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Structure and properties of $Pb(Lu_{1/2}Nb_{1/2})O_3$–$0.2PbTiO_3$ relaxor ferroelectric crystal

Ying Liu [a,c], Xiaoming Yang [b,c], Fachun Lai [a,**], Zhigao Huang [a], Xiuzhi Li [c], Zujian Wang [c], Chao He [c], Ju Lin [c], Xifa Long [c,*]

[a] College of Physics and Energy, Fujian Normal University, Fuzhou, Fujian 350117, China
[b] College of Materials Science and Engineering, Fujian Normal University, Fuzhou, Fujian 350117, China
[c] Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

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ABSTRACT

Ferroelectric crystal $Pb(Lu_{1/2}Nb_{1/2})O_3$–$0.2PbTiO_3$ (PLN–0.2PT) was successfully obtained by a top-seed solution growth technique. At room temperature the symmetry was orthorhomic according to X-ray diffraction (XRD). The super-lattice reflections were identified by XRD and transmission electron microscope (TEM). The micro-domain structure was detected by TEM. The temperature dependence of the dielectric constant (ε') shows a typical relaxor behavior. The temperature dependence of coercive electric field and remnant polarizations were investigated, which also shows the relaxor feature.

1. Introduction

Relaxor ferroelectrics or relaxors are a class of materials which possess peculiar structure and exhibits characteristic dielectric behavior with diffuse permittivity peaks. These peaks depend strongly on frequency compared with other normal ferroelectrics [1–4]. One view of relaxors is the existence of polar nanoregions (PNRs) or polar clusters, which can give rise to many specific properties [4–6]. The PNRs or polar clusters, can be thought as unusually large dipoles, whose direction and magnitude depend on the external electric field applied [6]. The relaxor behavior was first observed in the perovskites with disorder of non-isovalent ions such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) [7] and $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) [8].

$PbTiO_3$-based relaxor ferroelectric (PT-based relaxors) crystals with complex perovskite structure formula $(1-x)Pb(B_1,B_2)O_3$–$xPbTiO_3$ ($B_1 = Mg^{2+}$, Zn^{2+}, Sc^{3+}, In^{3+}, Yb^{3+} . . . , $B_2 = Nb^{5+}$, Ta^{5+}, W^{6+} . . .) have been the subject of intense research for the past several decades because of their interesting physical properties and potential applications in electronic devices. The typical examples are $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMNT) [9–11] and $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PZNT) [12–14], which exhibits remarkably high piezoelectric properties with low Curie temperature T_C (<170 °C) and relative low depoling temperature T_{RT} (<100 °C). Although PT-based relaxors were first reported nearly half a century ago, this field of research has experienced a revival of interest in recent years respect to the enhancement of the Curie temperature and depoling temperature. Example of these work include and not limited to $Pb(Yb_{1/2}Nb_{1/2})O_3$–$PbTiO_3$ (PYNT) [15,16], $Pb(Sc_{1/2}Nb_{1/2})O_3$–$PbTiO_3$ (PSNT) [17–19], $Pb(In_{1/2}Nb_{1/2})O_3$–$PbTiO_3$ (PINT) [20,21] and $Pb(Lu_{1/2}Nb_{1/2})O_3$–$PbTiO_3$ (PLNT) [22–26].

PLN–xPT ceramics have been investigated in the past few years. Antonova et al. reported the PLN–xPT ceramics system obtained by solid phase reactions, which has a MPB region in the range of $x = 0.38$–0.49 from a pseudomonoclinic (space group Bmm2) to tetragonal (space group P4mm) at room temperature [24]. The compositions within the MPB region show high Curie temperature ($T_C = 353$ °C) and good piezoelectric properties ($k_p = 0.66$, $k_t = 0.48$) [25]. Recently, the PLN–PT ceramics were also studied by Shen et al. in our laboratory [22]. The phase structure at room temperature changes from rhombohedral (space group R3m) to tetragonal (space group P4mm). The Curie temperature of the composition $x = 0.48$ is up to 375 °C and show good piezoelectric properties ($d_{33} = 350$ pC/N) [22]. The high Curie temperature and moderate piezoelectric coefficient of the PLN–PT system imply that the PLN–PT single crystal can be a promising material for high power transducer that has a wide working temperature range. Therefore, a series of PLN–xPT binary ferroelectric crystals were successfully obtained firstly by top-seed solution growth technique in our lab

* Corresponding author. Tel.: +86 591 83710369; fax: +86 591 83704907.
** Corresponding author. Tel.: +86 591 22868137; fax: +86 591 22868132.
E-mail addresses: laifc@fjnu.edu.cn (F. Lai), lxf@fjirsm.ac.cn (X. Long).

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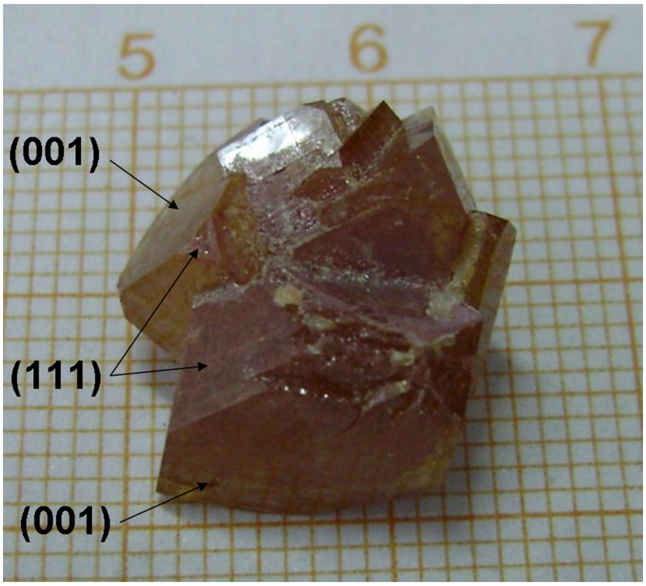

Fig. 1. As-grown PLN–0.2PT single crystal using TSSG method.

