Modified $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ Single Crystals for High Temperature Application

Shujun Zhang*[1], Jun Luo[2], Rob Shanta[3]
David W. Snyder[3], Thomas R. Shrout[1]
[1]Material Research Institute, Pennsylvania State University, University Park, PA, 16802
[2]TRS Technologies, Inc. 2820 E. College Ave., State College, PA, 16801
[3]Electro-Optics Center, Pennsylvania State University, Freeport, PA, 16229
* e-mail: soz1@psu.edu

ABSTRACT: The temperature usage range of rhombohedral $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMNT) piezoelectric crystals is limited by the Curie temperature (T_C) and further limited by the strongly curved morphotropic phase boundary (MPB). It is found in PMNT crystals that T_C decreases or keeps constant at low dc bias and then increases with increasing field, while the ferroelectric-ferroelectric phase transition temperature ($T_{F\text{-}F}$) decreases with increasing dc bias, expanding the tetragonal region and decreasing the overall temperature usage range. Modifications to Bridgman grown PMNT crystals have been made based on a perovskite tolerance factor relationship in an attempt to increase $T_{F\text{-}F}$, and the usage temperature range.

Key words: PMNT, Crystal growth, Piezoelectric, dc bias, Dielectric

1. INTRODUCTION

Relaxor ferroelectric single crystals based on the solid solutions $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMNT) and $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PZNT) have promising potential for applications in transducers and actuators due to their outstanding dielectric, piezoelectric and electromechanical properties [1-6]. However, the temperature usage range of these crystals is limited by their relatively low Curie temperature (T_C) and their strongly curved morphotropic phase transition temperature ($T_{F\text{-}F}$). Furthermore, piezoelectric crystals used in electromechanical devices are subjected to high electric fields, thus it is very important to understand the effect of external dc bias on the temperature usage range.

In this work, the dielectric behavior as a function of dc bias was studied to determine the application working range for PMNT crystals. To expand the temperature usage range, compositional modifications were implemented using the Bridgman growth method.

2. EXPERIMENTAL

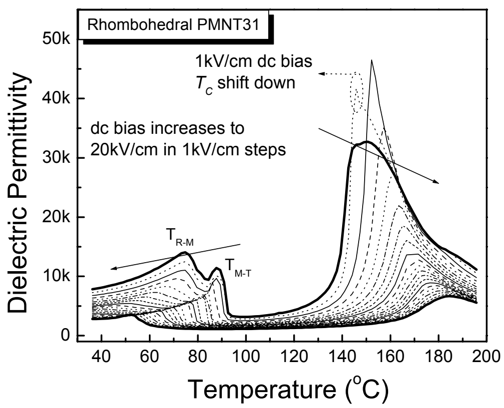
Pb_3O_4, TiO_2, the precursor $Mg_{1/3}Nb_{2/3}O_2$ [6] and small amount of modifications or dopants were used as starting materials, mixed and calcined at 880°C, and then pressed into cylindrical disks and sintered at 1250°C. The fired PMNT ceramics were used to grow single crystals using the modified Bridgman technique [5]. The obtained crystals were oriented along the crystallographic [001] direction using Back-reflection real-time Laue system (Multiwire Laboratory, Ltd.) and the obtained samples were cut and polished to $5x5x0.4mm^3$ in size and vacuum gold sputtered on the parallel large faces to form electrodes. The samples were poled at room temperature using 10kV/cm for 3 minutes. The dielectric behavior as a function of temperature and dc bias were performed on [001] poled PMNT33 samples using a multi-frequency LCR meter (HP 4284A) from room temperature to 250°C with a blocking-circuit designed to protect the LCR meter under high dc bias fields up to 20kV/cm, which was supplied by Trek 609C-6 high voltage dc amplifier. During the measurements, the samples were submerged in a high temperature insulating liquid to avoid arcing. High field measurements including polarization hysteresis (*P-E*) and strain-electric field curves (*S-E*) were measured at 1Hz frequency and fields of 10kV/cm using a modified Sawyer-Tower circuit and linear variable differential transducer (LVDT) driven by a lock-in amplifier (Stanford Research Systems, Model SR 830).

