Phase Coexistence of Temperature-Dependent Phase Transformation in Relaxor Ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ Single Crystal

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Phase Coexistence of Temperature-Dependent Phase Transformation in Relaxor Ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ Single Crystal

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Abstract

Coexistence of monoclinic and tetragonal domains is evidenced in a (001)-cut $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.61}\text{Ti}_{0.39}\text{O}_3$ (PMNT39%) single crystal from temperature dependent observation of domain structures and dielectric permittivity. The coexistence persists until the crystal transforms into the cubic phase near 455 K. As temperature increases, the monoclinic domains progressively transform to the tetragonal phase via polarization rotations of monoclinic distortions. This causes increasing volume of the tetragonal domain matrix as temperature increases before the cubic phase takes over.

I. Introduction

Relaxor-based ferroelectric (FE) single crystals $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ (PMNT $_x$) and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ (PZNT $_x$) exhibit extremely large electromechanical coupling factor k_{33} (>94%) and ultrahigh piezoelectric coefficient d_{33} (>2500 pC/N) [1]. The mechanism underlying the ultrahigh piezoelectric response lies in the polarization rotation from the rhombohedral (R) phase through the intermediate monoclinic (M) and orthorhombic (O) phases to the tetragonal (T) phase [2]. The intermediate phases strongly depend on PT content, temperature, strength of E-field and crystallographic orientation [3–5].

A modified phase diagram of PMNT $_x$ system has been reported by synchrotron X-ray powder diffraction measurements in unpoled ceramics of PMNT $_x$ for $31\% \leq x \leq 37\%$, in which various phase coexistences of R/M_C , T/M_C and $T/M_C/O$ were proposed for

31%, 33% and 35% PT compositions respectively [6]. Recent measurements of domain structures in a PMNT33% crystal revealed that the phase transformation from R to cubic phase is through polarization rotation with M distortion [4].

The discovery of the intermediate phases and polarization rotations has opened a new window for searching for the origin of high piezoelectric responses. However, whether these intermediate phases or phase coexistences are intrinsic, or are merely due to spatial segregation or to strain from domain mismatch is still not clear. It is important to understand how polarization rotation plays a role in phase transformations among various phases. In this report, domain structures and dielectric permittivity were investigated on a (001)-cut PMNT39% crystal.

II. Experimental Procedure

The lead magnesium niobate-lead titanate crystal PMNT39% was grown using a modified Bridgman method. The sample was cut perpendicular to the $\langle 001 \rangle$ direction. Gold electrodes were deposited on sample surfaces by RF sputtering for dielectric measurement. A Wayne-Kerr Precision Analyzer PMA3260A with four-lead connections was used to obtain dielectric permittivity. The temperature dependent dielectric permittivity is given in Fig. 1. The domain structures were observed by using a Nikon E600POL polarizing microscope with a $0^\circ/90^\circ$ crossed polarizer/analyzer (P/A) pair. The sample thickness is about $10\text{ }\mu\text{m}$. All P/A pair angles shown in Fig. 2 are with regard to the $[100]$ direction.

III. Review of Optical Extinction and Polarization

The propagation direction $\vec{k}$ of the polychromatic “white” light is along $[001]$ for this work. The most information is obtained from optical extinction, which occurs if all the following conditions are satisfied: (1) there must be no optical activity for the direction $\vec{k}$, (2) either $\vec{k}$ must lie along an optical axis, or if $\vec{k}$ is not along an optical axis, the incident $\vec{E}$ must lie along one of the two perpendicular axes in the plane perpendicular to $\vec{k}$ for which the optical-frequency permittivity is maximum or minimum. A clear analysis for the general extinction problem appears in Sommerfeld [7] and Hartshorne et al. [8]. The T and R

FIGURE 1 Temperature- and frequency-dependent dielectric permittivity.

