Materials Letters 164 (2016) 248–251

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

The effect of uniaxial pressure, temperature and electric field on the internal bias field in the lead-based piezoelectric ceramics

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ARTICLE INFO

Article history:
Received 7 April 2015
Received in revised form
30 October 2015
Accepted 31 October 2015
Available online 9 November 2015

Keywords:
Ceramics
Defects
Stability
Internal bias field

ABSTRACT

The internal bias field effects in ferroelectrics had been widely investigated in past decade, but the reasons for the formation of internal bias field are still a lot of disputes. Our works were focused on the external environment-dependent behaviors of the internal bias field, which is critical important to explain the cause for the internal bias field formation. Experiments result that a large internal bias field 4.2 kV/cm was obtained in the poled Mn-doped PNZST ceramics. A microscopic model for the domain-related ferroelectric effect in ceramics is proposed. It is also found that the internal bias field is stable under load the 90 Mpa uniaxial pressure and shows a good stability even after 10^7 fatigue cycles. This effect is related to the defect dipoles are rather stable due to the immobility of oxygen vacancies. Furthermore, it is suggested that the internal bias field can be decreased by increasing the temperature. These results provided direct critical experiment to understand the movement mechanisms of defect dipoles.

1. Introduction

Ferroelectric materials have a wide range of applications. Their electromechanical properties can be improved by doping with impurities in order to meet the requirements for particular applications [1,2]. As a typical feature, low-valence acceptor dopants result in asymmetric polarization–electric field (*P*–*E*) hysteresis loops which can be observed in many acceptor-doped ferroelectrics, such as Mn-doped PNZST and Mn-doped $BaTiO_3$ after poled [3,4]. The asymmetric *P*–*E* loop can be attributed to the emergence of an internal bias field E_i ($E_i = \frac{E_+ + E_-}{2}$) defined as the shift of hysteresis loop on the electric field axis (E_+ and E_- are the positive and negative intercepts of the hysteresis loop at the x-coordinate, respectively).

The effects of internal bias field on mechanical quality factor, aging change in the frequency constant and dielectric constant had been widely investigated in past decade. Several studies have been made on the origin of the internal bias field and showed it related to the stabilization of the domain walls [5–7]. Three competing mechanisms have been proposed to explain the domain stabilization. One is based on the charges gathering and drifting near the grain boundaries and other interfaces (surface effect) [5]. The other is based on the formation and reorientation of defect dipoles (domain wall effect) [6]. Another is based on the charged defects align with the polarization within ferroelectric domains (bulk effect) [7]. But there were still a lot of disputes on that which mechanism is dominant. Furthermore, a number of research has found that the large shape strain memory effect could been realized by the internal bias field. Thus, it is important to find out the cause of the formation of E_i and the factors which affect the E_i.

In the present work, we have proposed a microscopic model to illustrate the origin of the E_i, and also studied the external environment (including uniaxial pressure, electric cycling and temperature) –dependent behaviors of E_i. These results demonstrated that the stable E_i is quite for some specific actuator applications.

2. Experiment details

The general formula of the materials studied was $(Pb_{0.99}Nb_{0.02})[(Zr_{0.70}Sn_{0.30})_{0.52}Ti_{0.48}]_{0.98}O_3+x$ wt% MnO_2, Where $x=0$ and 0.4, respectively. Reagent-grade oxide powders, Pb_3O_4 (Purity 97.0%), ZrO_2 (99.0%), TiO_2 (98.0%), SnO_2 (99.0%), Nb_2O_5 (99.5%) and MnO_2 (90.0%), were used as the starting materials. They were stoichiometrically mixed and ball-milled in ethanol for 5 h. The dried powders were calcined at 850 °C for 2 h in air, and then pressed into 12-mm diameter disks at 200 MPa. The samples were sintered at 1300 °C for 3 h in a covered alumina crucible, and

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http://dx.doi.org/10.1016/j.matlet.2015.10.156

the pellets were polished to a thickness of 1 mm. Ag electrode paste was fired on both sides at 650 °C for 30 min. For ferroelectric characterization, electric poling was carried out at 200 °C with applying a dc field 30 kV/cm for 30 min. After poling, the samples was aged at room temperature for more than 15 days to establish a stable defect state.

The hysteresis measurements were performed in silicon oil, which can be heated from room temperature to 120 °C, under a triangular waveform with peak electric field values of ± 30 kV/cmm and a frequency of 0.05 Hz using the aid of a Sawyer–Tower circuit (TF analyzer 2000, aixACCT, Aachen, Germany). The uniaxial compressive stress was supplied by a homebuilt device of which the principle has been reported in detail [8]. The electric cycling experiment was conducted with a bipolar triangular electric signal with amplitude of 30 kV/cm at 1 kHz to 10^7 cycles.

3. Results and discussion

Fig. 1(a) shows the polarization–electric field (*P*–*E*) hysteresis loops for poled and unpoled Mn-doped PNZST ceramics. The unpoled sample exhibits a normal waist *P*–*E* loop, while a pronounced asymmetric *P*–*E* loop is presented after poling in agreement with the previous results for the poled hard ferroelectrics [3,4]. After poling, the *P*–*E* loop is displaced along the *E* axis with the internal bias field E_i=4.2 kV/cm and the remanent polarization increases from 20 μc/cm^2 to 40 μc/cm^2.

