The Nucleus ***54****, No. 1 (2017) 7-9*

www.thenucleuspak.org.pk

The Nucleus

ISSN 0029-5698 (Print)

ISSN 2306-6539 (Online)

Poling Field Induced Phase Transitions in [111]-oriented (1-x)Pb($Mg_{1/3}Nb_{2/3}$)O_3-xPbTiO_3 Single Crystal

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ARTICLE INFO

Article history :

Received : 31 August, 2106

Revised : 06 February, 2017

Accepted : 15 February, 2017

Keywords:

Phase Transitions

Relaxor ferroelectrics

Single crystal

PMN-PT

ABSTRACT

The effect of poling field on phase transitions of (1-x)Pb($Mg_{1/3}Nb_{2/3}$)O_3-xPbTiO_3 (PMN-xPT) [111]-oriented single crystal was examined through temperature dependent complex capacitance study. Two first order phase transitions from paraelectric cubic to ferroelectric tetragonal and then to ferroelectric rhombohedral phases were observed in the unpoled crystal. An additional low temperature anomaly was also observed at a temperature of ~40 ^{o}C in the field poled crystal. The new anomaly was associated to the field assisted monoclinic phase due to rotation of polarization vector.

1. Introduction

Relaxor ferroelectrics (RFEs) are a new generation of ferroelectric materials that in contrast to normal displacive ferroelectrics exhibit no long-range polar order in the absence of external electric field throughout the investigated temperature range. As a key feature, RFEs show a non-Debye type broad frequency dependent dielectric (ε) dispersion (due to polarization fluctuations) around/or below the temperature of dielectric maximum ($T_{\max}$), which is also one of the reasons to name them *relaxors*. RFEs show superior piezoelectric properties for compositions near the morphotropic phase boundary (MPB) (which separates ferroelectric tetragonal and rhombohedral phases) region *e.g.* very high electromechanical coupling factor (k_{33}~0.94) and piezoelectric coefficient (d_{33}~2820 pC/N) for (1-x)Pb($Mg_{1/3}Nb_{2/3}$)O_3-xPbTiO_3 (PMN-xPT) single crystals with x~33% [1]. MPB is actually a vertical region in the composition-temperature phase diagram of RFEs, where low symmetry ferroelectric metastable phases monoclinic (FEm) and orthorhombic (FEo) are present and may co-exist with ferroelectric tetragonal (P4mm) and rhombohedral (R3m) phases in the vicinity of its boundaries. Therefore, RFEs with composition around the MPB belong to an important group of materials for applications in electromechanical devices and transducer technology [1, 2].

The complex nature of physical behavior of RFE materials on one hand and giant piezoelectricity on the other hand, has greatly increased the quest to understand the relaxor phenomenon during the last two decades. The high electromechanical properties of (1-x)Pb($Mg_{1/3}Nb_{2/3}$)O_3-xPbTiO_3 (PMN-xPT) and (1-x)Pb($Zn_{1/3}Nb_{2/3}$)O_3-xPbTiO_3 (PZN-xPT) single crystals with MPB composition, have been associated to the polarization instability, which leads to easy rotation of polarization vector in the presence of external electric field [3-6]. In the presence of external *dc*-biasing field electromechanical response of the crystal can be modified through symmetry and domain structure changes. Due to polarization rotation possibility in PMN-xPT crystals around their MPB composition range, these crystals are very important from application point of view. In continuation of previous results [7], here it is reported the influence of *dc*-bias and poling field on the low field *ac*-response of MPB PMN-xPT [111]-oriented single crystal.

2. Experimental Procedure

[111]-oriented PMN-xPT single crystal with composition in the morphotropic phase boundary (MPB) region was investigated by measuring capacitance as a function of temperature and applied *dc* bias using Agilent 4294A impedance analyzer. The larger face of crystal normal to [111]-orientation was coated with silver paste and annealed at ~500 ^{o}C in air for ~30 min to ensure good Ohmic contacts. Three sets of experiments were performed at varying frequency of the probing signal (amplitude of 500 mV): (a) at zero *dc*-field heating and cooling of crystals and measurement of capacitance, (b) crystal poled at room temperature at a field of ~16 kV/cm and measuring in heating and cooling cycles, (c) fixed temperature in the tetragonal ferroelectric phase

(at ~125 °C) and measuring electric field-capacitance bipolar curve.

