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High Temperature Instabilities in $Sr_{0.75}Ba_{0.25}Nb_2O_6$ Ferroelectric Relaxor

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ABSTRACT

[001]-oriented tungsten bronze type $Sr_{0.75}Ba_{0.25}Nb_2O_6$ uniaxial relaxor ferroelectric single crystals have been examined by the temperature dependent complex capacitance study. The capacitance dispersion maximum temperature was observed at T~58 °C with strong frequency dependence above and below this temperature. At temperatures $T>T_{max}$ three additional instabilities were exhibited by the complex capacitance in the unpoled crystal during heating cycle whereas these instabilities could not be seen in the subsequent cooling cycle. Similarly these instabilities disappeared upon poling the crystal at room temperature. These additional high temperature instabilities of the metastable character were associated to different kinds of random inhomogeneous structures trapped in strong random field matrix of SBN-x uniaxial relaxor.

1. Introduction

Relaxor ferroelectrics (RFEs) have attracted a large number of researchers during the last few decades due to their interesting physical properties for industrial applications [1]. RFEs are structurally disordered materials consisting of two major classes: cubic perovskite-type ABO_3 oxides (e.g. $Pb(Mg_{1/3}Nb_{2/3})O_3$, PMN) and tungsten-bronze-type AB_2O_6 oxides (e.g. $Sr_xBa_{1-x}Nb_2O_6$, SBN-x). SBN-x ($0.25<x<0.80$) has unfilled tetragonal tungsten-bronze-type (TTB-type) structure and is an interesting candidate to understand the nature of relaxor ferroelectric materials due to its strong anisotropic nature of local polarization besides its excellent physical properties [2]. SBN-x is generally known as uniaxial RFEs because its local polarization vector is aligned along the single crystallographic direction in contrast to cubic perovskite relaxors.

The unit cell of TTB-type compounds is represented by the general formula $(A^{/})_2(A^{//})_4(C)_4(B^{/})_2(B^{//})_8O_{30}$, where the sites $A^{/}$, $A^{//}$, C, $B^{/}$ and $B^{//}$ can be partially or fully occupied by different cations resulting in lattice disorder due to missing charges. The structure consists of corner sharing NbO_6 octahedral units forming three kinds of channels (triangular, square, and pentagonal) along the polar *c*-axis. The pentagonal channels are partially occupied, squared are fully occupied while triangular ones are empty, which makes TTB-type structure as unfilled one consisting of 45 atoms at 46 sites of the general formula. Moreover broad distribution of Nb-O and Ba/Sr-O distances creates distortions in the oxygen octahedral units resulting in incommensurate modulations not present in cubic perovskite RFEs. These distortions in the octahedral units and incompletely filled structure (a source of random vacant sites) give rise to intense random fields which greatly influence the physical properties of RFEs.

As to the physical origin of relaxor state of these both kinds of oxide materials, it has been established in the light of available experimental data so far that the key role is played by the so-called polar nanoregions (PNRs) which appear right from the paraelectric phase and persist down to very low temperatures with either dynamic or frozen behavior. SBN-x crystals are ferroelectric for $x<0.6$ while relaxor properties have been observed for $x\geq 0.60$. To understand the interaction of PNRs with the strong random field matrix in SBN-x, studies have been carried out by dielectric [3, 4], X-ray diffraction [5], refractive index [6], Brillouin scattering [7-9], acoustic emission [10, 11], and second optical harmonics [12]. In the present article, the high temperature instabilities in [001] oriented $Sr_{0.75}Ba_{0.25}Nb_2O_6$ (SBN-0.75), RFE single crystals have been investigated by the low field alternating voltage capacitance measurements.

2. Experimental Procedure

[001]-plate SBN-0.75 single crystal was investigated by measuring capacitance as a function of temperature and using Agilent 4294A impedance analyzer. The sample was configured as a capacitor by coating the large face with silver paste and annealing at ~500 °C for ~30 minutes. The *ac* probing signal with amplitude of 500mV was applied along the measured direction ([001]) of the crystal. For temperature control; the crystal was placed in a THMSE600 heating/cooling stage (M/S Linkam, UK) with temperature accuracy of ±1.0 °C and stability of ±0.1 °C.

