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Aging Behavior and Electric Field Induced Instabilities in Lead Magnesium Niobate - Titanate Relaxor Ferroelectric Single Crystal

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Abstract. The aging characteristics and influence of electric field poling on the phase transitions in (1-*x*)Pb($Mg_{1/3}Nb_{2/3}$)O_3-*x*$PbTiO_3$ (PMN-*x*PT) [110]-oriented single crystal were examined through temperature dependent complex capacitance study. In addition to two phase transition anomalies exhibited by the crystal in the virgin state, other phase transition instabilities were observed in the complex capacitance of the crystal under the external applied electric field. The aging behavior deviated from the linear logarithmic law and followed the stretched exponential expression typical for relaxor ferroelectrics. Moreover, aging decreased with frequency while it became faster with increase in temperature towards the paraelectric – ferroelectric structural phase transition temperature.

Introduction

Single crystals of perovskite-based solid solutions of canonical relaxor Pb($Mg_{1/3}Nb_{2/3}$)O_3 (PMN) and classical ferroelectric $PbTiO_3$ (PT), commonly known as relaxor ferroelectrics (RFEs), are very important for ferroelectric industry due to their giant piezoelectric properties [1, 2]. It is generally agreed that the peculiar physical characteristics of RFE are attributed to the intrinsic inhomogeneity giving rise to static chemically ordered regions (CORs) and polar nanoregions (PNRs) at different length scales, exhibiting clear signatures of structural hierarchy in RFE materials [3]. In the presence of CORs and/or PNRs, RFE materials transform into an intermediate ergodic relaxor state at Burn's temperature (T_B) upon cooling from high temperature paraelectric state instead of directly developing a polar ferroelectric phase at Curie temperature (T_C). In RFEs, either $T_C \ll T_B$ or ferroelectric phase can only be attained by applying external electric field. It is important to remember that structural morphology of CORs is unchanged with temperature in contrast to PNRs that change their size and/or density and the crystal transform to a nonergodic glassy state below T_f, known as freezing temperature [4].

In spite of the extensive research carried out on (1-*x*)Pb($Mg_{1/3}Nb_{2/3}$)O_3-*x*$PbTiO_3$ (PMN-*x*PT) single crystals and other related perovskite oxides, the phase transition behavior exhibited by the dielectric properties of these materials especially near the morphotropic phase boundary (MPB) region remains far from clear. The structural investigations by high-resolution synchrotron x-ray diffraction [5] and further supported by the first principle calculations [6], established that MPB in RFE perovskite oxides is actually a narrow region consisting of monoclinc and other mixed phases, that contribute to the possible giant piezoelectric activity through rotation of polarization vector. It has been argued that the phase structure near the MPB region is highly unstable with nearly degenerate phase energies and even a small external electric field can induce phase transitions (of metastable nature in some instances) by altering the phase energies. Therefore, field induced polarization rotation results in the formation of intermediate monoclinic (M) and/or othorhombic (O) phases in the MPB region with their co-existence along with rhombohedral (R) and tetragonal (T) phases at the extremities of MPB.

In the presence of external electric field, the crystal attains non-equilibrium state and with the passage of time the system tries to return to its equilibrium state by exhibiting changes in induced physical properties through aging process. Aging depends on sample conditions such as temperature, strength of applied electric-field etc. In continuation of previous work [7-9], here are reported the electric field induced phase instabilities and aging behavior in PMN-*x*PT [110]-oriented single crystal.

Experimental Procedure

Complex capacitance of the [110]-plate PMN-*x*PT single crystal with composition in the morphotropic phase boundary (MPB) region (*x*~33%) was measured as a function of temperature and applied *dc* bias (+40V) using Agilent 4294A impedance analyzer. A second set of same measurements was taken in narrow temperature range (*T*~50-120°C) by poling the crystal using high voltage power supply ES-5R1.2 (M/S Matsusada Inc., Japan). The amplitude of the probe *ac* signal was of the order of 1 volt for all experimental conditions. Aging of complex capacitance was observed on the unpoled crystal well inside the ferroelectric region at temperatures of 40°C and 120°C. The experimental details can be found elsewhere [7, 8]. Electric field was applied along [110] direction and resulting changes in the complex capacitance were monitored along the same direction of the crystal.

Results and Discussion

The complex capacitance, $C^*(\omega,T)$, consisting of real, $C'(\omega,T)$, and imaginary, $C''(\omega,T)$ parts ($C^*(\omega,T) = C'(\omega,T) - iC''(\omega,T)$), is a general electrical parameter which is experimentally measured for dielectric characterization of ferroelectric and/or piezoelectric materials. Where, $\omega = 2\pi f$ and T are angular frequency of the *ac* probing signal and sample temperature, respectively. The complex capacitance, in turn, is proportional to the complex dielectric function, $\varepsilon^*(\omega,T) = \varepsilon'(\omega,T) - i\varepsilon''(\omega,T)$.

