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Phase transition and piezoelectric response under electric field in PMN-PT crystals

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Abstract The phase transition between the ferroelectric and relaxor states for (1-x)Pb($Mg_{1/3}Nb_{2/3}$)O_3-xPbTiO$_3$ (PMN-PT) single crystals at low PT (x=0.21) was identified using high-resolution X-ray diffraction. The characterization of the dielectric and pyroelectric currents determined the properties of the polar state. The temperature stability region of the polar phase was enlarged with increasing bias field, and the corresponding polarization and piezoelectric properties were enhanced. Non-linearity of the electric displacement and loss under high ac fields was investigated by laser interferometry at a frequency of 40 kHz well below the resonant frequency. A linear displacement was obtained up to a large alternating current-field of 125 V/mm with an almost negligible second order harmonic component. The optimal d_{33} improvement was 1,339 pm/V found for the [001] orientation. Such disclosure of phase stability and enhanced performances under high external field will be useful to determine their practical applications for resonant power transducers and quasi-static actuators.

Keywords Phase transition · Piezoelectric response · PMN-PT crystals

1 Introduction

During the last decade, investigations on lead-based single crystals have evidenced the outstanding properties achieved for the relaxor ferroelectric materials (1-x)Pb($Mg_{1/3}Nb_{2/3}$)O_3-xPbTiO$_3$ (PMN-PT) and (1-x)Pb($Zn_{1/3}Nb_{2/3}$)O_3-xPbTiO$_3$ (PZN-PT) [1, 2]. Especially, the high piezoelectric charge coefficient d_{33} (~2000 pC/N) and electromechanical coupling factor k_{33} (~90%) exhibits a magnitude of ten for the former and 1.5 for the latter in comparison with lead zirconate titanate [1–4]. Regarding their applications for resonance and quasi-static transducers, more attention should be paid to the losses and to the linearity of the macroscopic response under high external fields. A high linearity and low losses (both electrical and mechanical) are strongly required for most applications [5]. Few studies have been focused on this topic and most of the published results were devoted to the characterization and applications of PMN-PT crystals near the morphotropic phase boundary (MPB, i.e. x=0.35) [2–4]. Therefore, there is a need for a better understanding of the behavior of piezoelectric crystals under high power driving conditions which may cause large dynamical stress and heat dissipation. However, these MPB crystals, despite their low dielectric loss at low field, possess a complex ferroelectric domain and phase structure which induces fatigue and depoling under mechanical and electrical stress [6]. It would be quite interesting to explore some less complex single phase materials, despite their slightly lower properties at low level.

The stability of a ferroelectric phase depends on the electrical and mechanical boundary conditions. At a given temperature, application of an electric field and elastic stress can lead to polarization switching and even to phase transitions, which dramatically alter the electromechanical properties of the crystal, as well as induce cracking and

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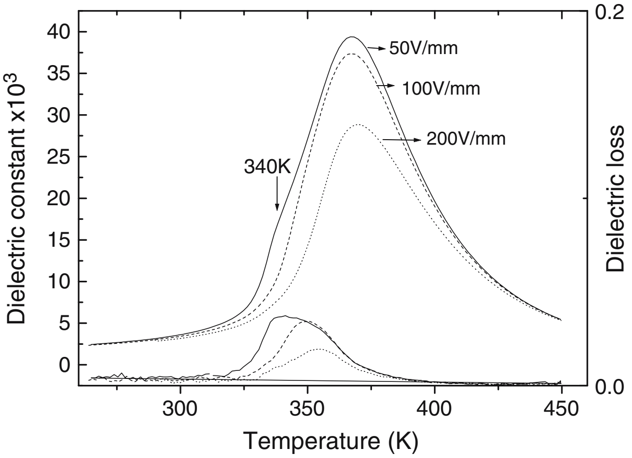

Fig. 1 Complex permittivity at 1 kHz during field cooling for the <001>-oriented PMN-0.21PT crystals

fatigue which may lead to early failures in working conditions. In the present work, the behavior of PMN-PT ($x=0.21$) single crystals is investigated under different electrical and thermal conditions in order to determine the limits of their applicability. Disclosure of phase stability in relation with performances under high E-field is useful to determine the limits of their practical applications in resonant power transducers and quasi-static actuators.

