Time evolution of polar regions in (Sr_{0.65}Ba_{0.35})_2NaNb_5O_{15} single crystal

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The linear, second-order and third-order dielectric susceptibilities $\chi_1$, $\chi_2$, $\chi_3$ of a (Sr_{0.65}Ba_{0.35})_2NaNb_5O_{15} (SBNN) single crystal have been measured. Strong relaxation was found in all investigated dielectric susceptibilities near the phase transition. The time dependence of linear and third-order dielectric susceptibility can be explained as the effect of polar nano-clusters evolution. Near the phase transition, the net polarization of the crystal, monitored by second-order dielectric susceptibility, changes both its value and orientation. Measurements of the pyroelectric effect indicate that the non-zero net polarization in SBNN crystals appears spontaneously. In addition, the ferroelectric phase transition in SBNN showed many features of a first-order phase transition.

Keywords: Relaxor; Phase transition; Linear and nonlinear dielectric susceptibilities; Aging; Polar nano-regions

1. Introduction

The strontium–barium–sodium niobate compound (Sr_{x}Ba_{1-x})_2NaNb_5O_{15} (SBNN) is a lead-free ferroelectric relaxor. Similarly to strontium–barium niobate (SBN), it has a tungsten bronze type crystal structure [1]. However in contrast to SBN, the crystal structure is a filled type. Since sodium atoms shift the Curie temperature up to $T_C \sim 472$ K in comparison with $T_C \sim 354$ K for SBN61, this material is a better candidate than SBN for electro-optical, dielectric and piezoelectric applications [1, 2]. Similarly to SBN, the [001] SBNN orientated crystal shows typical relaxor behaviour. Generally speaking, relaxors, such as PbMn_{1/3}Nb_{2/3}O_{3} (PMN), (PMN)_{1-x}(PbTiO_3) (PMN-PT), (Pb_{1-x}La_x)(Zr_{y}Ti_{1-y})_{1-x/4}O_3 (PLZT) [3] and Sr_{x}Ba_{1-x}Nb_2O_{6} [4], exhibit aging, which can be detected in the linear dielectric response. In addition, aging of the third-order dielectric susceptibility of a relaxor was found in the 9/65/35 PLZT ceramics [5]. The aging of dielectrics refers to the

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gradual change (mostly decreasing) of the dielectric susceptibility when a sample is kept under a fixed environmental condition, such as a constant temperature and/or a constant applied electric field. In this work, we have studied the dielectric properties of a \((\text{Sr}_{0.65}\text{Ba}_{0.35})_2\text{NaNb}_5\text{O}_{15}\) single crystal in the direction parallel to the [001] polar \(c\)-axis. The compound \((x = 0.65)\) under investigation is close to the morphotropic phase boundary (MPB) composition \((x = 0.6)\) [6]. The linear, second-order and third-order nonlinear dielectric susceptibilities \(\chi_1, \chi_2, \chi_3\) have been systematically measured, while these linear and nonlinear dielectric susceptibilities are defined by the following \(P-E\) relationship: \(P(E) = \varepsilon_0(\chi_1E + \chi_2E^2 + \chi_3E^3 + \ldots)\), where \(P\) is the polarization and \(E\) is the applied electric field along the polar \(c\)-axis.

Two different measurements have been carried out. First, the linear and nonlinear dielectric susceptibilities were measured in the variable cooling ramp regime. Secondly, measurements of the linear and nonlinear dielectric susceptibilities were performed in the interrupted cooling ramp regime (isothermal aging). In order to describe the experimental data obtained from the second type experiments mathematically, the stretched exponential law [7] was used:

\[
\chi(t) = \chi_\infty + \Delta \chi \exp\left\{-(t/\tau)^\beta\right\}.
\]

We also report here pyroelectric measurements on a non-poled SBNN sample.

