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Self-polarized high piezoelectricity and its memory effect in ferroelectric single crystals



Chao He ^a, Zujian Wang ^a, Xiuzhi Li ^a, Xiaoming Yang ^a, Xifa Long ^{a, **}, Zuo-Guang Ye ^{b, *}

^a Key Laboratory of Research on Chemistry and Physics of Optoelectronic Materials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, China

^b Department of Chemistry and 4D LABS, Simon Fraser University, Burnaby, British Columbia, V5A 1S6, Canada

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ABSTRACT

In ferroelectric materials, significant piezoelectric response only occurs after poling by an external electric field applied along a certain crystallographic direction, and the piezoelectric effect generally disappears upon heating to the Curie temperature (T_C) where the poled state vanishes. This thermally induced depoling often restricts the temperature range for the applications of piezoelectric devices. It has been a challenge to develop materials that exhibit high piezoelectric performance that is not affected by electric poling, nor thermal depoling. Here we report an unusual piezoelectric effect found in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbSnO}_3\text{-PbTiO}_3$ ternary ferroelectric crystals which exhibit a relatively high piezoelectricity (with the piezoelectric coefficient $d_{33} = 1350\text{--}1400$ pC/N) without undergoing any poling process. Moreover, this high piezoelectric performance is retained after repeated thermal annealing at temperatures above T_C , showing a piezoelectric memory effect. This uncommon piezoelectric effect is explained by a self-polarization mechanism based on the defect-dipoles formed in the crystals due to the presence of mixed valence states of $\text{Sn}^{2+/4+}$. The defect-dipoles generate internal bias electric fields which, in turn, provide the stabilizing and restoring forces leading to preferred orientation states and the retention of spontaneous polarization. This mechanism offers a new perspective for designing novel piezoelectric materials with high performance and a wide temperature range of operation.

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1. Introduction

Crystal defects are known to have important effects on such properties of materials as mechanic, optical, magnetic, electric, and so on. Therefore, it is possible to develop or modify functional materials by introducing certain kinds of defects into the crystal lattices artificially. Of various kinds of crystal defects, point defects (dopant, vacancy, solute atoms, etc.) exist inevitably in ferroelectric crystals and may strongly affect their phase transition (the Curie point [1,2]) and electric properties, such as, coercive field [1,2], aging [3,4], resistivity [5], fatigue [6–8], hardening [9], softening [9], etc., and thereby their potential applications. One of the approaches used to generate point defects is to introduce different-valence elements into the lattice so that vacancies can be formed

due to charge neutralization. For example, oxygen vacancies can be generated by an acceptor dopant replacing the B site ions with a lower valence ion in perovskite ABO_3 compounds. Consequently, defect-dipoles are formed due to the movements of highly mobile oxygen vacancies, which align in a certain permissible direction. These ordered defect-dipoles provide a driving force that stabilizes the domain structure [10].

Utilizing the significant deformation that is generated during 90° domain switching in ferroelectric crystals and a general symmetry-conforming principle for point defects [11,12], large recoverable electro-strain was realized in BaTiO_3 crystal [13]. Unfortunately, the alignment of defect-dipoles in crystals is random in most cases. Previous studies showed that the orientation of defect-dipoles takes place via oxygen vacancy octahedral rotation or oxygen vacancy diffusion [10]. Lambeck and Jonker [3,14] further suggested that the alignment of defect-dipoles can occur along the direction of the spontaneous polarization which aligns in the polar axes according to the symmetry of the ferroelectric phase. It becomes difficult to mediate the structure and properties of the crystal using this kind of defect-dipoles. If all the defect-dipoles

* Corresponding author.

** Corresponding author.

E-mail addresses: hechao@fjirsm.ac.cn (C. He), lxif@fjirsm.ac.cn (X. Long), zye@sfu.ca (Z.-G. Ye).

align in a preferred direction during the crystal growth process, they could provide strong enough ‘bias fields’ to orient (or pole) the domain/polarization in a highly consistent direction. Such a “self-poled” state should exhibit high piezoelectricity without undergoing any poling process [15,16]. Based on this concept, we have synthesized and characterized the $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbSnO}_3\text{-PbTiO}_3$ (PMN-PSn-PT) ferroelectric crystals where point defects are introduced artificially by the mixed valence states of tin, i.e. $\text{Sn}^{2+}/\text{Sn}^{4+}$. It is found that the PMN-PSn-PT crystals exhibit very high piezoelectric response without poling, indicating the presence of a self-polarized state with preferred orientation of polarization. More interestingly, this self-polarized state is stable against thermal annealing at temperatures above T_C , pointing to a new type of defect-dipole-engineered ferroelectric crystals that exhibit piezoelectric memory effect. This phenomenon is different from the self-polarization state reported in thin films that undergoes depolarization upon heating [15,16]. In bulk ferroelectric materials, the self-polarization phenomenon was found in some order-disorder-type organic ferroelectric materials, such as doped triglycine sulphate (TGS) crystals (the TGS family) [17–20]. Pure TGS crystal has the disadvantage that it depolarizes with time [18]. In order to overcome this defect, a series of dopants have been tried. In some doped TGS single crystals, a fully poled state exists below the Curie point in the absence of any external fields [17–20]. For these self-polarization doped TGS single crystals, the dipole cannot be inverted, i.e. they exhibit a permanent dipole, an asymmetry in hysteresis loop, a single domain state and no depolarization [17,18]. The permanently poled state for the doped TGS single crystals was explained by the chemical bias effect [19]. On the other hand, the self-polarization effect had rarely been observed in bulk perovskites, especially not in the high-performance relaxor-based piezoelectric single crystals. So the discovery of self-polarization and the related piezoelectric memory effect in PMN-PSn-PT crystals could provide a new insight into their mechanisms and a novel approach for the fabrication of highly stable piezoelectric devices.

