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# The effect of electrical conductivity on the polarization behavior of the relaxor–ferroelectric $Sr_{0.33}Ba_{0.67}Nb_2O_6$

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**Abstract**

This paper presents a study of the effect of electric field-induced charge carriers on the switching kinetics of a $Sr_{0.33}Ba_{0.67}Nb_2O_6$ crystal. We discuss investigations on the temporal behavior of the electric polarization by means of hysteresis loops and switching current registration. It has been found that the switching kinetics can be approximated by a stretched exponential function, widely used in dielectric relaxation studies. These results prove the existence of random electric fields in a relaxor–ferroelectric $Sr_{0.33}Ba_{0.67}Nb_2O_6$ single crystal.

## 1. Introduction

Strontium barium niobates, SBN ($Sr_xBa_{1-x}Nb_2O_6$, $0.25 \leqslant x \leqslant 0.75$), have promise for use in optics and piezoelectric devices due to their large electro-optical and relatively high nonlinear optical coefficients [1]. Doping SBN with rare-earth or alkali ions improves the properties via a significant increase of the electro-optical coefficients [2]. The controlled manipulation of domain structure via external electric fields is an important factor in many applications. Switching of SBN crystals under electric field pulses revealed specific features of this process related to the relaxor properties of this material, with an open tungsten bronze structure, in which only five of six available positions of $Sr^{2+}$ and $Ba^{2+}$ cations are occupied [3]. These unfilled sites, randomly distributed in each unit cell, create local lattice distortion. Macroscopically these effects appear as non-coincidence of trajectories of hysteresis loops, $D$–$E$, in the course of repeated field cycling [4–6]. This process was accompanied by a considerable decrease in the amplitude of polarization (the so-called fatigue effect). The known instability of its switching parameters with the elapse of time (revealed as the ageing effect) are also related to a specific feature of the switching process. It was detected by various methods and was accounted for by freezing or pinning effects [7–9]. A model based on the assumption of charge disorder giving rise to random fluctuations of the crystalline internal field has been proposed to explain the dielectric relaxation and switching behavior in relaxor–ferroelectric crystals [10].

The concept of random crystalline internal electric fields and their influence on the domain dynamics in relaxor SBN crystals has been widely accepted. Kewitsch *et al* [11] have reported on the optically induced domain reversal when the crystal is illuminated. Granzow *et al* [12] have found that the ageing process of SBN doped with Ce ions was suppressed when the sample was illuminated. It was concluded that external illumination releases the mobile carriers, which compensate the sources of random fields, giving rise to depinning of the domain walls.

The purpose of this work was to study the effect of the field-induced charge carriers on the switching kinetics in SBN ($x = 0.33$; SBN:33). The main reason for this choice is that SBN:33 crystals exhibit a large leakage current, whose contribution to the measured polarization is significant. It is well known that with Sr content increasing, SBN crystals exhibit lower leakage current and higher breakdown voltage [13]. Polarization switching proceeds by nucleation and growth of domains. Two stages of the polarization reversal process: a fast one (on the timescale of milliseconds) and a slow one (which lasts over seconds) can be distinguished in SBN crystals, even under electric fields exceeding the coercive field [14]. The slow switching process was investigated for many ferroelectric crystals by observation of the domain structure by the nematic liquid crystal (NLC) decoration technique. However, the orientational contrast of the NLC for domains in SBN was too weak for observing domains during switching [15]. This paper presents the investigation of the fast switching process in an electric field range exceeding the coercive field. We have investigated the temporal behavior of the polarization by means of hysteresis loop and switching current registration.