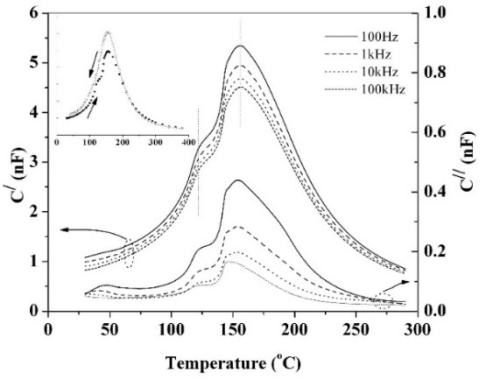

Fig. 1. Real ($C'(\omega,T)$) and imaginary ($C''(\omega,T)$) parts of the complex capacitance of unpoled [110]-plate PMN-PT single crystal at some selected frequencies. Inset shows $C'(\omega,T)$, measured in heating and cooling cycles at a frequency of 10 kHz.

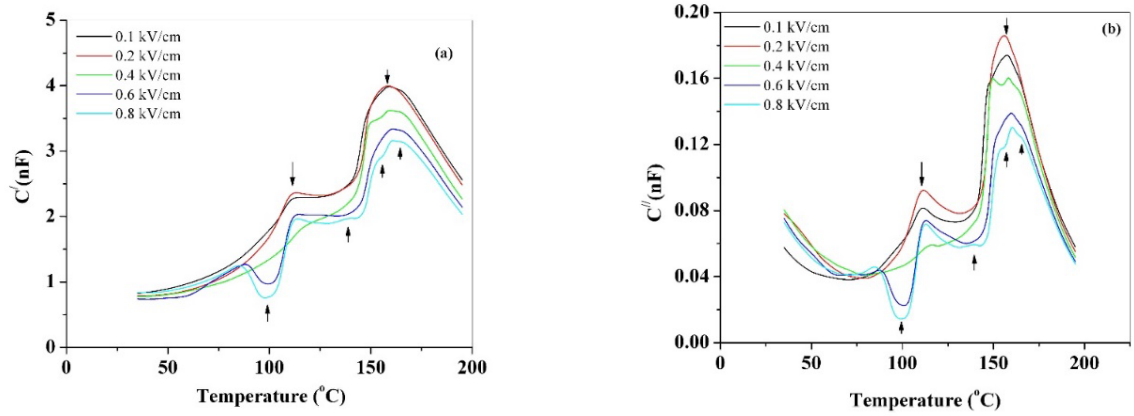

Fig. 2. Temperature dependent real ($C'(\omega,T)$) (a) and imaginary ($C''(\omega,T)$) (b): parts of complex capacitance of the [110]-plate PMN-PT single crystal measured under different *dc*-bias conditions. Down and up arrows indicate zero-field and field induced anomalies, respectively.

The temperature and frequency dependence of the measured complex capacitance of [110]-oriented PMN-xPT single crystal in unpoled state is shown in Fig. 1. Two phase transition instabilities, from ferroelectric rhombohedral to ferroelectric tetragonal (T ~ 125°C) and then to

paraelectric cubic phase (T ~ 156°C) were clearly observed in heating the crystal from room temperature. These two temperatures are indicated by vertical dotted lines in Fig. 1.
Fig. 2 shows the *in-situ* field induced response of the crystal at low electric fields (< 1.0 kV/cm). It is interesting to note that visible fluctuations in the complex capacitance could be seen in the vicinity of both the phase transition points at electric fields of $E \geq 0.4$ kV/cm as indicated by upward short arrows in Fig. 2. With further increasing electric field, the low temperature peak becomes sharper and an additional instability (a dip at T ~ 90°C) appears below the rhombohedral – tetragonal phase transition point. These instabilities may be associated to the rotation/alignment of polarization vector under the influence of external electric field giving rise to various monoclinic phases [9].

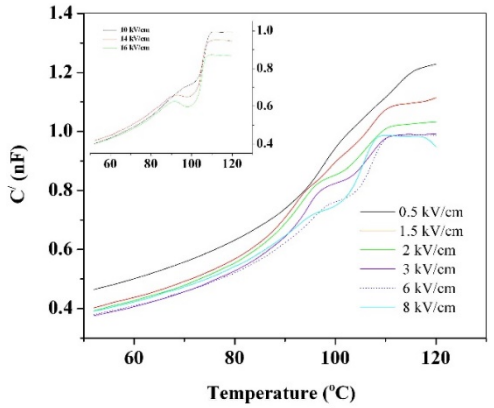

Fig. 3. Electric field poling effect on the capacitance of the ferroelectric tetragonal – rhombohedral phase transition of PMN-PT single crystal. Capacitance changes for high field poling are shown as an inset for the sake of clarity.

