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Composition dependence of field induced phase transformations in $[0\,1\,1]_C$ PIN–PMN–PT relaxor ferroelectric single crystals with d_{322} piezoelectric mode

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Abstract

Relaxor ferroelectric single crystals are used in sonar, medical ultrasound, accelerometers and energy-harvesting applications due to their large electromechanical coupling. In this work, the compositional dependence of the electromechanical properties of $[0\,1\,1]_C$ cut relaxor ferroelectric lead indium niobate–lead magnesium niobate–lead titanate single crystals, $x\mathrm{Pb(In_{1/2}Nb_{1/2})O_3}$–$(1\text{-}x\text{-}y)\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$–$y\mathrm{PbTiO_3}$ (PIN–PMN–PT) was determined. The effect of increasing the concentration of lead indium niobate (xPIN) and increasing the concentration of lead titanate (yPT) on compositions near the morphotropic phase boundary was explored. Specimens were subjected to combined electrical, mechanical and thermal loading. The electric field induced changes of polarization and strain were measured at a series of preload stresses and the stress induced polarization and strain changes were measured at a series of bias electric fields. This was repeated at several temperatures. Evidence of a phase transformation from ferroelectric rhombohedral to ferroelectric orthorhombic was observed in the form of jumps in strain and electric displacement at critical field levels. The linear piezoelectric constant, dielectric permittivity, elastic compliance, thermal expansion, pyroelectric coefficient and rate of change of the material properties with temperature were determined including a scalar measure of electromechanical work indicating the start of the field induced phase transformation.

Keywords: Ferroelectric; Single crystal; Phase transformation; PIN–PMN–PT; Helmholtz energy density

1. Introduction

Relaxor ferroelectric single crystals are used in advanced sonar transducers and medical ultrasound transducers [1–5] due to their enhanced electromechanical properties [6–8]. The anisotropic in-plane strain of the $[0\,1\,1]_C$ cut has been used as a test-bed to study the behavior of magnetoelectric heterostructures under biaxial strain loading [9,10]. Single crystals display reduced hysteresis when loaded in certain crystallographic directions [8]. They also display a diffuse phase transition about the Curie temperature [11].

The properties of relaxor ferroelectric single crystals depend on composition and crystal cut. The binary crystal of lead magnesium niobate–lead titanate, $(1\text{-}x)\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$–$x\mathrm{PbTiO_3}$ (PMN–PT), with compositions near the morphotropic phase boundary (MPB) on the rhombohedral side ($x = 0.28$ to 0.33) has a coercive field $E_C \approx 0.25\ \mathrm{MV\,m^{-1}}$, a rhombohedral to tetragonal phase transition temperature $T_{R/T} < 100\ ^\circ\mathrm{C}$, and a Curie temperature $T_C \approx 150\ ^\circ\mathrm{C}$ [12–15]. The elastic, piezoelectric and dielectric coefficients have strong temperature dependence, and the range of operating electric field is reduced to zero

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as $T_{R/T}$ is approached. This has led to the development of ternary crystals with a higher $T_{R/T}$. The addition of lead indium niobate (PIN) to PMN–PT has increased $T_{R/T}$ to 137 °C and T_C to ∼200 °C [14–18] with minimal degradation of the piezoelectric or electromechanical properties. Ternary lead indium niobate–lead magnesium niobate–lead titanate, $x\mathrm{Pb(In_{1/2}Nb_{1/2})O_3}$–$(1\text{-}x\text{-}y)\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$–$y\mathrm{PbTiO_3}$ (PIN–PMN–PT) [19–22] can be grown in large boules with high quality [14,18,19]. Ternary PIN–PMN–PT single crystals have higher phase transition thresholds, higher Curie temperatures and a higher coercive field (E_C up to 0.7 MV m^{-1}) [14,16–18,23] than binary PMN–PT. This expands the thermal and electrical operating ranges and reduces the temperature dependence of the material constants [14,24].

PIN–PMN–PT at room temperature with zero externally applied loads can be in either the ferroelectric rhombohedral (FE_R) phase (at low PT compositions) or the ferroelectric tetragonal (FE_T) phase (at high PT compositions) [25]. These two phases are separated by a MPB. The material properties are a function of electrical and mechanical load, temperature, composition and orientation. Fig. 1 shows the room-temperature and zero-load phase diagram of PIN–PMN–PT. The rhombohedral phase is to the left of the MPB and the tetragonal phase is to the lower right. The dotted curve separating the two phases represents the MPB. The six dots represent the compositions characterized in this study.