## 2. Experimental details

SBN crystals with tetragonal tungsten bronze structure belong to the point group with $4mm$ symmetry at room temperature [3]. Single crystals of SBN were grown by the Czochralski method applying an induction furnace. High purity powders of $SrCO_3$, $BaCO_3$ and $Nb_2O_5$ were used as starting materials and all the components were mixed in a ratio corresponding to composition $Sr_{0.5}Ba_{0.5}Nb_2O_6$. Single crystals were grown in an iridium crucible in a nitrogen and oxygen atmosphere. An oxygen-poor atmosphere affects the oxygen stoichiometry, and significantly reduces the optical quality in the SBN samples. To obtain transparent samples, the SBN crystals were annealed at the temperature 1473 K for 3 h. The transition temperature, defined as the temperature at which the low frequency dielectric constant reaches its maximum, was found to be equal to 389 K [16]. While the melt composition is given by the initial weights, it is difficult to determine the accurate composition in non-congruently grown crystals. The results of the x-ray powder diffraction (XRD) analysis indicated that the parameter $x$ in the $Sr_xBa_{1-x}Nb_2O_6$ formula was shifted to $x = 0.33$ in the crystal. It was found that the crystal had tetragonal structure with lattice cell parameters $a = 12.4826(6)$ Å, $c = 3.9819(4)$ Å, $V = 620.42$, $Z = 5$.

Polarization switching measurements were carried out on a $c$-cut SBN sample (normal to the polar direction) having an electrode area of 0.2 $cm^2$ and a thickness of 0.27 mm. Hysteresis loops were obtained by means of a modified Sawyer–Tower bridge using an ac electric field of 50 Hz. The switching currents were measured by applying square-wave electric pulses amplified with a Kepco bipolar amplifier, model BOP500. The voltage across the 50 Ω resistor, connected in series with the crystal sample, was measured using a digital oscilloscope. The electrical measurement were carried out with air-drying silver paste as the electrodes.

## 3. Results

Microscopic observation of the newly created (in the electric field) domains (observed on the polar surface) revealed that SBN:33 crystals are inhomogeneous; regions may exist that exhibit

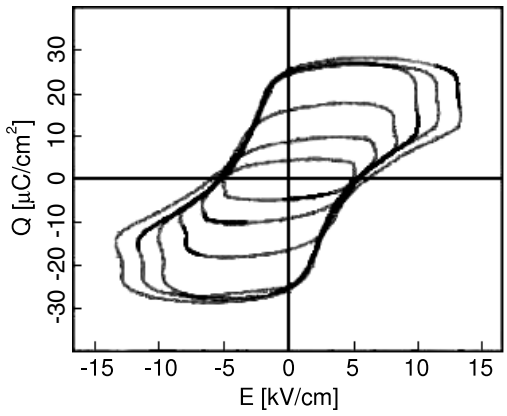


**Figure 1.** Family of hysteresis loops for increasing amplitude of the ac field at frequency of 50 Hz.

switchable polarization (high density of nucleated domains) and there are parts with more fixed polarization in which the nucleation is suppressed. In many crystal samples the observed inhomogeneous distribution of nucleated domains may be liquidated during the annealing of the sample above the Curie temperature. Annealing lowers the threshold nucleation field, which is equal to the static coercive field of the crystal, increases the number of nuclei active in an electric field, and enhances the dynamic mobility of the domain walls. For instance, the value of the coercive field, $E_c$, decreases in a freshly annealed crystal sample by about 20%. However, in freshly annealed crystal samples the switching parameters changed with the elapse of time. The experiments were carried out a few days after the annealing of the sample, so that the domain structure was more stable and the domain structure, in an electric field, changed nearly reproducibly in repeated experiments in the same conditions. Prior to the measurements the sample was electrically de-aged by using a bipolar rectangular pulse train ($\pm 10$ kV cm$^{-1}$ 1 Hz, 100 pulses). The results presented refer to one chosen SBN:33 crystal sample.

### *3.1. Hysteresis loop measurements*

The main characteristic of a ferroelectric is its hysteresis loop (HL), obtained when the crystal sample is switched from one saturated state of polarization to another with an applied electric field. The polarization charges, accumulated on the crystal surface, result from various effects of the crystal bulk, such as changes in the domain structure and leakage currents. The build-up of an electric screening field near the electrodes also affects the switching charges [17]. It is difficult to distinguish between these individual effects by means of hysteresis loop measurements. Figure 1 shows the shape of HL for the SBN crystal sample at various amplitudes of an ac field. The anomalous shape of HL is characteristic for ferroelectric crystal with a large conductivity. At low $E$, HL has a near-square shape relative to $D$–$E$ axes, indicating an abrupt change of the domain orientation. The HL are nearly symmetric; this indicates the lack of a built-in internal field. The coercive field, $E_c$, defined as the field at which half of the polarization is reversed, $E_c = 5 \pm 0.6$ kV cm$^{-1}$, is nearly independent of the ac field amplitude. The switched charge, $Q$, gradually increases with increasing electric field and saturates at $E \approx 11$ kV cm$^{-1}$, with the saturation value of the charge density 26.5 $\mu$C cm$^{-2}$. Similarly, as was observed for homogeneous crystals, the field at which $Q(E)$ tends to saturation was about twice $E_c$. In the SBN crystal sample, the switched charge is controlled not only by the field amplitude, but also by the electric field duration