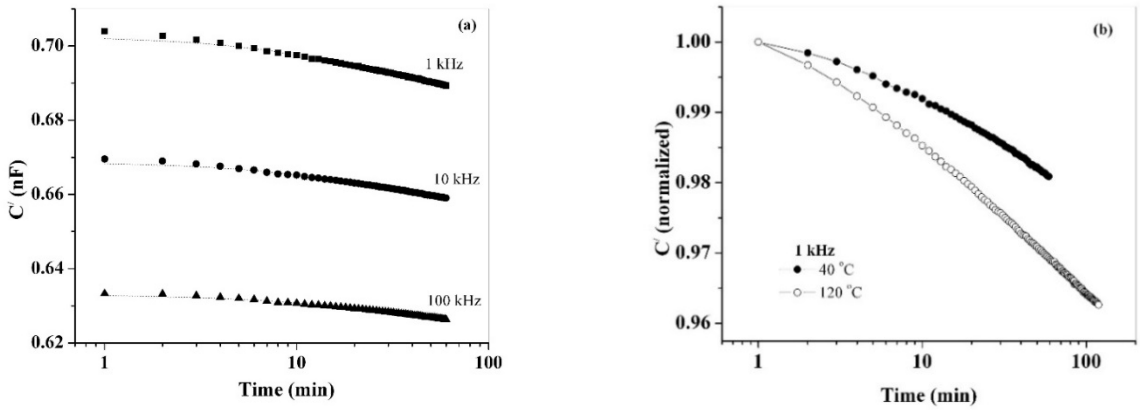

Fig. 4. Frequency dependence of the real part of complex capacitance at aging temperature of T ~ 40°C (a) and normalized aging data measured at two temperatures (b).

Another set of data were recorded by poling the crystal under varying external fields and then measuring the impact of poling field strength on the complex capacitance of the crystal. These experiments were performed in the ferroelectric regime (T~120°C) and real part of capacitance data are plotted in Fig. 3. With increasing poling field, a clear shift in the phase transition boundary was observed for rhombohedral – tetragonal phase transition and an additional phase develops at T ~ 95°C at higher poling field *i.e.* $E \geq 1.5$ kV/cm which seems to transform into a downward dip with even higher poling fields $E \geq 14$ kV/cm.

The low-field aging behaviour in the complex capacitance of [110]-oriented PMN-33%PT single crystal was investigated at two different aging temperatures (T= 40°C and T=120°C) below the dielectric maximum temperature, T_{max}, (paraelectric cubic to ferroelectric tetragonal phase transition temperature) as a function of frequency of the probing *ac* signal. Fig.4a shows representative data measured at an aging temperature of T ~ 40°C. It can be seen that aging behaviour of crystal does not follow the general linear logarithmic time equation as in case of normal ferroelectric materials but rather it follows the stretched exponential law expressed as [8]:

$$C(\omega,T) = C_{\infty}(\omega,T) + C_1 exp[-(t/\tau)^{\upsilon}] \quad (1)$$

Here, first term on right side of the above equation is independent of time, and the second part of the expression depends on time and this term becomes zero under infinite time scale ($t\rightarrow\infty$), t is aging time and τ (time constant) represents the aging rate.

It is important to note that although the fit of the data to the above relation seems good but the fitting parameters were not reliable. This discrepancy probably may be associated to insufficient data points where the capacitance would show flat response after full relaxation. The experiments for longer time were not possible due to experimental constraints. In order see unquestionable difference in the measured aging rate, the data points for the two temperatures were normalized with respect to the initial capacitance and are plotted in Fig. 4b. This shows clearly that aging rate at T = 120°C is higher than that for T = 40°C similar to that reported for other relaxor oxides [10]. As to the frequency dependence of aging behaviour at the aged temperatures, an increase in the time constant τ while a decrease in C_{∞} and C_1 was observed with increasing frequency. This is typical for relaxor materials originating from pinning of the polarization components with low time constant. In contrast to relaxors, aging in normal ferroelectrics is related to the stabilization and/or re-arrangement of macroscopic domain structure/configuration in presence of structural defects. In RFE, CORs, PNRs originating from chemical and structural inhomogeneities are responsible for the deviation of aging process from the linear logarithmic time law.

Summary

In summary, the electric field induced instabilities and aging effects in the low field *ac* response of [110]-oriented PMN-*x*PT single crystal in the MPB composition range was investigated by temperature dependent complex capacitance measurements. The phase transition characteristics under the applied electric filed and pre-poled conditions were studied as a function of temperature. A clear shift in the phase transition boundary and additional instabilities were observed under the external electric conditions which were attributed to the electric field assisted rotation of polarization vector. The aging rate showed decreasing trend with increasing frequency whereas; the aging rate increased with rise in temperature indicating that aging is thermally activated process.

Acknowledgements

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