Domain wall motion is the dominant loss mechanism in ferroelectrics. In certain crystal cuts the crystals can be loaded both electrically and mechanically without producing a driving force for domain wall motion. This is often referred to as domain engineering. The $[011]_C$ cut and poled crystals are in a domain-engineered two-variant state that results in a negative d_{322} piezoelectric coefficient, a positive d_{311} piezoelectric coefficient, low hysteresis and dielectric loss, and high electromechanical coupling efficiency [26–28]. As the electric field and the stress are increased, the material undergoes a field induced phase transformation. This results in hysteresis, a significant increase in dielectric loss, and the introduction of nonlinear material behavior. The field induced phase transformation is from FE_R to ferroelectric orthorhombic (FE_O) under mechanical and electrical loading of the $[011]_C$ cut [29–31]. The effect of the FE_R–FE_O transformation is observed as a jump in strain and electric displacement as well as an order of magnitude decrease in the piezoelectric, compliance and dielectric constants [32,33].

Fig. 2a and b depict the cubic referenced coordinate system and the $[011]_C$ crystal cut, a 45° rotation about the $[100]_C$ axis. When the crystal is poled along the $[011]_C$ direction, the FE_R crystals forms a macroscopic $mm2$ symmetry [27,34,35] with the two $[111]_C$ FE_R variants closest to the poling direction being populated. The volume average remanent polarization (P_r) is in the $[011]_C$ direction. The $[011]_C$ direction is denoted the x_3 axis, the $[0\bar{1}1]_C$ direction the x_1 axis, and the $[100]_C$ direction the x_2 axis. The cubes shown in Fig. 2 are oriented with the quasi-cubic lattice.

In applications the crystals are often mechanically preloaded in the $[100]_C$ direction and unipolar electric field is applied in the $[011]_C$ direction. This stress and this electric field each produce a driving force for the FE_R to FE_O phase transformation. Under small applied stress and electric field at room temperature the crystal is in the two-variant $[111]_C$ rhombohedral state with the volume average P_r in the $[011]_C$ direction as shown in Fig. 2b. As the compressive stress (σ_{22}) increases beyond a certain threshold in the $[100]_C$ direction, the FE_R–FE_O phase transformation occurs as shown in Fig. 2c. As electric field (E_3) increases in the $[011]_C$ direction beyond a certain threshold the same FE_R–FE_O phase transformation occurs, as shown in Fig. 2d. Concurrent $[100]_C$ mechanical loading and $[011]_C$ electrical loading drive the FE_R–FE_O phase transformation at lower threshold levels than either load alone. When the $[011]_C$ poled crystal passes through the

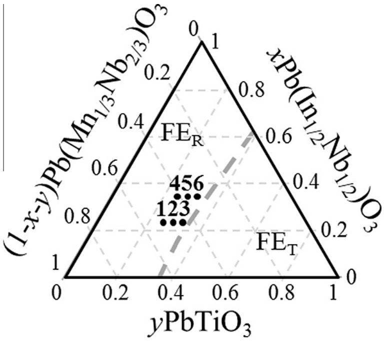

Fig. 1. PIN–PMN–PT phase diagram at room temperature with zero mechanical or electrical loading. The points represent the compositions characterized in this study.

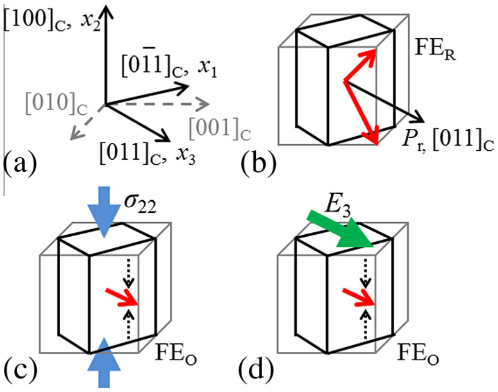

Fig. 2. Domain states and field driven transformations for $[011]_C$ cut and poled ferroelectric PIN–PMN–PT single crystals. (a) The 45° axes rotation associated with the $[011]_C$ cut. (b) At room temperature with no external loads FE_R PIN–PMN–PT is in a two-variant rhombohedral domain state with polarization in $[111]_C$ and volume average remanent polarization (P_r) in $[011]_C$. (c) Application of mechanical loads in $[100]_C$ and (d) electrical loads in $[011]_C$ induce a FE_R–FE_O phase transformation with polarization in $[011]_C$.