FIGURE 2 Temperature-dependent domain structures. The domains showing extinction for $P/A:0^\circ$ and $P/A:5^\circ$ are tetragonal (T) and monoclinic (M) phases, respectively. The region at 452 K with extinction for all P/A angles is the cubic (C) phase.

phases have uniaxial strain tensors with principal axes and polarization $\mathbf{P}$ along $\langle 001 \rangle$ and $\langle 111 \rangle$, respectively. For the O phase observed in perovskites, the strain tensor and index ellipsoid are biaxial, with principal axes (for one example) along $[101]$, $[10\bar{1}]$, and $[010]$ and $\mathbf{P}$ along $\pm[101]$ or $\pm[10\bar{1}]$. Monoclinic or triclinic phases allow $\mathbf{P}$ to vary continuously via distortions away from T , R , or O symmetry. Monoclinic cell strain tensors are biaxial, with one principal axis along $\langle 001 \rangle$ or $\langle 110 \rangle$, and the other two axes and $\mathbf{P}$ in arbitrary perpendicular directions. The $\langle 001 \rangle$ case corresponds to the M_C cell based on the primitive ($Z = 1$) cubic unit cell, while the $\langle 110 \rangle$ case corresponds to the M_A and M_B cells based on the double-size ($Z = 2$) orthorhombic cell.

Figure 3 shows the (001) -cut projection (with all four sides folded out) of relations among the various phases and corresponding polarizations. Squares indicate the directions for tetragonal polarization vectors $\mathbf{P}$, triangles for rhombohedral $\mathbf{P}$'s, and circles for orthorhombic $\mathbf{P}$'s. Solid, dashed and dash-dot lines indicate possible $\mathbf{P}$ directions for monoclinic M_A or M_B cells. Dotted lines alternating between rectangles and circles indicate possible $\mathbf{P}$ directions for monoclinic M_C cells.

Domains that are optically inactive for $\vec{k}$ along $[001]$ will have optical extinction for optical electric field along the radial and circumferential axes indicated by solid crossed lines inside the symbols. Solid lines between some symbols indicate no shift in extinction

FIGURE 3 Relation between polarizations and various phases projected on (001) plane. The notation of M_A -, M_B -, and M_C -type monoclinic phases follows that found in Ref. [9].

directions away from those in symbols connected by these lines. Lines for the remaining $Z = 2$ (dashed and dash-dot) and all $Z = 1$ (dotted) M polarization directions indicate shift in extinction direction away from radial and circumferential. The central “black” square indicates extinction for any optical field direction.

IV. Results and Discussion

The temperature- and frequency-dependent dielectric permittivity shown in Fig. 1 exhibits a maximum near 450 K and an extra broad step that is associated with a weak frequency dispersion at lower temperatures near 200 K. As seen in Fig. 2, the domain matrix at 228 K exhibits a complicated coexistence of monoclinic (M), T_{001} and non- T_{001} tetragonal domains. When observing the (001)-cut sample along [001] between a crossed P/A pair, the optical extinction angle for the non- T_{001} tetragonal domains is 0° measured from the $\langle 001 \rangle$ axis, as shown at P/A: 0° in Fig. 2. The T_{001} tetragonal domains, which correspond to the “black” square in Fig. 3 and give extinction at every P/A angle, are distributed all over the domain matrix as dark spots seen at all temperatures in every picture of Fig. 2, for example the pictures at P/A: 45° .

We see no evidence for O domains. Of the 12 O domain types, 8 would give the same extinction angle of 0° as T domains, but 4 would give extinction at 45° , as shown in Fig. 3. However, Fig. 2 shows no evidence for 45° O domains.

The coexistence of M and T domains persists until the crystal transforms entirely into the cubic phase near 455 K, consistent with the ϵ' maximum at $T_m \sim 450$ K seen in Fig. 1. At 228 K and 293 K in Fig. 2, some M domains seen in color for P/A: 0° show extinction for

P/A:5°. Others that are brighter at 5° show extinction at −5°. This indicates similar M and T polarization directions, so from Fig. 3 it appears that the monoclinic phase is M_A or M_C but not M_B . As temperature increases, polarizations of the monoclinic domains progressively rotate via monoclinic distortions to reach tetragonal phase directions. This causes increasing volume of the tetragonal domain matrix as temperature increases. This progressive evolution between M and T domains may cause the gradual permittivity anomaly seen up to 240 K.

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