Electric-field-induced phase transitions of <001>-oriented $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ single crystals

W. Ren, L. Han, R. Wicks, G. Yang and B. K. Mukherjee*
Department of Physics, Royal Military College of Canada, Kingston, Ontario, K7K 7B4, Canada

ABSTRACT

Electric-field-induced phase transitions and piezoelectric properties of <001>-oriented $Pb(Mg_{1/3}Nb_{2/3})O_3$–32%$PbTiO_3$ (PMN-PT) single crystals have been investigated as a function of temperature. It was found that the phase transitions and piezoelectric properties for PMN-PT crystals are strongly dependent on temperature. The measurements of polarization and longitudinal strain as a function of a unipolar electric field show that the field for the induced monoclinic-tetragonal phase transition decreases linearly with temperature in the range between 23 ºC and 75 ºC. Raising the temperature can stabilize the tetragonal phase in <001>-oriented PMN-PT crystals. The effective longitudinal piezoelectric constant, d_{33}, in the monoclinic phase increases with temperature. Meanwhile in the field-induced tetragonal phase, d_{33} is much smaller and has little change with temperature. The electric-field-induced phase transition from a cubic phase to a tetragonal phase was observed at 125 ºC.

Keywords: PMN-PT single crystals, phase transitions, field dependence, piezoelectric constants, temperature dependence

1. INTRODUCTION

Single crystals of the relaxor ferroelectric solid solution families $Pb(Mg_{1/3}Nb_{2/3})O_3$ - $PbTiO_3$ (PMN-PT) and $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PZN-PT) are currently being studied extensively due to their high-electric-field-induced strains[1,2,3,4]. The PMN-PT and PZN-PT single crystals in the rhombohedral phase, particularly those with compositions around the morphotropic phase boundaries (MPBs), exhibit high piezoelectric coefficients ($d_{33} \sim 2000$ pC/N), high electromechanical coupling coefficients ($k_{33} \sim 0.90$) and electric-field-induced longitudinal strains up to 1.7 % when poled along the pseudocubic <001> direction. All these properties are superior to those of the commonly used lead zirconate titanate (PZT) ceramics and make PMN-PT and PZN-PT single crystals promising materials for transducer, sensor and actuator applications, such as medical ultrasound imaging systems, underwater sonar projectors and telecommunication systems.

The excellent properties of PMN-PT and PZN-PT single crystals are believed to originate from the MPBs and related effects. Recently, metastable monoclinic ferroelectric phases have been observed around the MPBs between rhombohedral and tetragonal ferroelectric phases, first in PZT and then in PZN-PT and PMN-PT systems[5,6,7,8]. Xu *et al.* have observed both a rhombohedral *3m* phase and a monoclinic *m* phase in the PMN-33%PT crystals under polarization microscopes[7]. Ye *et al.* have found an M_A type monoclinic phase in PMN-35%PT crystals poled along <001> direction using high-resolution synchrotron x-ray diffraction methods[8]. More recently, Noheda *et al*[9]. have carried out systematic investigations on the PMN-xPT system with x between 30% ~ 39%. Their synchrotron x-ray diffraction measurements indicated that a M_C type monoclinic phase coexisted with other phases, either rhombohedral or tetragonal, around the MPB[9]. Guo *et al.* have confirmed the presence of the M_C monoclinic phase in the poled PMN-PT crystals by dielectric and piezoelectric measurements[10].

The monoclinic phase around the MPB in the PMN-PT system increases the possible polarization states in the crystal and enhances dielectric and piezoelectric responses. On the other hand, it makes the system more complicated. As a result, the piezoelectric properties and phases of PMN-PT crystals around the MPB strongly depend on the crystal

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* mukherjee@rmc.ca

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composition, orientation, electrical condition and temperature. For practical applications, especially for actuator applications, it is particularly important to know the piezoelectric responses of the single crystals as a function of the driving electric field and the temperature and to know the effect of phase transitions on the piezoelectric properties. An experimental investigation of such responses for PZN-PT single crystals has been reported by us earlier[11]. The present work extends that experimental investigation to the case of PMN-32%PT single crystals.