2. Experimental

The SBNN single crystal was grown by the Czochralski method. A sample of dimensions \(4 \times 6 \times 0.4 \text{ mm}^3\) was cut from a crystal boules. The polar \(c\)-axis is along [001] of the tetragonal phase, which is the main surface direction of the sample. Vacuum deposition of copper and subsequent gold films onto the major faces produced the electrodes. Measurements of the dielectric susceptibilities were made using an HP 4263B LRC meter. Then, simultaneous measurements of the real parts of the linear and nonlinear dielectric susceptibilities of SBNN were carried out using an experimental set-up described in [8]. During this experiment, a 1 kHz a.c. field with an amplitude of \(E = 50 \text{ V cm}^{-1}\) was applied to the sample. Such amplitude of the applied field is typical for this type of measurement and is generally kept much lower than the coercive field. Prior to each measurement on cooling, the sample was refreshed at a temperature of \(573 \text{ K}\) for 20 minutes.

3. Results and discussion

The temperature dependence of the linear dielectric susceptibility has been measured at four different frequencies: \(10^2, 10^3, 10^4\) and \(10^5\) Hz. The results are shown in figure 1 for both cooling (figure 1a) and heating (figure 1b) cycles. The cooling/heating rate was set at \(2 \text{ K min}^{-1}\). The peak temperature, \(T_{\text{max}}\), increases from 472.6 to 473.9 K during the cooling process (figure 1a) and increases from 474.9 to 475.4 K during the heating process (figure 1b) while the frequency is increased from 100 Hz to 100 kHz. An increase in the measuring frequency leads to a decrease in the dielectric susceptibility and also causes peak broadening. In the ferroelectric phase, below \(T_{\text{max}}\), the SBNN sample displays strong frequency dispersion. In addition, weak dispersion is also observed in the paraelectric phase...
immediately above $T_{\text{max}}$. This dispersion behaviour below and above $T_{\text{max}}$ indicates the presence of relaxing polar regions.

Figure 2 shows the temperature dependence of the linear and nonlinear dielectric susceptibilities $\chi_1$ (a), $\chi_2$ (b) and $\chi_3$ (c) measured on cooling (with variable cooling ramp regime) with several different cooling rates. At a first glance (figure 2a) one notices the strong cooling rate dependence of the linear dielectric susceptibility in the
temperature range $460 \leq T \leq 500$ K. This cooling rate dependence manifests near $T_{\text{max}}$ only, and is visible both in the ferroelectric and in the paraelectric phases. When the cooling rate is decreased from 8 to 0.12 K min$^{-1}$, the peak value of $\chi_1$ decreases approximately by a factor of 2. Such behaviour indicates that, near the phase transition point, the SBNN crystal is in a non-equilibrium state. Therefore, the isothermal aging process of the linear dielectric susceptibility should be observed near $T_{\text{max}}$. The temperature dependence of the second-order dielectric susceptibility,
The non-zero value of $\chi_2$ is observed not only in the ferroelectric phase but also in the paraelectric phase. The second-order dielectric susceptibility is non-zero only for the macroscopically non-centrosymmetric systems. On the contrary, one obtains $\chi_2 = 0$ in the case of macroscopically centro-symmetric systems, i.e. in systems for which the net polarization vanishes. In order to explain the occurrence of $\chi_2$ in the paraelectric phase we postulate that the presence of polar regions causes the breaking of global inversion symmetry. Such behaviour has already been observed in pure and chromium-doped strontium–barium niobate crystals. As shown in figure 2(b), the peak value of the second-order dielectric susceptibility decreases when decreasing the cooling rate. Hence, the non-equilibrium nature of the SBNN crystal near the phase transition is confirmed by these observations. The relative change of the peak value of $\chi_2$ is higher than that observed in linear dielectric susceptibility. The temperature interval in which $\chi_2$ is non-zero coincides with the temperature interval in which strong cooling rate dependence of the linear dielectric susceptibility has been observed. The temperature dependence of the third-order dielectric susceptibility, $\chi_3$, is presented in figure 2(c). Similarly to $\chi_1$, the value of $\chi_3$ strongly depends on the cooling rate and decreases when the cooling rate decreases.

