cm}^2$. The values were $22.7 \pm 0.7 \mu\text{C}/\text{cm}^2$ and $24.3 \pm 0.3 \mu\text{C}/\text{cm}^2$,

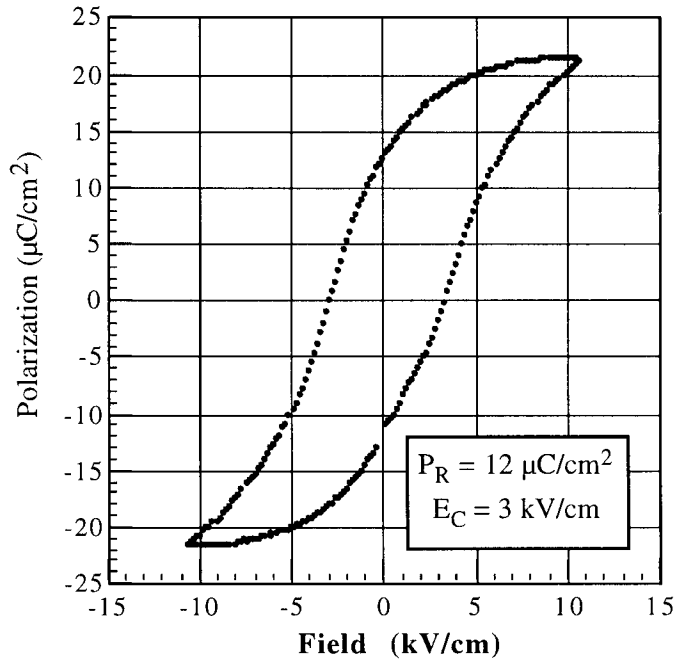


Fig. 5. Bipolar polarization as a function of electric field for (001) TGG grown BaTiO₃ single crystal.

respectively, for 3 ± 1 vol% porosity. It is believed that the values observed were due to a combination of the lower density and the inability to completely pole the crystals.

The unipolar strain (S_{33} , if the measurements were along the polar direction) versus electric field is shown for TGG and TSSG crystals in Fig. 6 (bottom). From this curve, significant domain reorientation is observed for the TGG crystal at fields up to 65–75 kV/cm, above which the strain behavior begins to saturate. For the TSSG crystal, the hysteresis-minimized strain response saturates at $E > 15$ kV/cm. If the two curves are compared, it can be observed that the TGG crystal may not have reached full saturation. This is direct evidence that some domains are pinned, and even very large E-fields cannot align them. By calculating the slope in the saturated high-field region, the piezoelectric coefficient, d_{33} , was found to be ~ 140 pC/N. This value is higher than for the TSSG crystal (125 pC/N), which also indicates that, even at high E-fields, the strain still includes a contribution from domain reorientation. A summary of polarization, coercive field, and piezoelectric coefficients calculated from the polarization measurements is presented in Table II.

It has been reported that {111} directions are the directions along which the maximum effective d_{33} can be achieved in a BaTiO₃ crystal [19]. A question arose as to whether the concept of crystallographic engineering could be applied to TGG crystals. Therefore, the polarization and strain behavior of TGG-grown crystals also was measured for crystals grown from a (111) template orientation. The unipolar strain versus electric field curve exhibited significant domain reorientation up to electric fields of 10 kV/cm, above which the strain behavior begins to sat-