3. RESULTS AND DISCUSSION

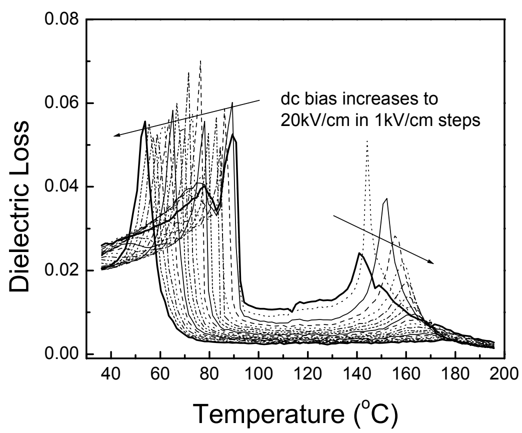
3.1 Dielectric behavior with dc bias

Fig. 1 shows the dielectric permittivity and dielectric loss as a function of temperature for a [001] poled PMNT31 single crystal sample, measured at 100kHz under various applied fields. The dc bias was increased incrementally from 0kV/cm to 20kV/cm in 1kV/cm steps. As shown in Fig. 1a, the dielectric permittivity maximum initially becomes sharper and higher at low dc bias, and then decreases and becomes more diffuse, shifting to higher temperatures with increasing dc bias. This behavior is in good agreement with reported results for PMNT with low PT content [7-9]. It should be noted that when the dc bias is small

(~1kV/cm), T_C of the PMNT31 crystal is found to shift downward, and then strongly increases with fields above 1kV/cm. However, the ferroelectric phase transition temperatures T_{R-M} and T_{M-T} are found to shift to lower temperatures with increasing dc bias. The dielectric peak at the rhombohedral to monoclinic phase transition becomes more diffuse when the dc bias is larger than 4kV/cm, implying the coexistence of rhombohedral and monoclinic phases, which disappear above 10kV/cm and only the electric-field-induced monoclinic phase is observed at room temperature. The dielectric loss exhibits similar behavior as the dielectric permittivity under different dc bias, as shown in Fig. 1b.



(a)



(b)

Fig. 1 Dielectric permittivity (top) and dielectric loss (bottom) as a function of temperature and dc bias at 100kHz for PMNT31 single crystals.

The T_C and T_{M-T} (monoclinic to tetragonal phase transition temperature) as a function of dc bias for rhombohedral PMNT31 crystals are summarized in Fig. 2, where the T_C is found to increase linearly with a dc bias field above 3kV/cm, while T_{M-T} decreases, demonstrating that an external dc bias will stabilize the tetragonal phase of PMNT31 crystals [10].

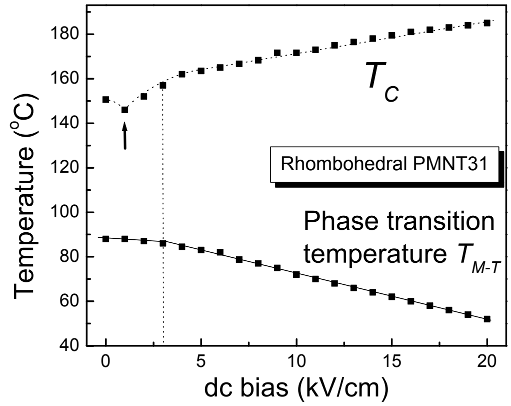


Fig. 2 Curie temperature and phase transition temperature as a function of dc bias for PMNT33 single crystals.

In general, rhombohedral PMNT single crystals are used below their ferroelectric phase transition temperature owing to the change of the piezoelectric properties. Fig. 3 shows the usage temperature range for rhombohedral PMNT single crystals, in which one can see that the usage range decreases with increasing dc bias field. Fig. 4 gives the phase diagram of the PMNT system as a function of dc bias, in which the tetragonal phase region is expanded, limiting the application temperature usage range.