3. Results and Discussion

Fig. 1 shows real part (C') of the measured complex capacitance and dissipation factor (D), related to imaginary part of complex capacitance (C''), of unpoled [111]-oriented MPB PMN-*x*PT single crystal as a function of temperature and frequency. The value of x (mole%) for crystal under study was estimated to a good approximation from $T_c = 5x\text{-}10$, where, T_c is Curie temperature of PMN-*x*PT in its phase diagram [8]. The measured capacitance is a complex parameter that may be represented as: $C^*(\omega,T) = C'(\omega,T) - iC''(\omega,T)$ [9], where, $\omega=2\pi f$ is angular frequency of the probing signal and T is temperature. These data were recorded during heating cycle only. In the investigated temperature range, the complex capacitance diverges at temperatures of ~152 °C (strong peak) and ~75 °C (weak peak). This divergence of dielectric parameters was associated to: (i) phase transformation from paraelectric cubic (PEc) to ferroelectric tetragonal (FEt) and (ii) FEt to ferroelectric rhombohedral (FEr) phases, respectively [10, 11]. Dissipation factor shows a peak for PEc to FEt transition but FEt to FEr phase transition cannot be identified. Both the phase transition anomalies exhibit a clear temperature hysteresis in heating and subsequent cooling cycle (inset Fig. 1), exhibiting first order nature of both the anomalies. The capacitance decreases with increasing frequency at PEc to FEt phase transition temperature similar to those of normal ferroelectrics and a significant frequency dispersion is observed below T~135 °C. The dissipation factor shows rising trend with decreasing frequency above PEc – FEt temperature, which may be associated to the thermally activated *ac*-electrical conductivity arising from oxygen vacancy transport in the bulk [12].

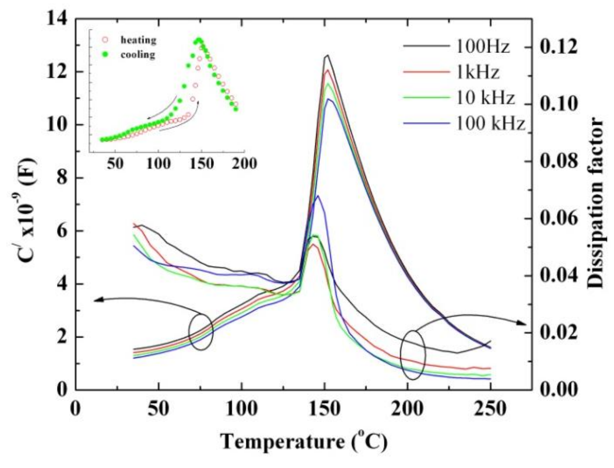

Fig. 1: Real part of complex capacitance (C′) and dissipation factor (D) of the unpoled [111]-oriented PMN-PT single crystal at some selected frequencies. Inset shows heating and cooling data of the unpoled crystal measured at a frequency of 1 kHz

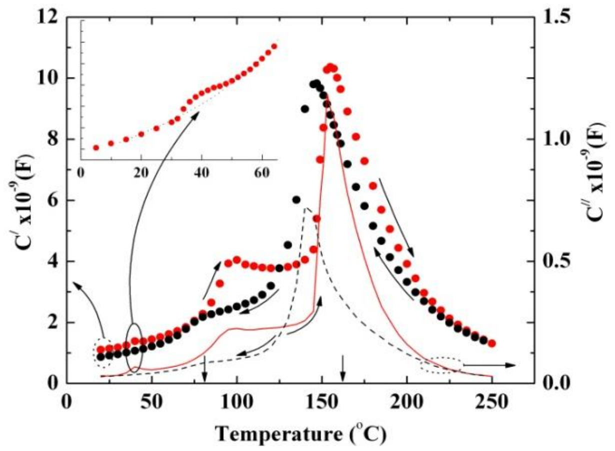

Fig. 2: Temperature dependent complex capacitance of [111]-oriented poled crystal measured in heating and subsequent cooling cycles. Inset shows enlarged view of the low temperature anomaly observed at T~40 °C (dotted line is just a guide to eye)