2 Experimental procedure

High quality PMN-PT crystals were grown using a modified Bridgman technique described elsewhere [7]. Crystals were cut into rectangular-shaped specimens (about $6\times6\times0.45$ mm^3) with large faces along <001>, <111> and <110> directions, respectively. Thin films of Cr/Au electrodes (~130 nm) were sputtered on the large faces. Their complex dielectric permittivity was investigated at 1 kHz in the temperature range 270~470 K with a heating rate of 1.5 K/min, using a liquid nitrogen cryo-furnace (SMC Air liquid) and a HP4192A impedance analyzer. Samples were poled during direct current (DC) field cooling (FC) procedures. The polarization current was measured with a programmable electrometer (KEITHLEY 617) during decreasing temperature from 470 K to 270 K at the rate of 1.5 K/min with different poling fields. X-ray diffraction was performed on a high-accuracy two axes diffractometer using Cu-K_β monochromatic radiation issued from a Rigaku rotating anode (RU300, 45 kW, 300 mA). Crystals were mounted on a HUBER goniometric head and, in the Bragg–Brentano geometry, the diffraction angles were measured with a precision better than 0.002° (2θ).

A double-beam laser interferometer (Polytec OFV 502) system was used to measure the surface sample displacement applied by different alternating current (AC) fields. The sample was fixed at some nodal points by the edges of the holder. The voltage response from the heterodyne detection is sent to a lock-in amplifier (Stanford Research System SR844 RF). The complex piezoelectric response at

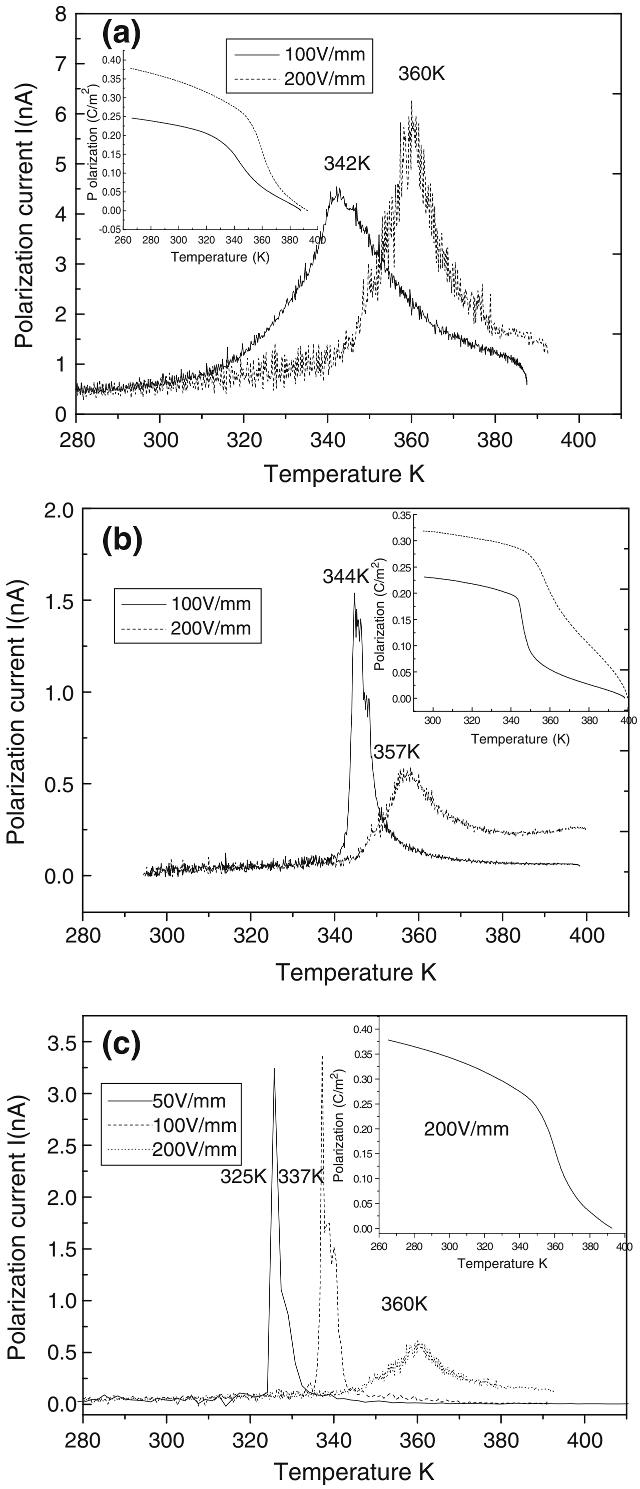

Fig. 2 Polarization currents change and polarization (*inset*) during field cooling for PMN-0.21PT crystals along (**a**) <001>, (**b**) <110> and (**c**) <111> directions, respectively

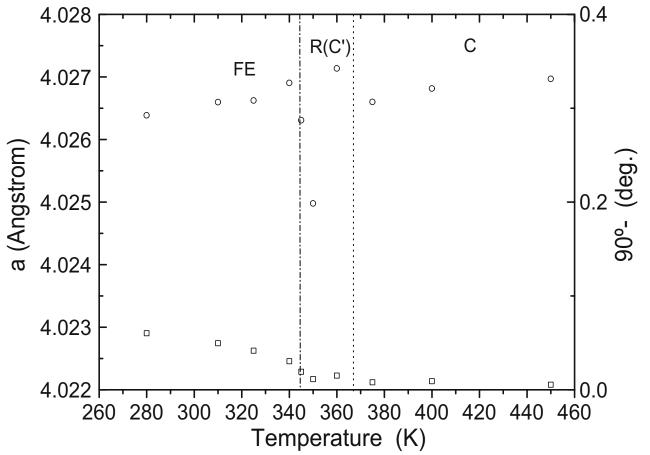

Fig. 3 Lattice parameters of the unit cell for the <111>-oriented PMN-0.21PT crystals during poling under bias field (100 V/mm) cooling

f and 2*f* (40 and 80 kHz) far below the first resonance frequency (5 MHz) was measured.