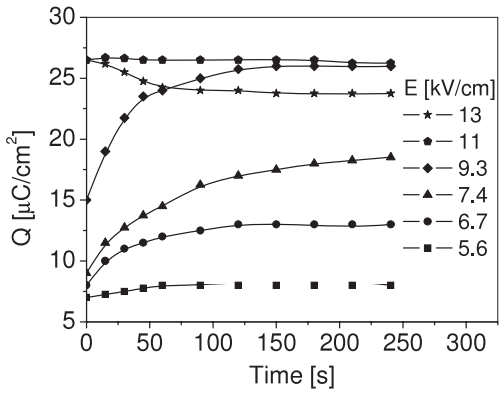


**Figure 2.** The time dependence of the switched polarization from the moment of applying the ac field at frequency 50 Hz.

(the so-called rejuvenation process). The temporal behavior of the switched charge density at various amplitudes of an ac field is shown in figure 2. The amplitude of the polarization, under repeating field cycles, increases with the elapse of time (rejuvenation process). At about 11 kV cm$^{-1}$ the HL comes to saturation and $D$–$E$ loops become reproducible.

The time in which the HL can reach its saturation state depends not only on the magnitude of the ac field, but also on the state of ageing of the sample. The annealing of an aged crystal sample above the Curie temperature or applying a large electric field to overcome the internal field may fully restore the HL of the aged sample to its initial saturation state of polarization. This phenomenon was attributed to depinning of domains that were pinned during the ageing process. This is supported by decreasing of the $E_c$ after rejuvenation.

The so-called fatigue effect, defined as a loss of switchable polarization after repeated HL measurements, which has often been observed during repeated HL measurements on SBN crystals, was insignificant for the pure SBN:33 crystal sample examined. Once the saturation state of the switched charge is attained (at $E \sim 2E_c$), there was observed a small decrease of the HL height due to the fatigue effect. The switched charge value dropped by about 5% after several minutes (i.e. $10^5$ cycles). It is difficult to interpret the polarization switching behavior when both the free and the bound charges are contributing to the measured polarization.

### *3.2. Switching current measurements*

The measured current transients in static electric fields enable a more detailed interpretation of polarization switching than the conventional $D$–$E$ loop method.

- The polarization reversal can occur more completely under a dc field than under an ac field.
- In the HL measurements, crystal samples are often heated by a hysteresis loss. The measurements of $i(t)$ were carried out in a single-pulse mode.

Four square-wave voltage pulses were applied (10 ms wide) as shown in figure 3(a). The switching current response is shown in figure 3(b). To compare the results obtained by the two methods, the width of the pulse was the same as it was for the ac field (at frequency 50 Hz). Provided that the pulse duration exceeds the switching time, the first positive and/or negative pulse will be a switching pulse. The subsequent pulses of the same polarity (non-switching pulses) caused the appearance of dc current only, without domain switching. The crystal sample does not reveal backswitching currents after the switching pulses are completed;

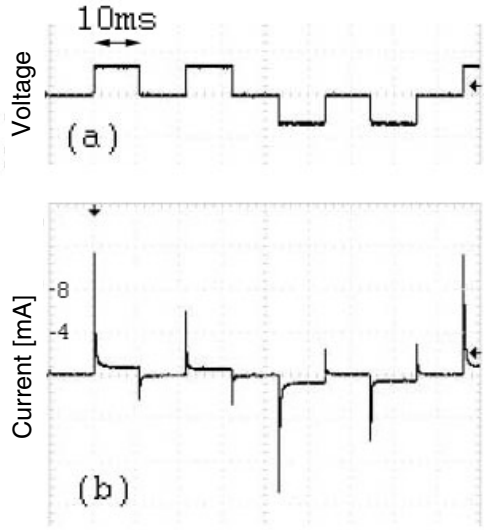


**Figure 3.** Applied voltage pulses (a) and switching current response at $E = 7.4$ kV cm$^{-1}$ and 10 ms pulse duration (b).