Figure 3 shows the measured pyroelectric effect of non-poled SBNN crystal during the cooling and heating processes. The rate of temperature change was set to $T = 10$ K min$^{-1}$. Measurement of the pyroelectric effect on a non-poled SBNN crystal confirmed that non-zero net polarization spontaneously and gradually appears in the SBNN crystal during the cooling process. During the heating process, the net polarization gradually decreases and finally vanishes; however, a polarization tail still persists above $T_{\text{max}}$—showing strong thermal hysteresis.

Typical temperature dependences of the linear and nonlinear dielectric susceptibilities, measured at $f = 1$ kHz in the interrupted cooling ramp regime, is shown in figure 4. The crystal was cooled from a temperature far above $T_{\text{max}}$ with a cooling rate of 2 K min$^{-1}$ (curves AB). At the isothermal aging temperature of $T_{a} = 469.9$ K, the cooling process was stopped and the temperature was maintained for 10 h (curves BC). Then, the crystal was re-heated (curves CA). Such experiments were repeated for several values of $T_{a}$ in the temperature range $455 \leq T \leq 490$ K. In figure 5, the time dependences of $\chi_1$, $\chi_2$ and $\chi_3$ obtained for isothermal aging at a temperature of $T_{a} = 469.9$ K are presented. These results correspond to curves BC in figure 4. For all linear and nonlinear dielectric susceptibilities, strong time dependence has been observed. In the investigated temperature range and time range, all aging curves can be best fitted using the stretched exponential function of equation (1). The stretched exponential function has four adjustable parameters: $\chi_{\infty}$ (equilibrium value of susceptibility), $\Delta \chi$ (total change of susceptibility), $\tau$ (characteristic relaxation time) and $\beta$ (stretching exponent). The use of other functional forms [7] such as biexponential, inverse logarithmic, and power-law decay prove to be less successful. For example, the power-law decay function gives negative values of the equilibrium value for the linear dielectric susceptibility in the paraelectric phase. The curves that best fit the stretched exponential function at $T_{a} = 469.9$ K are plotted in figure 5 (solid lines). In a short time interval ($t < 100$ s) after interrupting the cooling process, a difference between the fitting function and the experimental data has been observed. Fitting in a long time interval (10 h) provides the extrapolated value of the initial susceptibility at $t = 0$. This value is higher than that observed
immediately after interruption of the cooling process due to susceptibility aging during the cooling process.

The temperature dependence of the initial value, \( \chi_0 = \chi_1(t = 0) = \chi_\infty + \Delta \chi_1 \), the equilibrium linear dielectric susceptibility, \( \chi_\infty \), and the characteristic relaxation time are shown in figure 6. It can be seen (figure 6a) that the peak of the initial susceptibility is higher and sharper than that observed experimentally at the same cooling rate. Such behaviour agrees with the trend shown in figure 2(a). A higher cooling rate results in a decrease in the cooling time; therefore the time of aging during the cooling process is shorter and the linear dielectric susceptibility becomes higher.

Figure 3. Results of pyroelectric measurements carried out on a non-poled SBNN crystal: (a) pyroelectric current, (b) net polarization.
The equilibrium value of the linear dielectric susceptibility is smaller even than that obtained at a cooling rate of 0.12 K min$^{-1}$ (see figure 2a). In practical experiments this equilibrium value is unattainable owing to the very long relaxation time. The shortest estimated value of the relaxation time is 283 s (figure 6b), but above $T_{\text{max}}$ the relaxation time rapidly increases. When the temperature is a few degrees above $T_{\text{max}}$, the estimated value of relaxation time will exceed $10^4$ s. The peak position in the

Figure 4. Linear (a), second-order (b) and third-order (c) nonlinear dielectric susceptibilities obtained during examination of the aging process in the interrupted cooling ramp regime. Curve AB—cooling with rate 2 K min$^{-1}$, BC—isothermal aging at temperature $T_a = 469.9$ K for 10 h, CA—heating of the sample.
temperature dependence of the equilibrium linear dielectric susceptibility appears 5 K above that registered during experiments. However, at this temperature, polarization appears spontaneously in the cooling process (see figure 3b).