2. EXPERIMENT

<001>-oriented single crystals of PMN-PT, with the nominal composition of 32% PT and grown by a flux method, were provided by TRS Ceramics Inc. and have been investigated. The plate samples had dimensions of 5 mm × 5 mm × 1 mm and were prepared with gold electrodes. Before measurements, all samples were poled at fields of 4 MV/m in silicon oil at room temperature.

A differential variable reluctance transducer (DVRT) and a modified Sawyer-Tower circuit were used to measure the field-induced longitudinal strain and the polarization responses respectively. The experimental arrangement of the system is schematically drawn in Fig. 1. The STEP Electromechanical Response Characterization program was used to generate a required waveform for a power amplifier and at the same time to acquire strain and polarization data[12]. A Trek 610D power amplifier was used to supply samples with amplified high voltages. Unipolar electric fields with a frequency of 1 Hz were applied to the specimens along their <001> directions. The samples were immersed in silicon oil that could be heated from room temperature to 145 °C. The silicon oil also helps to prevent arcing when a high voltage is applied.

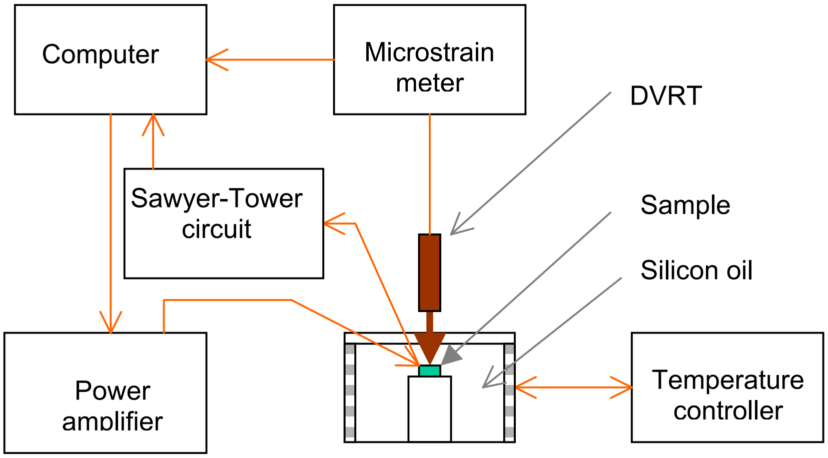

Figure 1. Schematic of the experimental arrangement of the DVRT system.

3. RESULTS AND DISCUSSION

Figure 2 shows the measured polarization and longitudinal strain of the poled PMN-32%PT crystal samples as a function of the unipolar field at various amplitudes from 1 MV/m to 4 MV/m. The plots clearly show that both polarization and strain increase linearly with applied field with a small hysteresis. The calculated effective longitudinal piezoelectric constant $d_{33} = \Delta S_3/\Delta E_3 \approx 1380$ pm/V. This value is smaller than the value (~ 1750 pm/V) for the poled PMN-31%PT reported by Guo *et al.*[13], but higher than the value (~ 900 pm/V) for the poled PMN-33%PT crystals reported by Bokov *et al.*[14]. These values result from contributions by the mixture of phases around the MPB for the crystals. As indicated by Noheda *et al.*[9], the phases around the MPB are very sensitive to the chemical compositions of the materials. Based on their synchrontron x-ray diffraction analysis for the PMN-PT system, the main phase for the PMN-PT system with PT composition between 31% and 33% is the ferroelectric M_C monoclinic phase acompanied with a secondary phase. The secondary phase is a rhombohedral one for PMN-31%PT and a tetragonal one for PMN-33%PT.[9] It is well known that for PMN-PT crystals poled along pseudocubic <001> direction, the longitudinal piezoelectric constant d_{33} in a rhombohedral phase is much higher than that in a tetragonal phase. This result suggests that it is important to control possible variations in the chemical composition of the PMN-PT single crystals as the nature of the phases and the piezoelectric properties are very sensitive to the chemical composition near the morphotropic phase boundary.