2. Experimental procedures

The PMN-PSn-PT ternary ferroelectric crystals were grown by the conventional flux method using the $\text{PbO-H}_3\text{BO}_3$ complex flux. The oxides powders, including PbO , TiO_2 , SnO_2 , MgO and Nb_2O_5 , were used as starting materials. A series of PMN-PSn-PT ferroelectric single crystals with various compositions were obtained. As a representative example, the studies of the 0.542PMN-0.077PSn-0.381PT single crystals were reported here. Other crystals were found to exhibit the same features in terms of structure and electric properties. The crystal structures of the grown crystals were examined by power X-ray diffraction (XRD) using a Rigaku diffractometer (Rigaku, Japan). The composition of the grown PMN-PSn-PT crystals was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, JY Ultima-2, France).

For electrical property measurements, the grown crystals were sliced into wafers parallel to the $(001)_{\text{cub}}$ planes, polished and coated on both sides with silver paste as electrodes. The dielectric properties were measured using a computer-controlled Alpha-A broadband dielectric/impedance spectrometer (Novocontrol GmbH, Germany). The polarization under electric field was displayed using an aix-ACCT TF2000 analyzer (at $f = 2$ Hz). The piezoelectric coefficient d_{33} was measured using a quasi-static d_{33} m (Institute of Acoustics, Chinese Academy of Sciences, Model ZJ-4AN). The strain induced by unipolar or bipolar electric field was measured using an aix-ACCT TF2000E analyzer. The recycling heat treatments were carried in which the samples underwent an annealing process at 200°C for 4 h, which was repeated eight times while piezoelectric coefficient d_{33} value was measured after each

treatment.

The valence states of tin were analyzed using X-ray photoelectron spectroscopy (XPS) (VG - Escalab 250). The electron paramagnetic resonance (EPR) measurements were performed with Bruker ELEXSYSE500 spectrometer at room temperature. A polarized light microscope (PLM, Nikon ECLIPSE LV100POL, Japan) was employed to examine the domain configuration and phase transitions on platelet samples with a thickness of about $50\mu\text{m}$. PFM investigations were carried out on a commercial atomic force microscope (Cypher, Asylum Research, USA) using Asylum Research Pt-coated Si probes.

3. Results

3.1. Crystals

The as-grown PMN-PSn-PT crystals exhibit a reddish color, an intergrowing pseudo-cubic morphology and a size of 5–12 mm, as shown in Fig. 1a. The actual chemical composition of the grown crystals was determined to be 0.542PMN-0.077PSn-0.381PT based on the data from an inductively coupled plasma atomic emission spectroscopy (ICP-AES), which was slightly deviated from the nominal composition as a result of compositional segregation in this ternary system. The powder XRD patterns (of crushed crystals) measured at room temperature indicate a pure perovskite phase for the grown crystals (Fig. 1b). More detailed analysis of the (200) reflection around $2\theta = 45^\circ$ shows that it is composed of only one single peak, indicating a rhombohedral symmetry at room temperature (see Fig. 1c).

3.2. Phase transition

To investigate the phase transitions in the PMN-PSn-PT crystals, the temperature dependences of the dielectric constant (ϵ') and dielectric loss ($\tan\delta$) of an unpoled $[001]$ -oriented PMN-PSn-PT crystal platelet were measured upon heating at the frequencies of 1 Hz to 1 kHz and the results are shown in Fig. 2. The sharp peak of the dielectric constant at 155°C (at 1 kHz) corresponds to the Curie temperature T_C . In addition, a small dielectric peak appears around 45°C at all frequencies which indicate a ferroelectric-ferroelectric phase transition, most likely a rhombohedral - tetragonal transition (at T_{RT}). The phase transitions at T_C and T_{RT} suggest that the

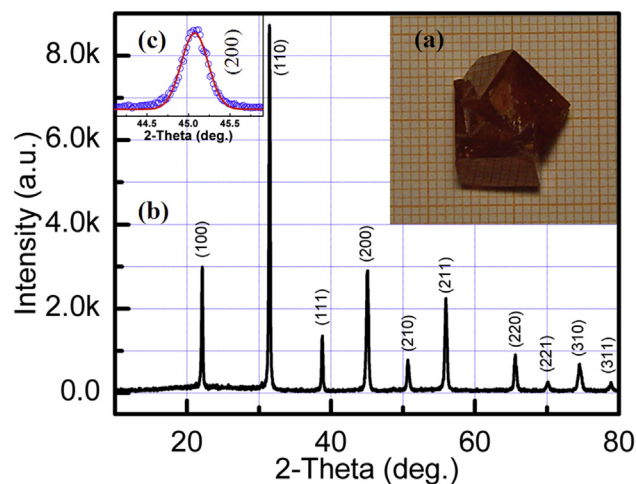


Fig. 1. (a) As-grown PMN-PSn-PT single crystals. (b) Powder XRD patterns of the grind PMN-PSn-PT crystals, indicating a pure perovskite structure. (c) Pseudo-cubic (200) reflections deconvoluted with the rhombohedral symmetry.

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