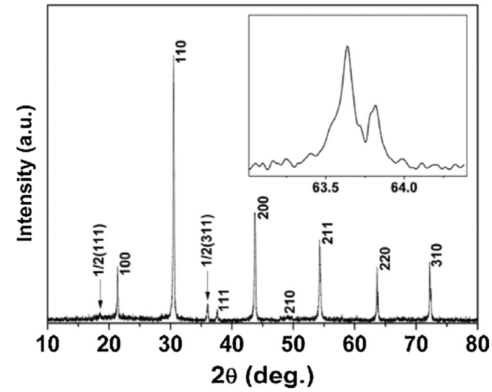

Fig. 2. X-ray powder diffraction patterns of the crashed PLN–0.2PT crystal with super-lattice reflections peak. The split in the fundamental lines around $2\theta = 64^{\circ}$ insert clearly show the orthorhombic phase.

with the purpose of high temperature application. The crystal with composition $x = 0.49$ shows high Curie temperature ($T_C = 360\,^{\circ}C$) and good piezoelectric properties ($d_{33} = 1630$ pC/N) [27]. The major studies of PLN–xPT crystal structures focus on the MPB region transition from Rhombohedral to Tetragonal phase. Broadening of the phase transition, dielectric dispersion, and the characteristic features of ferroelectric relaxors were observed within the concentration interval of $0.1 < x < 0.3$ in PLN–PT ceramics [24] and $x < 0.4$ in PLN–PT single crystals [27]. In these regions, PLN–PT system exhibits typical relaxor characteristics but the Curie temperature deviates from the ideal linear relationship between $0 < x < 1$. In this paper, the growth, structure and properties of PLN–0.2PT relaxor ferroelectric crystal are reported.

2. Experimental procedures

2.1. Crystal growth

Due to the high melting point of Lu_2O_3, a top seeded solid solution growth method was chosen to grow PLNT single crystal. Such a method also offers more advantages in growing single crystals of good quality and high compositional homogeneity. The flux is PbO–H_3BO_3. The starting chemicals and the ratios of flux to solute are described in Ref. [27]. The detailed growth process is similar to the one described by He et al. [28]. Finally, the single crystal has been obtained, as shown in Fig. 1.

2.2. Property characterization

The actual chemical compositions of the grown crystal was determined to be $x = 0.2$ by inductively coupled plasma atomic emission spectroscopy (*ICP-AES*, JY Ultima-2, France). The phase and structure of the grown crystal was carried out by X-ray diffraction analysis using Cu-Kα radiation (*DMAX*2500, Rigaku, Japan) at room temperature. Fine crystal powder for the electron microscopy study was polished mechanically and measured on a transmission electron microscope (TEM) (*Tecnai F20 FEG*, FEI, America). For electric characterization, the sample was sliced from the as-grown crystal along <0 0 1> direction, polished and coated with silver paste as electrodes. Measurements of the dielectric constant and loss tangent (tanδ) were carried out by computer-controlled Alpha–broadband dielectric/impedance spectrometer (Novocontrol GmbH, Germany) with an AC signal of 0.5 V (peak-to-peak) applied. Polarization hysteresis loops were displayed by standard ferroelectric test system (TF Analyzer 2000E, *aix-ACCT*, Germany) at $f = 2$ Hz, combined with a high-voltage supply amplifier/controller (*Model 610E*, Trek, America) and an environmental test chamber (*DELTA 9023*, DELTA, America) with temperature varies from room temperature up to 130 °C. Poling was performed by applying a DC electric field of 20 kV/cm along the <0 0 1> direction of the crystal at 60 °C for 15 min, and then keeping the field on while cooling down to room temperature. The piezoelectric coefficients were measured using a quasi-static

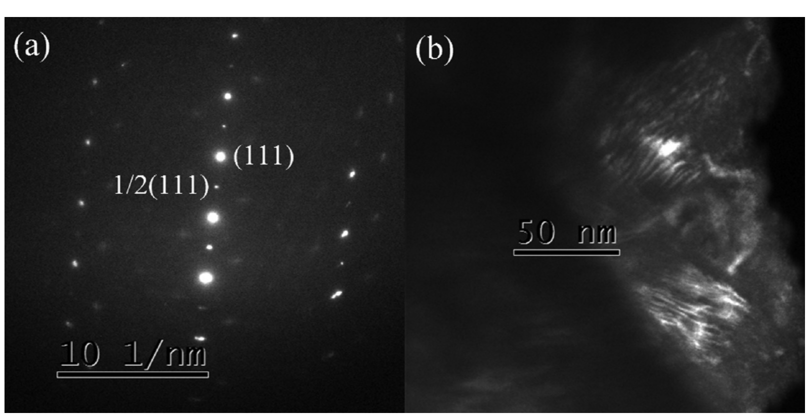

Fig. 3. Electron diffraction patterns of ferroelectric phase obtained (a) super-lattice reflections and (b) micro-domains configurations under TEM.