we thus confirm the absence of an internal bias field. Moreover, the switched charges calculated under the switching current curves, corresponding to positive and negative voltage pulses, have nearly the same values (within an accuracy of a few per cent) for a given value of an electric field. This additionally confirms the absence of a backswitching process for the SBN:33 sample examined. The data presented in figure 3(b) demonstrate that a leakage current causes a definite contribution to the switching current, seen as a plateau dc current ($i_{\rm dc}$), recorded after a transient current peak. From the current plateau $i_{\rm dc}$, it is possible to estimate the dynamic conductivity, $\sigma$, induced by the applied switching voltage, as $\sigma = i_{\rm dc}\cdot E^{-1}$, where $i_{\rm dc}$ is the dc current density. Figure 4 shows $i_{\rm dc}$–$E$ characteristics of SBN:33 at room temperature. In the low electric field of 7 kV cm$^{-1}$, the current density is of the order of $10^{-3}$ A cm$^{-2}$; thus the dynamic conductivity induced by the applied field is $3 \times 10^{-7}$ $\Omega^{-1}$ cm$^{-1}$. The conductivity measured (with an HP capacitance bridge) at a weak (0.1 kV cm$^{-1}$) ac field at 1 kHz was $4.6 \times 10^{-9}$ $\Omega^{-1}$ cm$^{-1}$, which is two orders of magnitude lower than the dynamic conductivity induced by the applied switching field of 7 kV cm$^{-1}$. The leakage current density increased rapidly as we applied an electric field higher than 12 kV cm$^{-1}$. The dc current density was increased by over one order of magnitude while applying 13 kV cm$^{-1}$. The recorded current $i_{\rm dc}$ represents the conductive current flowing in an external short circuit connecting to switching electrodes. The conductivity is connected with mobile charges, which can move in the SBN lattice along the $c$-axis in structure channels existing in the $P_{\rm s}$ direction. Similar $i_{\rm dc}$–$E$ leakage current characteristics have been reported for SBN ceramic samples [13].

The area under the switching current curves in figure 3(b) is proportional to the amount of the switched charge, and hence to the polarization. The total charge switched during a complete reversal of the polarization is expressed by the formula $Q = \int i\,{\rm d}t = 2P_{\rm s}\cdot S$, where $P_{\rm s}$ is the spontaneous polarization and $S$ is the electrode area [18]. We have subtracted the non-switching current from the switching one and the difference $i(t)$, for various values of $E$, is shown in figure 5. The increase of $E$ from 9.3 to 11.1 kV cm$^{-1}$ causes $i_{\rm max}$ to nearly double, whereas the switching time $t_{\rm s}$ changes insignificantly. It must be noted that when complete switching occurs, $i_{\rm max} \sim 1/t_{\rm s}$. The switching current pulse $i(t)$ provides integral information