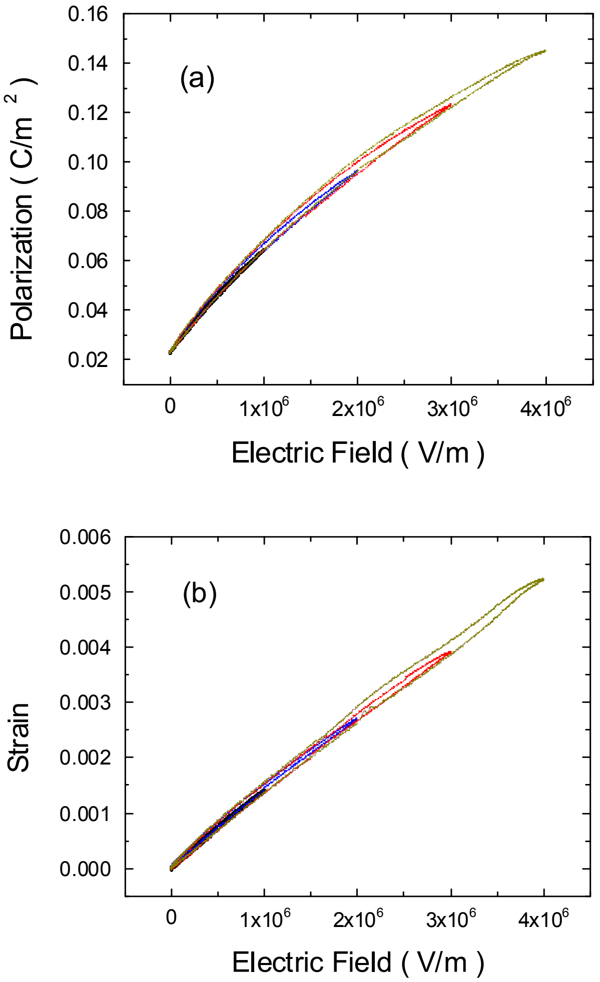

Figure 2. Unipolar electric field dependence of (a) the polarization and (b) the strain response of PMN-32%PT single crystals.

Polar states of the PMN-PT system can be changed by an applied electric field and this process is very susceptible to change of temperature. The temperature dependence of the polarization and the longitudinal strain versus unipolar field along the <001> direction is shown as a function of unipolar field in Fig. 3 and Fig. 4. The behavior of the polarization and that of the strain under a unipolar field are very similar. Upon applying the electric field, the polarization vector rotates to the <001> direction. The PMN-PT materials change crystal symmetry from the monoclinic phase (and also possible rhombohedral phase) to the ferroelectric tetragonal phase, resulting in an electric-field-induced phase transition, as shown in Fig. 3. The electric field for the phase transition is strongly temperature-dependent. Fig. 5 shows the temperature dependence of the phase transition field. As in the case of PZN-PT single crystals[11], the phase transition field of PMN-PT crystals decreases almost linearly with temperature. The effective piezoelectric constants