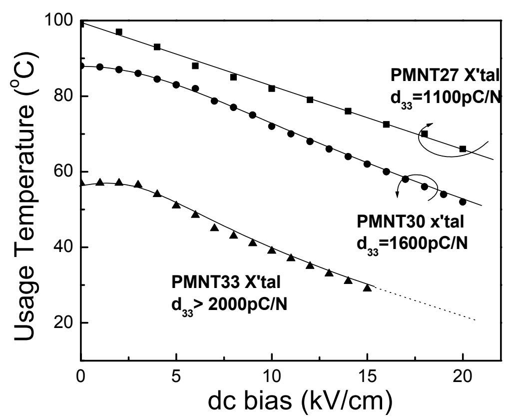


Fig. 3 The usage temperature range for rhombohedral PMNT single crystals as a function of bias.

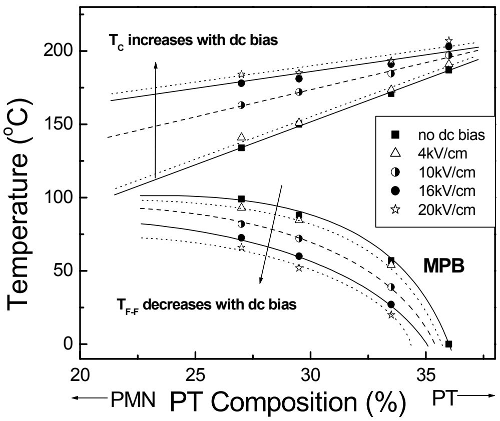


Fig. 4 Phase diagram for PMNT single crystals under different dc bias fields.

3.2 Growth and Characterization of modified PMNT single crystals.

As mentioned above, PMNT single crystals used in electromechanical devices are limited by a low Curie temperature and a strongly curved MPB, further limited when used under a dc bias. It is desired to obtain single crystals with high ferroelectric phase transitions and high piezoelectric properties, from the viewpoint of applications. Three approaches have been used to expand the temperature usage range of rhombohedral single crystal perovskites [11-13]. First, dopant modifications were made to PMNT systems, this approach was selected owing to the commercial viability of PMNT using Bridgman growth; second, crystal growth of other systems with much higher Curie temperature, such as $Pb(Yb_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ near the MPB composition, the highest T_C for a relaxor-PT system reported, being on the order of ~350°C [14-15]; and third, crystal growth of novel MPB compositions in the $Bi(Me)O_3$-$PbTiO_3$ family, which was found to exhibit T_Cs >450°C and T_{R-T} >300°C [16-18].

In this work, we focused on the modification of PMNT single crystals using the Bridgman method which has been commercialized over the past few years [19-20]. In this study, relatively small A- site and/or large B-site ions (compared to the effective ion radius of $Mg_{1/3}Nb_{2/3}O_2$) were used as the dopants in the PMNT system with the dopant level maintained lower than 5mol% in order to obtain good quality crystals. Selection of A and/or B-site modifications was to decrease the perovskite tolerance factor, which should increase T_C and effectively stabilize the rhombohedral phase [21-22]. As shown in Fig. 5, PMNT single crystals with different modifications (15mm in diameter and 80mm in length) were grown by the Bridgman method with good quality crystals obtained.

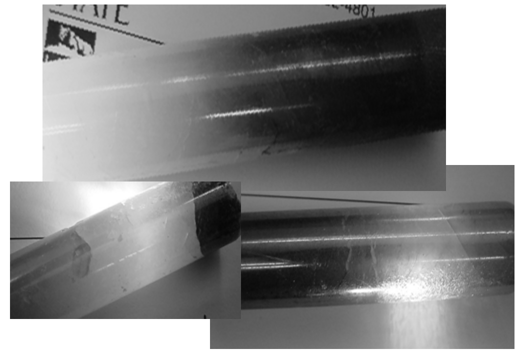


Fig. 5 Photos of the PMNT crystals with different modifications grown using the Bridgman method.