These results can be explained by taking into account the defects redistribution and the interaction of the domain walls during the poling process. It is well known that MnO$_2$ addition into the PZT-based ceramics can't change the solubility limit. The B-site ions in the perovskite structure (Zr^{4+}, Ti^{4+}) are substituted with the Mn ions which have lower valences (Mn^{2+} or Mn^{3+}), creating oxygen vacancies as follow [9]:

$$Mn^{3+} \rightarrow^{Zr^{4+},Ti^{4+}} Mn'_{Zr,Ti} + \frac{1}{2} V_o^{\cdot\cdot} \tag{1}$$

$$Mn^{2+} \rightarrow^{Zr^{4+},Ti^{4+}} Mn''_{Zr,Ti} + V_o^{\cdot\cdot} \tag{2}$$

The Mn ion is more thermodynamically stable in the valence state of 3+ at the sintering temperature range. In additionally, the existence of Mn^{3+} was also confirmed by electron spin resonance [9]. Oxygen vacancies ($V_o^{\cdot\cdot}$) will be introduced by valence compensation and then the defect dipoles P_d can be formed by the

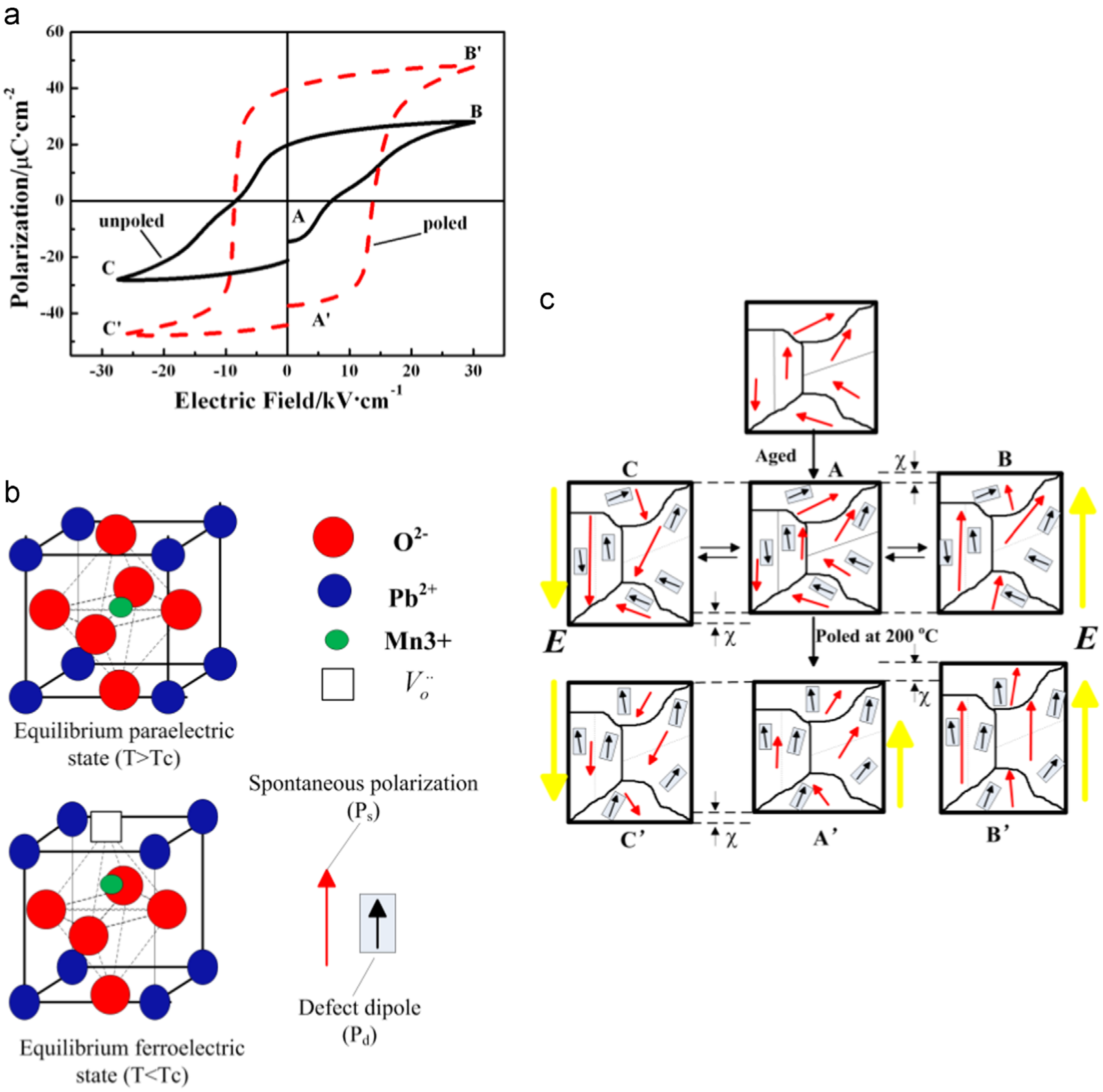

Fig. 1. (a) *P*–*E* hysteresis loops for poled and unpoled Mn-doped PNZST ceramics, (b) defect symmetry principle in ABO$_3$ structure, (c) domain switching process.