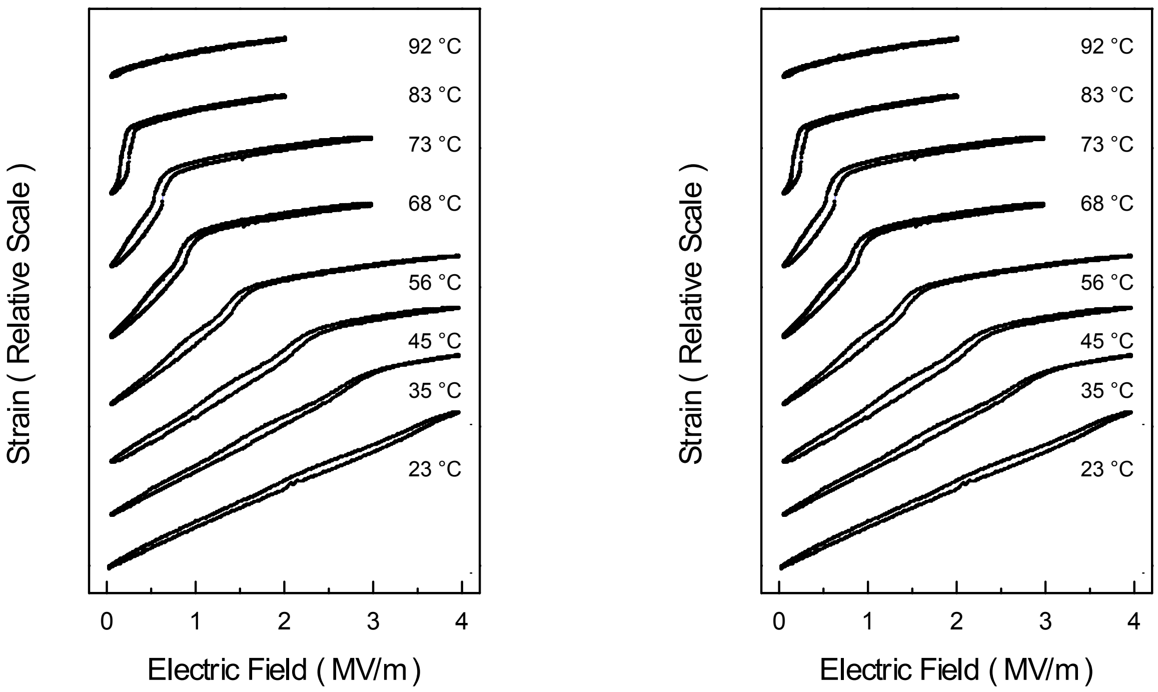

Figure 3. Unipolar electric field dependence of the polarization and the strain response of PMN-32%PT single crystals at temperatures ranging from 23 ºC to 92 ºC.

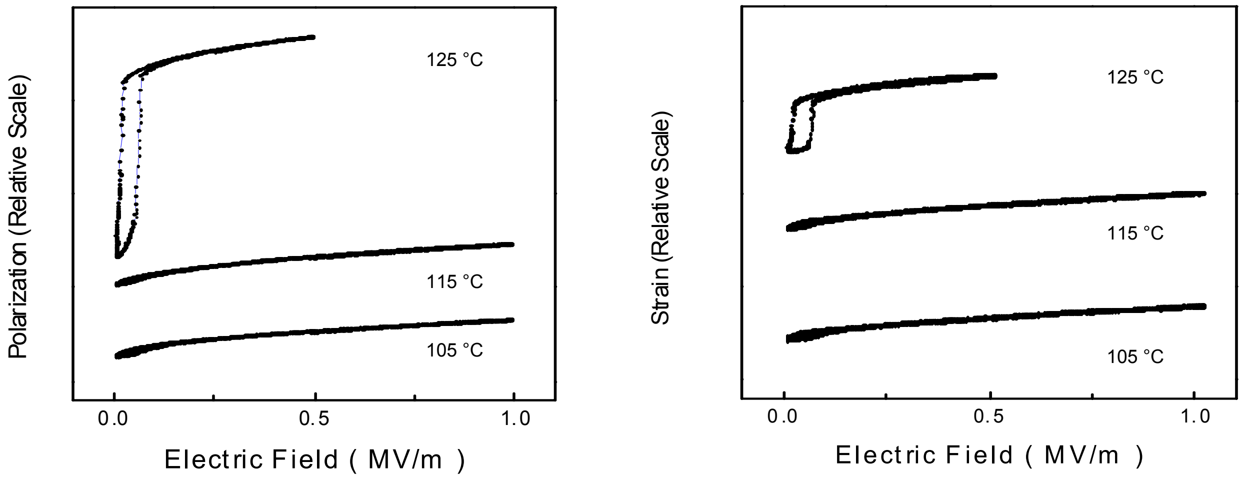

Figure 4. Unipolar electric field dependence of polarization and strain responses of PMN-32%PT single crystals at temperature range from 105 ºC to 125 ºC.