3. Results and Discussion

The temperature dependent frequency dispersion curves of SBN-0.75 crystal exhibited by the complex capacitance, $C^*(f, T) = C'(f, T) - iC''(f, T)$, at some selected frequencies (f) of the low field probing alternating voltage are shown in Fig. 1 and Fig. 2. The real part of the complex capacitance

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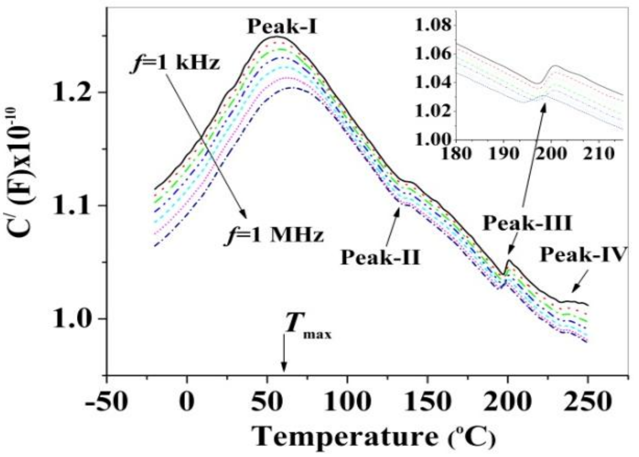

Fig. 1: Temperature dependence plot of the real part of the low field capacitance of SBN-0.75 crystal at some selected frequencies.

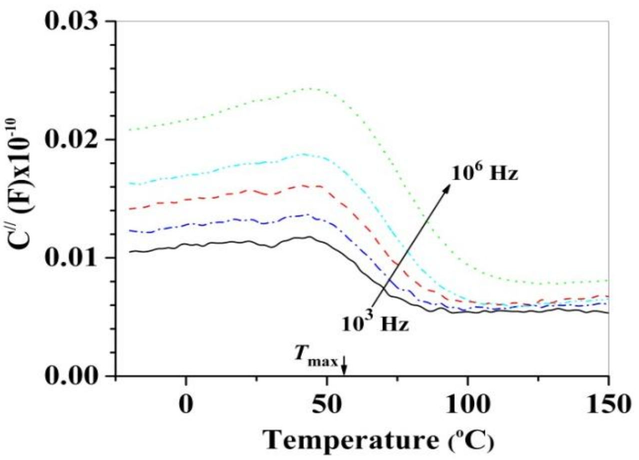

Fig. 2: Frequency dispersion curves of the imaginary part of the complex capacitance (C'') of SBN-0.75 crystal as a function of temperature.

(C') or the ordinary capacitance shows a typical relaxor behavior (Fig. 1) as maximum in the capacitance (Peak-I) decreases and shifts towards higher temperature with increasing frequency. Therefore, Peak-I represents the RFE diffuse phase transition temperature and may be denoted by $T_{max}(f)$. This relaxor type feature is also reflected by the imaginary part of the capacitance, $C''(f)$, related to the dielectric loss part of the frequency response (Fig. 2), i.e., peak value of $C''(f)$ rises and shifts towards higher temperature with increasing frequency. This behavior of $C''(f)$ is in good agreement with reported data for SBN-0.60 [13]. The high temperature data of complex capacitance has been removed because it is markedly increased due to some conduction mechanism of hoping charges with appropriate relaxation time constant. This means that inverse of the time constant of hoping charges is less than the frequency of the applied probing alternating voltage signal which supports movement of charge carries in the highly uneven energy landscape. The hoping of charge carries becomes pronounced with increasing temperature (T>250 °C for C') as can be seen in low frequency part of Fig. 3b. An interesting feature of the data shown in Fig. 1 is that the $C'(f)$ shows larger dispersion for $T<T_{max}(f)$ relative to that for $T>T_{max}(f)$, which seems logical because high temperature dispersion consists of universal relaxation process only whereas; low temperature dispersion consists of universal and conventional relaxation processes [14].

There are three additional instabilities in the capacitance – temperature plots (Fig. 1) at T~ 142 °C, 200 °C and 234 °C denoted by Peak-II, Peak-III, and Peak-IV, respectively. Upon subsequent cooling the crystal and by pre-poling at room temperature these instabilities could not be observed. These instabilities exhibit strong frequency dependence as is clarified by logarithmic frequency – capacitance plots at different temperatures shown in Fig. 3a (Peak-II and Peak-III) and Fig. 3b (Peak-IV). It is interesting to note that close to the instability temperature, the frequency seems to be clamped while capacitance shows linear frequency dependence for equal temperature intervals.