3 Results and discussions

The temperature dependence of the dielectric constant and dielectric loss of <001>-oriented PMN-PT (x=0.21) single crystals upon DC field cooling was shown in Fig. 1. The temperature T_m at the maximum of relative permittivity is of about 365 K and a low temperature anomaly was well observed at 340 K under field 50 V/mm, which also tends to persist on the plots of dielectric loss, related to the poling of the crystal. The polarization current under field cooling is given in Fig. 2 for the PMN-0.21PT single crystals. It is worth to notice that the temperature of current peak seems to be dependent on the applied field and does not vary with orientations, e.g. at about 342, 344, and 337 K (100 V/mm) along <001>, <110> and <111> directions, respectively. The temperature of peak corresponds to the transformation from a nonpolar state towards a polar one (jump in polarization). It is also compatible with the tendency of increased polarization under higher bias field. The current peak along <111> is much narrower than those along <110> and <001> orientations, which shows that the ferroelectric state is probably rhombohedral and more stable at low temperature [8]. Furthermore, at 50 V/mm along <111>, the current peak observed at lower temperature (325 K) indicates the kinetic phenomena of domain motion or the existence of a threshold field [9]. With increasing DC field to 200 V/mm, the current peak becomes broad, exhibiting the higher transition temperature (~360 K) approaching T_m, which im-