Figure 7(a) shows the temperature dependence of the initial and the equilibrium values of the third-order dielectric susceptibility, \( \chi_0 = \chi_3(t = 0) = \chi_\infty + \Delta \chi_3 \) and \( \chi_\infty \), respectively, together with characteristic relaxation time. In comparison with
the linear susceptibility the nonlinear susceptibility experiences much intensive aging. It is clearly indicated from the experimental data that the third-order dielectric susceptibility will eventually vanish. Near $T_{\text{max}}$, the equilibrium value of $\chi_3$ reaches only five per cent of that registered during experiment. The peak temperature of $\chi_3$ agrees with that of $\chi_1$. Taking into account the equilibrium value of the third-order dielectric susceptibility, one can conclude that the strong nonlinearity of the SBNN crystal observed near the phase transition is due to the fact that the crystal is not in

Figure 6. Temperature dependence of the initial, $\chi_0$, equilibrium, $\chi_{\infty}$, and the measured linear dielectric susceptibilities (a) and the characteristic relaxation time of aging of the linear dielectric susceptibility (b) of the SBNN crystal.
its equilibrium state. The temperature dependence of the characteristic relaxation time of aging of $\chi_3$ is similar to that of $\chi_1$, but the estimated value is much smaller. Aging of $\chi_3$ is faster than the aging of $\chi_1$, both in isothermal processes and during continuous cooling. The time dependence of the linear and third-order dielectric susceptibilities can be explained as an evolution effect of the polar nano-regions.

The net polarization of the crystal was monitored by the second-order dielectric susceptibility. An aging of $\chi_2$ is observed both during cooling...
(figure 2b) and at a constant temperature $T_a$ (figure 5b). In contrast with the odd-order dielectric susceptibilities, $\chi_{31}$ changes its sign during the isothermal aging process. The sign change of $\chi_{31}$ results from the change of the direction of net polarization. During the cooling process, more polar regions are formed with polarization pointing ‘down’. This was confirmed by the measurements of pyroelectric effect. At constant temperature, the structure of polar regions evolves with time towards the equilibrium state and the ratio of the ‘down’ to ‘up’ orientated polarization regions also changes with time. After a certain time, the net polarization may vanish when the ‘up’ and ‘down’ polar regions have nearly the same contributions. Consequently, $\chi_{2}$ also becomes zero. The reorientation of polar regions will continue until the equilibrium value of $\chi_{2}$ is reached, which is a small positive value. The possible origin of reorientation and growth of polar regions is due to the presence of an internal bias field.

The change of the second-order dielectric susceptibility, $\Delta \chi_{2}$, during isothermal aging is shown in figure 8. The peak temperature of $\Delta \chi_{2}$ agrees with $T_{\text{max}}$. At this same temperature, maximum aging was observed in both the linear and the third-order dielectric susceptibilities. The observed thermal hysteresis in $T_{\text{max}}$ (figure 1) and in net polarization (figure 3b) indicate that the phase transition in the SBNN crystal is of first order. Moreover, the third-order dielectric susceptibility does not change its sign at the phase transition, i.e. it is positive both in the ferroelectric and paraelectric phases (figure 2c). This kind
of behaviour is a strong indication of a first-order phase transition, as discussed in earlier investigations of strontium–barium–sodium niobate [9].

In conclusion, we have investigated both the linear and nonlinear dielectric susceptibilities of an SBNN crystal with composition near to that of MPB. The main results can be summarized as follows.

- SBNN single crystals exhibit strong dielectric nonlinearity near the phase transition temperature.
- Such strong dielectric nonlinearity of SBNN observed during the cooling process originates from the non-equilibrium nature of the crystal.
- A strong aging effect has been observed in both linear and nonlinear dielectric susceptibilities.
- Net polarization spontaneously and gradually appears during the cooling process in SBNN single crystals.
- The observed aging process is the result of the time evolution of polar regions, including their growth and/or reorientation.
- The phase transition that occurs in SBNN shows many first-order transition signatures.

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References