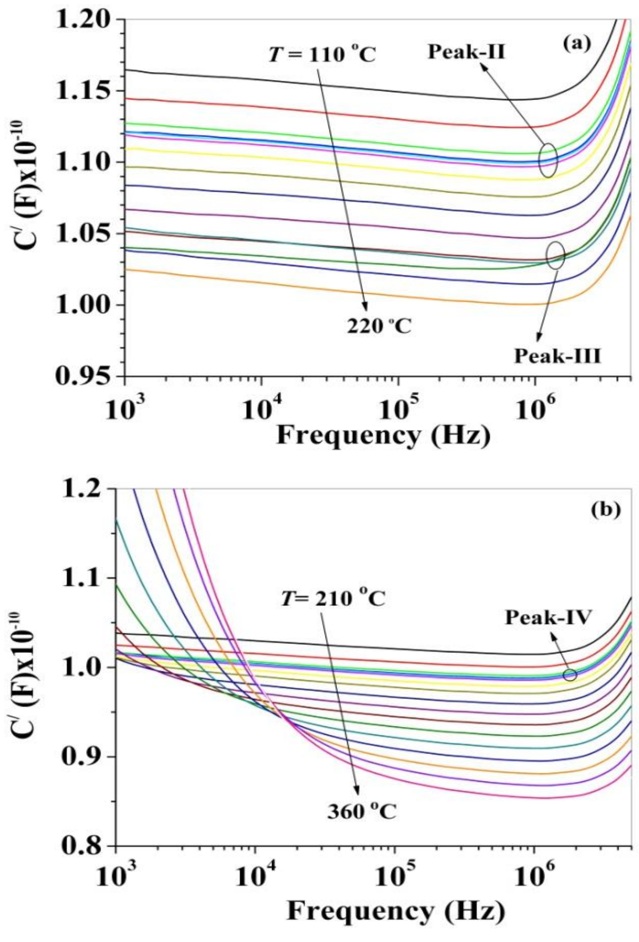

Fig. 3: Capacitance versus logarithmic frequency plot of SBN-0.75 crystal measured at different temperatures above $T_{max}(f)$: (a) Peak-II and Peak-III, (b) Peak-IV, respectively.

The frequency response of the anomaly at T~234 °C resembles with that at T~142 °C, whereas the anomaly at T~200 °C seems to be rather sharp and apparently different in nature (enlarged view is shown as an inset in Fig. 1). This temperature is very close to T^* (~193 ^oC) for SBN-0.75 [100]-plate crystal as observed by acoustic emission technique [10] and no anomaly could be seen in the vicinity of T_B (~350 ^oC). The exact nature of these instabilities observed at $T>T_{max}$ is not known; however, it is proposed that these instabilities may not be neither related to T_B (~350 ^oC) or T^* nor show structural phase transformation (due to clear relaxor nature in this temperature range), but may indicate the presence of random structures/inhomo-geneities (domain like or clusters of PNRs) trapped in strongly quenched random fields (RFs) matrix. It is thermal flipping and/or wall movement of these domain structures that give rise to high temperature anomalies of metastable character. Temperature dependence of the optical second harmonic generation signal in SBN-*x* crystals [12] shows a very complex pattern of activation energies indicating existence of different patterns of local polar region depending on crystal composition, however; additional studies are required to confirm the exact nature of high temperature instabilities observed in SBN-0.75 crystal.

4. Summary

In summary, the low field *ac* response of [001]-oriented uniaxial single relaxor ferroelectric crystals of SBN-0.75 composition were investigated by temperature dependent complex capacitance measurements. The temperature and frequency dependence of complex capacitance exhibited a typical relaxor behavior with T_{max}~58 ^oC (at f~10 kHz). Above T_{max} three additional instabilities were observed at temperatures T~ 142 ^oC, 200 ^oC and 234 ^oC in the unpoled crystal during heating cycle whereas these instabilities could not be seen in the subsequent cooling cycle and upon poling the crystal at room temperature. These additional high temperature instabilities of the metastable character were associated to different kinds of inhomogeneous random structures trapped in strong random field matrix of SBN-*x* relaxor.

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