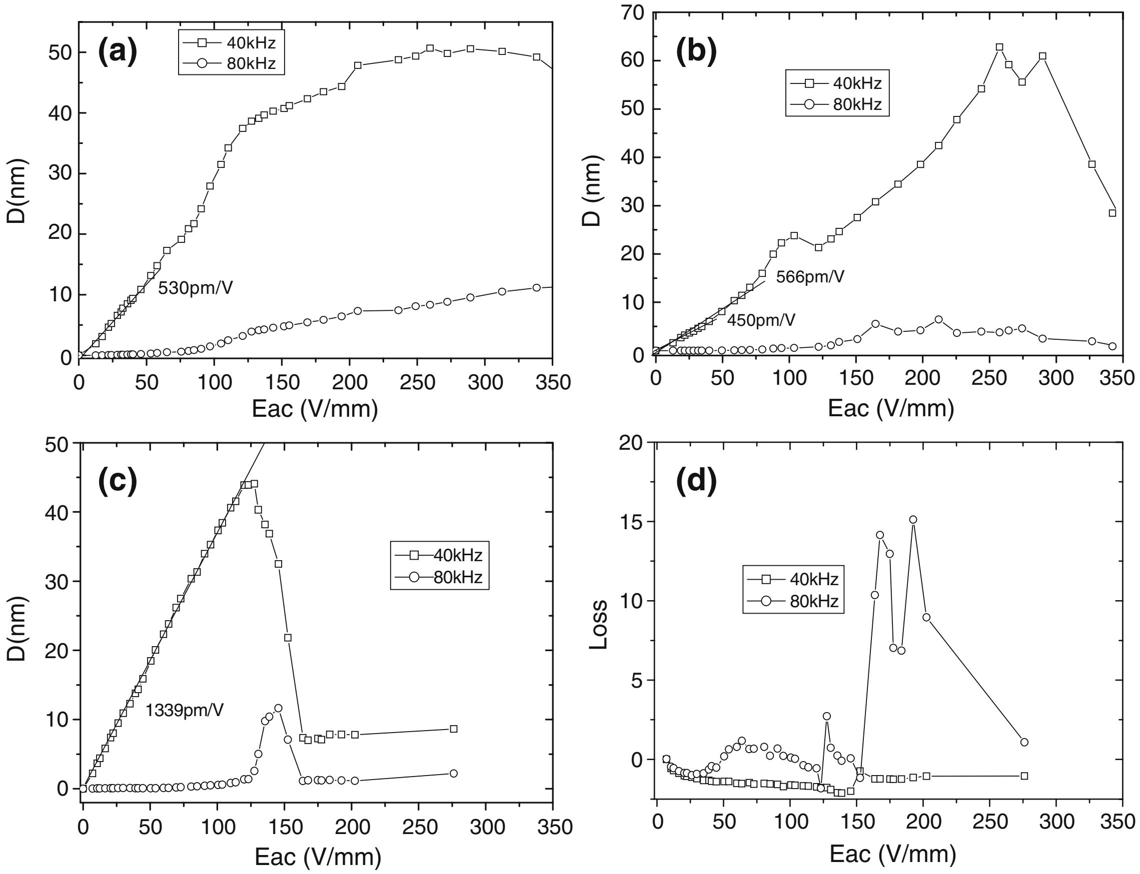

Fig. 4 Piezoelectric strain responses of PMN-0.21PT crystals with increasing ac field for: (**a**) <111> (FC 100 V/mm), (**b**) <110> (FC 400 V/mm), and (**c**) <100> (FC 200 V/mm) directions and (**d**) elastic losses in the <100> (FC 200 V/mm) direction with increasing driving ac field

plies the enlarged temperature stability region of the polar state. It seems that the DC field at around 200 V/mm is enough for poling the crystal during the FC procedure.

Further investigation was done to determine the transition from the relaxor cubic phase [R(C')] to the ferroelectric phase (FE) by X-ray diffraction of <111>-oriented PMN-0.21PT crystals during DC field (100 V/mm) cooling. As deduced in Fig. 3, the crystal shows clearly a cubic phase above 370 K. Below 345 K, the appearance of doublet diffraction pattern stemming from cubic (222) diffraction peak implies the partially poled state. The lattice parameters *a* and deviation angle ($90°–\alpha$) from the cubic phase (C) confirm the existence of the polar rhombohedral phase, deduced from $(22\overline{2})$ and (222) diffraction peaks, which are consistent with those found in pure PMN [10] and PZN [11].

Figure 4 shows the electric displacement and loss of PMN-0.21PT crystals sustained up to an AC field of around 350 V/mm for frequencies f=40 kHz and 2f=80 kHz at room temperature. The piezoelectric response deduced from displacement vs. electric field was about 530 pm/V and 450 pm/V for <111> poled at 100 V/mm and <110>-oriented crystals poled at 400 V/mm (Fig. 4(a), (b)), respectively. The first non-linearity appears at around Eac=70–80 V/mm for these two directions, however the linear region of piezoelectric response increases a little in the poled <111>-oriented crystal (Fig. 4(a)). The main cause for such phenomena may be the self-heating of the sample resulted from the increase of the electrical losses (the mechanical losses should be neglected since the sample is not at resonance). In the <001>-oriented poled samples, piezoelectric response can reach 1,339 pm/V (FC poling at 200 V/mm, Fig. 4(c)) and a larger linear response was gained up to Eac=125 V/mm with a negligible second order harmonic component. Above this field, the sudden disappearance of the piezoelectric response happens when the ac field approaches the coercive field E_C at the actual temperature of the crystal. The heating of the crystal due to the increase of the electric losses (Fig. 4(d)) explains the depoling at a field which is lower than coercive field at room temperature. Above this threshold field, the piezoelectric response would not be recoverable. A significant part of the piezoelectric response of the bulk ferroelectric materials originates from the displacement of domain walls. This extrinsic contribution to the piezoelectric properties is undesired since it is nonlinear, hysteretic, and dispersive, even at weak-to-moderate driving fields [12–15]. The application of high electric field improving the piezoelectric response and linear region is favorable in the application of PMN-PT crystals operated for high power transducers and miniaturized piezo microelectro–mechanical systems.

These results are consistent with those obtained previously on rhombohedral PMN-PT crystals exhibiting large piezoelectric coefficients when poled in a <001> or <110> direction [3, 16] compared with <111> direction, which is directly related to the engineered domain structure: an effective four-domain state (4R) for the <001> poled crystals and a two-domain state (2R) for the <110> poled crystals [16]. The <001> poled crystals provide high longitudinal piezoelectric coefficient d_{33}, while the two-domain <110> poled crystals give high transverse piezoelectric coefficient d_{31} and d_{32}. In PMN-0.21PT crystals, a large linear response and low second order harmonic response were observed in 4R state. The <001> poled crystal exhibits a good domain compatibility leading to low nonlinear effects.

4 Conclusions

The phase transition between the relaxor and rhombohedral ferroelectric state in PMN-PT (x=0.21) crystals was analysed using polarization current, and high-resolution X-ray diffraction. The temperature region of the polar phase stability tends to be enlarged with increasing bias field, and the corresponding polarization and piezoelectric linearity were enhanced. Piezoelectric strain measurements show that a linear response is obtained up to Eac=125 V/mm ([001] poled by FC 200 V/mm) with a negligible second order harmonic component. PMN-PT (x=0.21) crystals with the [001] engineered domain states could be a promising material compared with MPB crystals for high power acoustic transducers or high strain linear actuators.

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