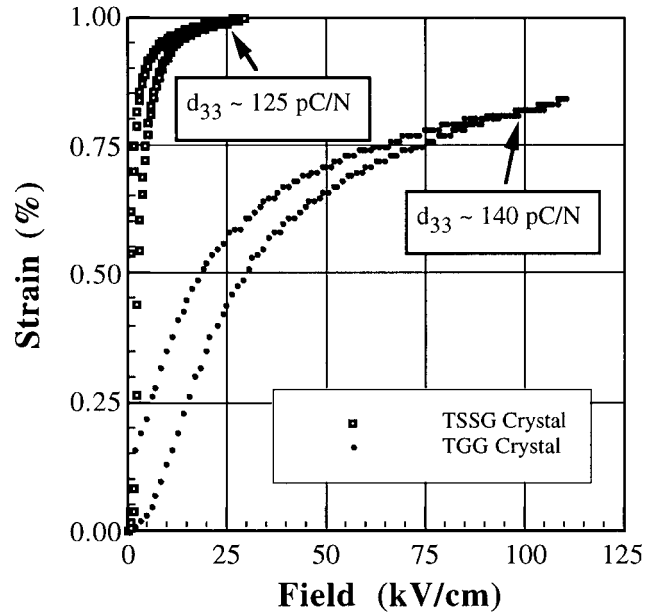
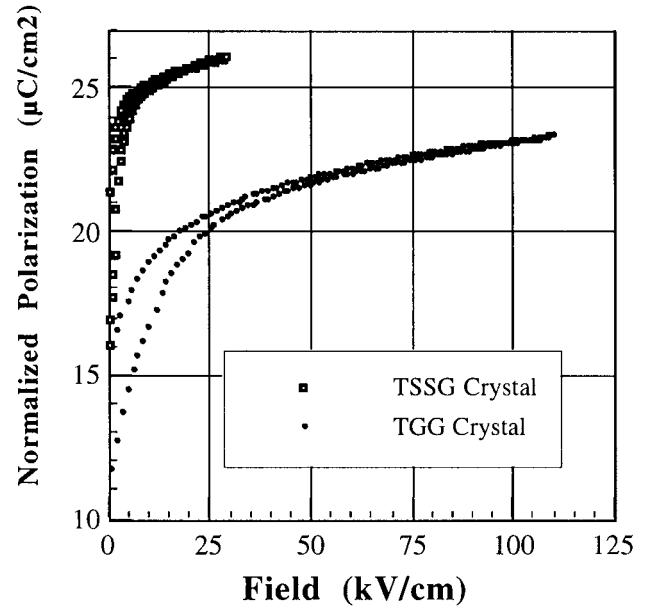


Fig. 6. Unipolar polarization (normalized) (top) and strain (bottom) as a function of electric field at high applied electric fields for (001) TGG and TSSG grown BaTiO₃ single crystals.

urate. By calculating the slope in the saturated region, the piezoelectric coefficient, d_{33} , was ~ 260 pC/N. This value is higher than for (001) (polar axis) oriented tetragonal BaTiO₃ crystals and confirms that this technique is viable for TGG crystals as well.

C. Electromechanical Coupling, Piezoelectric, and Elastic Properties

Fig. 7 shows the electromechanical coupling coefficients, k_{33} and k_{31} , as a function of DC bias for a (001) crystal. The observed increase in coupling coefficients with DC bias is consistent with the observation that as-poled crys-