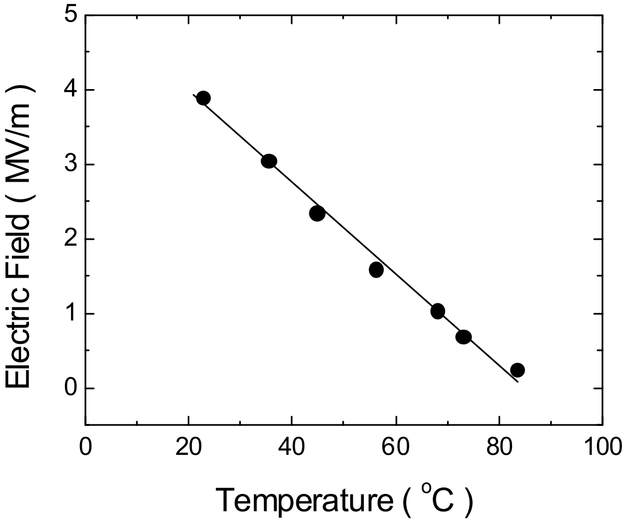

Figure 5. Phase transition fields of PMN-32%PT crystals as a function of temperature.

d_{33} in the monoclinic phase and in the field-induced tetragonal phase were calculated from the plots in Fig. 3 and Fig. 4 and are shown in Fig. 6. The d_{33} in the monoclinic phase increases with temperature from 1380 pm/V at 23 °C to 3904 pm/V at 73 °C. In contrast, the d_{33} in the induced tetragonal phase changes much less with temperature (from 380 to 490 pm/V) when the temperature is below 100 °C and there is only a small increase after temperature is above 100 °C. This result confirms that the piezoelectric constants in the tetragonal phase are much smaller than those on the rhombohedral side of the MPB. In practical device applications, it is desirable to ensure that the PMN-PT materials are not in the tetragonal phase and in order to ensure this the maximum applied electric field that can be applied decreases with temperature as indicated by the results shown in Fig. 5.

As shown in Fig. 3 and Fig. 4, the electric field for the induced phase transition decreases with increasing temperature, which suggests that upon heating the polarization vector moves more easily toward the <001> direction under the applied unipolar electric field. At temperatures above 90 °C, the PMN-PT crystal samples are in the tetragonal phase even without any electric field being applied. Thus, the tetragonal phase is a favorable state for <001>-oriented PMN-PT single crystals under a unipolar field applied along the <001> direction. The crystal samples exhibit a stable ferroelectric tetragonal phase in the temperature region from 92 °C to 115 °C. Further increasing the temperature breaks down the long-range order of the ferroelectric tetragonal phase and transforms the samples from a tetragonal phase to a cubic phase, and, as shown in Fig. 4, the crystals are in a cubic state at a temperature of 125 °C. But the cubic phase is in an electrically active state at this temperature. The tetragonal distortion c_t / a_t can be easily induced even under a very small electric field along the <001> direction. Figure 4 shows that the phase transition from a cubic to a tetragonal happens at a very low field and is hysteretic. The crystal samples are in a field-induced tetragonal phase at the field of 0.064 MV/m.

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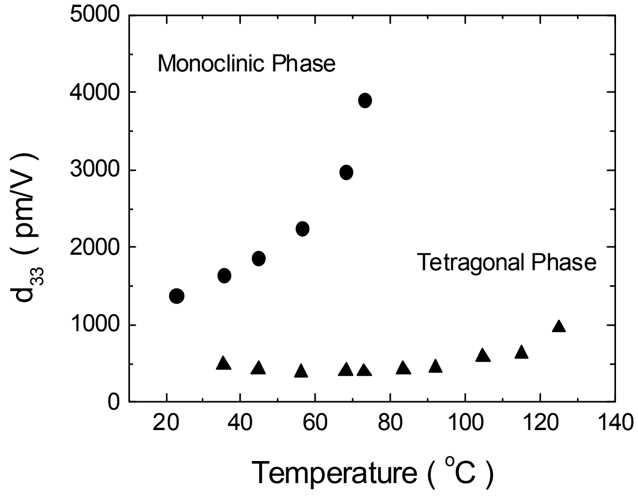

Figure 6. Temperature dependence of d_{33} in the monoclinic phase and the tetragonal phase respectively in PMN-32%PT single crystals.

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