Fig. 2 shows temperature dependence of the real and imaginary parts of the complex capacitance of [111]-oriented MPB PMN-*x*PT single crystal pre-poled at room temperature by applying a *dc* electric field of E~16 kV/cm. The data plotted were measured in heating and subsequent cooling cycles. A visible effect of the *dc* poling electric field on the two phase transition anomalies (PEc-FEt and FEt-FEr) can be seen in these data at temperatures of ~155 °C and ~95 °C, respectively. The PEc-FEt region became narrower due to shift of FEt temperature to higher side by almost 20 °C and the FEr-FEt phase transition temperature increased from ~80 °C to ~95 °C. The shift in FEr-FEt boundary actually occurs at very low poling field (~0.2 kV/cm) as observed previously [7]. A significant increase in capacitance of the crystal suggests a strong coupling between poling field and capacitance. After subsequent cooling the crystal from high temperature, the depoled behavior of the crystal

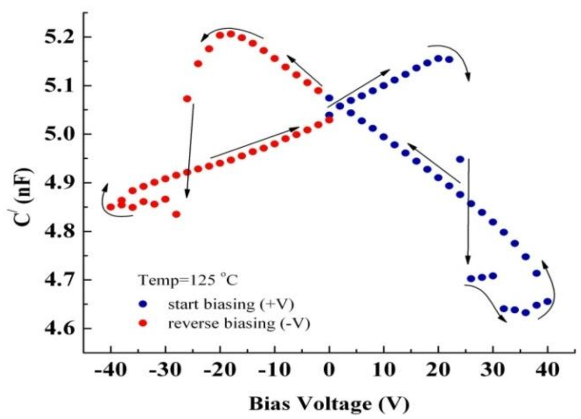

Fig. 3: Capacitance versus bias-voltage bipolar plot for [111]-oriented PMN-PT crystal measured at 125 °C well inside the ferroelectric tetragonal phase

is reproduced. The strong coupling between capacitance and applied field is clearly visible in the bias-voltage bipolar plot (look like wings of a bat) of capacitance measured at 125 ^oC well inside the tetragonal phase of [111] crystal (Fig. 3).

An important observation of these experiments is the presence of a new discontinuity at temperature of ~40 ^oC in capacitance of the poled crystal. This anomaly has not been reported previously in electrical measurements. As the order of magnitude of discontinuity was small, the measurements were repeated carefully a number of times with smaller temperature intervals during heating and cooling cycles. It was finally confirmed that a small anomaly was indeed present in poled crystal spanning temperature ranging from ~32 $\rightarrow$ 46 ^oC. Enlarged view of which is shown as an inset in Fig. 2. An important feature of this anomaly is that it disappears during cooling cycle (crystal heated from 5 $\rightarrow$ 60$\rightarrow$5 ^oC). This low temperature anomaly may be the appearance of a monoclinic phase induced by poling field assisted rotation of spontaneous polarization [7, 13]. Further experiments are in progress to investigate in detail the existence of this low temperature anomaly in PMN-*x*PT MPB single crystals with different orientation and origin.

4. Summary

In summary, the low field *ac* response of [111]-oriented PMN-*x*PT single crystal in the MPB composition range was investigated by temperature dependent complex capacitance measurements. A new low temperature anomaly at ~40 ^oC was observed in the complex capacitance of the field poled crystal which was associated to the monoclinic phase induced by poling field forced rotation of polarization vector. Bias voltage bipolar plot measured at a temperature of ~125 ^oC (well inside tetragonal phase) showed good field-capacitance coupling in the crystal.

Acknowledgement

PMN-*x*PT crystals were kindly provided by Professor Yao Xi of Xi'an Jiaotang University, China.

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