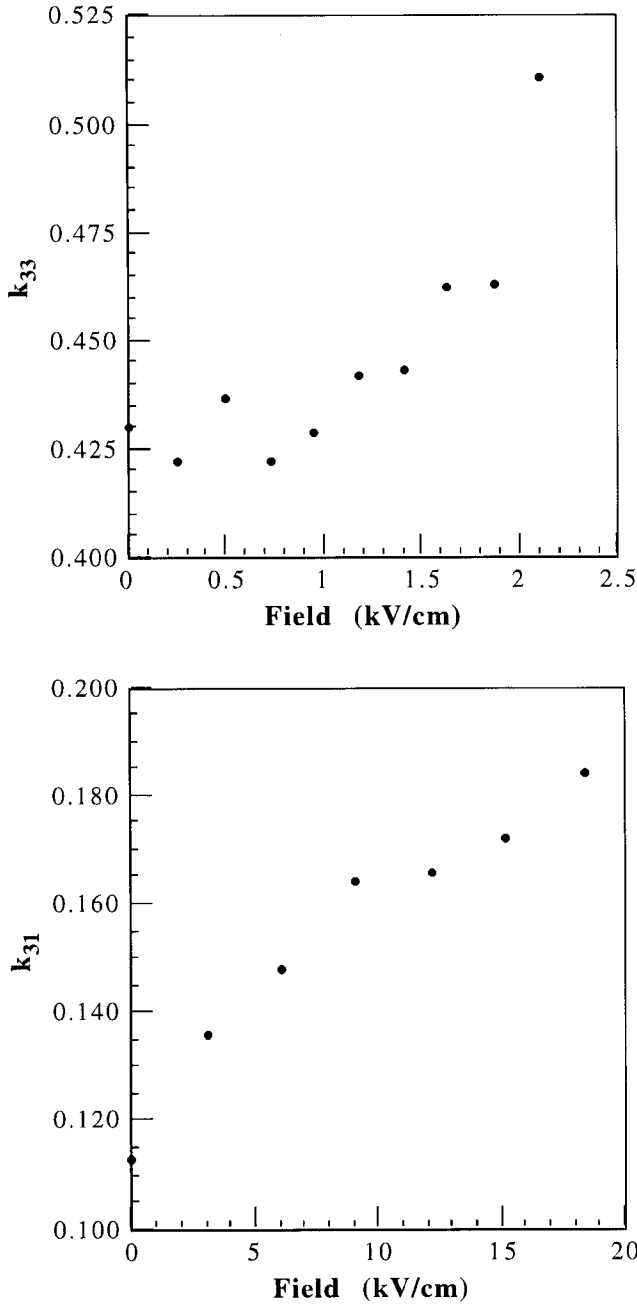


Fig. 7. Electromechanical coupling coefficients, k_{33} (top) and k_{31} (bottom) as a function of DC bias for (001) TGG grown BaTiO₃ single crystal.

tals had low remanent polarizations. The value increases from 0.42 (no bias) to 0.51 at ~ 2 kV/cm. As shown by the previous data, a much higher electric field ($E > 60$ – 80 kV/cm) is necessary to achieve a single domain state; therefore, a higher k_{33} value may have been achieved, if higher fields could have been applied. Fig. 7 (top) shows the transverse electromechanical coupling coefficient as a function of DC bias. As in the case for the longitudinal coupling coefficient, an increase in magnitude with increasing DC bias is observed; however, the field is still too low to achieve a single-domain state. The maximum value of k_{31} was 0.18, which is significantly lower than

the expected value of 0.32 [16], [20]. The magnitude of the electromechanical coupling coefficients also is influenced by the presence of voids because, as shown previously, these macro-defects can impede domain wall motion. The resulting difficulty in fully poling these crystals results in lower observed electromechanical coupling coefficients at the achievable electric fields. There is also sample-to-sample variability in the ability to achieve a well poled state, which probably accounts for the low k_{31} values relative to the observed k_{33} . Even when the fields are high, the samples partially depole upon the removal of the field, indicating that the domain state is not stable.

Table III shows the electromechanical properties calculated using the IEEE resonance technique. For elastic compliances, s_{ij}^D (open circuited sample) and s_{ij}^E (short circuited sample), the values were higher than expected. The effect of porosity on these values was calculated using mixing rules. It was found that, as the volume percent porosity increases, Young's modulus decreases, and hence the compliance increases [21]. However, the amount of increase cannot sufficiently account for the total increase in the values shown in Table III. Therefore, the increase in the values must be associated with the lower electromechanical coupling coefficients and higher values for the dielectric constant. The calculated piezoelectric coefficient, d_{33} , has a value of approximately 135 pC/N, and any errors from the calculation of this value should cancel out. This is in good agreement with the value calculated from high-field polarization data (Fig. 6). The piezoelectric coefficient, g_{33} , was calculated to be 30.6 Vm/N as compared to 57.5 Vm/N for fully poled BaTiO₃ single crystals (its value is lower primarily because of the higher value of $\varepsilon_{33}^T/\varepsilon_0$). The piezoelectric coefficients, d_{31} and g_{31} , measured from transverse properties show similar results to that of the longitudinal results with values lower than expected. The elastic compliances, however, match literature values closely.

IV. CONCLUSIONS

Single crystals of BaTiO₃ were grown by TGG, and the dielectric properties and crystal quality were evaluated and compared to high quality TSSG crystals. The effect of porosity on the dielectric constant is that the TGG crystals behave similar to a 0-3 composite in which the second phase is air, therefore, decreasing the dielectric constant with increasing porosity. Another effect of porosity on the TGG crystals was an observed difficulty in poling the crystals even under high fields (100 kV/cm), caused by the pinning of domain walls. The result of this is a lower remanent, P_R , and saturation polarization, P_{sat} , value and a higher coercive field, E_c . Due to the porosity, the DC bias applied during resonance measurements was not high enough to achieve a single-domain state; therefore, lower electromechanical coupling coefficients were observed. It is likely that the properties of these crystals may be improved further by eliminating the porosity from the crystals.

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