Fig. 6 shows the dielectric permittivity and dielectric loss as a function of temperature and frequency for a B-site modified PMNT30 crystal. The Curie temperature was found to increase by 5°C when compared to the pure counterpart. It is worthy to note that the ferroelectric phase transition is located at 110°C, almost 15°C higher than the T_{R-T} value of PMNT crystals with similar Curie temperature, expanding the usage temperature range for the modified PMNT crystals.

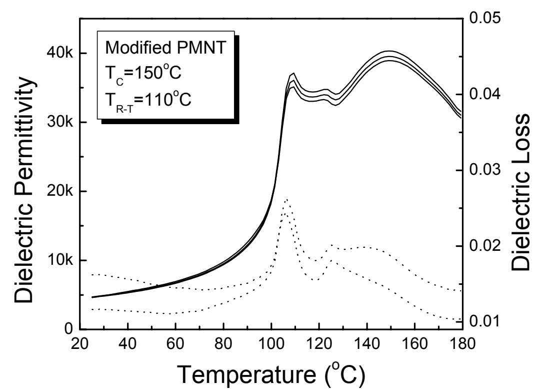


Fig. 6 Dielectric permittivity and dielectric loss as a function of temperature for a B-site modified PMNT.

Fig. 7 presents the bipolar polarization hysteresis and strain electric field curve for a B-site modified crystals, in which the remnant polarization and coercive field are found to be 25.5μC/cm^2 and 3.1kV/cm, respectively. The coercive field is larger when compared to the pure counterpart (~2kV/cm), which relates to the higher Curie temperature. Fig. 8 gives the unipolar strain behavior as a function of electric field. The strain level at 10kV/cm is found to be 0.15% and with very low hysteresis. The piezoelectric coefficient calculated from the slope of the strain-field curve and found to be 1500pm/V, very similar to values of pure PMNT30 crystals (~1400-1800pC/N).

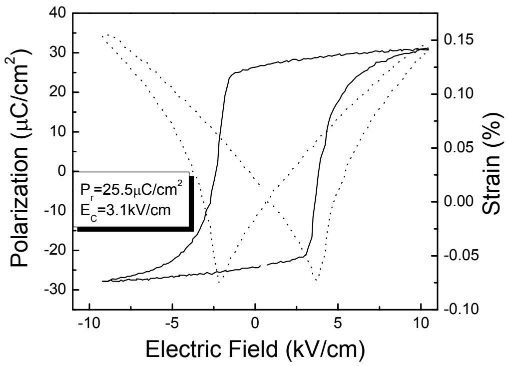


Fig. 7 Polarization and strain as a function of electric field for a B-site modified PMNT crystals.

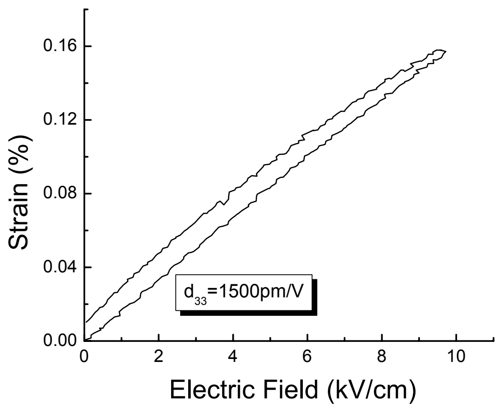


Fig. 8 Unipolar strain as a function of electric field for a B-site modified PMNT crystals.

4. CONCLUSION

Piezoelectric single crystals with high Curie temperature are of interest for the next generation of high performance actuators and transducers, requiring a broad temperature usage range. The T_C of PMNT single crystals increases with external dc bias field, while the ferroelectric phase transition $T_{F\text{-}F}$ shifts downward, limiting the temperature usage range of the crystals. The modification of PMNT single crystals, where it is found that the replacement of B-site ion $Mg_{1/3}Nb_{2/3}O_2$ with larger radius ion gives rise to the enhanced T_C and $T_{R\text{-}T}$ because of the smaller tolerance factor, increasing the temperature usage range, meanwhile maintaining the still high piezoelectric properties.

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