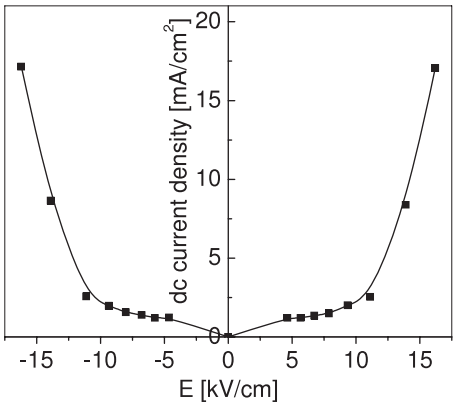


**Figure 4.** Leakage current characteristics of SBN:33 crystal sample at room temperature.

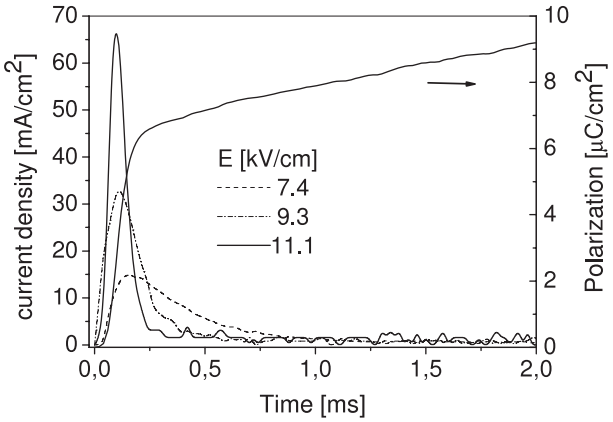


**Figure 5.** Time dependence of the switching current for various amplitudes of the pulse electric field. The switched polarization $P(t)$ is calculated from switching current $i(t)$ at $E = 11.1\ \mathrm{kV\ cm^{-1}}$.

about all randomly polarized regions. One can deduce the details of the kinetics of the domain reversal process by analyzing the shape of the current curve. It is well known that domain reversal process in monodomain crystal sample is accomplished by nucleation, either in the bulk or at the surface, followed by rapid growth across the crystal in the polar direction and subsequent sideways motion of domain walls [18]. In usual homogeneous ferroelectrics the switching process proceeds very slowly under low external fields and is strongly enhanced when approaching the coercive field $E_c$. The fast switching occurs when the applied field is generally of the order of $2E_c$. For such high $E$ the density of nucleated domains may be so large that it nearly prevents the sideways domain wall motion. As a result, one current peak was observed, of several microseconds' duration.

For SBN:33 crystals, unlike homogeneous ones, the kinetics of the polarization switching in a given field $E$ is contributed to by fast and slow (of the order of tens of seconds) components. Thus a slow current tail with a time of many milliseconds is observed even at large fields (twice $E_c$) when the main current peak is of the order of microseconds. One can presume that the main current peak (duration of about 0.2 ms), obtained at $E = 11.1\ \mathrm{kV\ m^{-1}}$, corresponds to domain

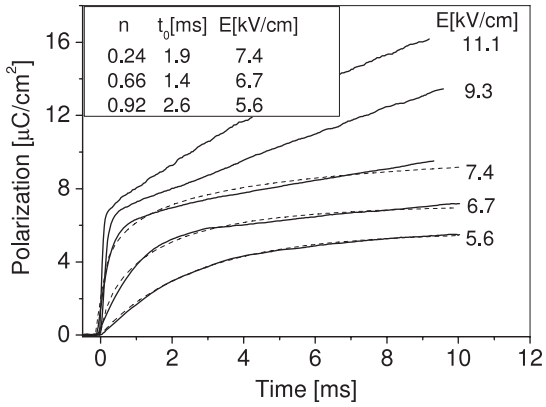


**Figure 6.** Kinetics of polarization switching at various amplitudes of the pulse electric field acquired by integration of the switching current. We convert $i(t)$ to $P(t)$ after non-switching current subtraction.

nucleation and growth in the polar direction, and the subsequent decay to sideways domain wall motion. Thus the switching times of SBN crystal samples exceed by several orders of magnitude the switching times of usual homogeneous ferroelectrics, and may be accounted for by the relaxor origin of SBN crystals.

The rate of polarization switching at constant $E$ can be found from the switching current $i(t)$, by integration of $i(t)$ from $t = 0$ to the instant $t$. The result obtained, for $E = 11.1$ kV m$^{-1}$ and 2 ms pulse duration, is shown in figure 5 and that for the total pulse duration of 10 ms is presented in figure 6. The essential difference of the observed curves $P(t)$ from the case of usual homogeneous crystals is their saturation behavior. For homogeneous crystal, the switching curves taken at different fields, higher than the coercive field, typically saturate at the same value, corresponding to the complete polarization reversal. For the SBN:33 crystal sample examined the saturation value of the switched polarization increases with increase of the electric field, as is shown in figure 6. For low $E < 8$ kV cm$^{-1}$ (small value of the dc current) partial 'freezing' of the polarization is observed. In such cases, the relaxation of the polarization during the switching process is well described by a Kohlrausch, Williams and Watts (KWW) stretched exponential function $P(t) = P_0[1 - \exp(-t/\tau)^n]$ with $0 < n < 1$, widely used in dielectric relaxation studies [19]. The fits are represented by the broken lines in figure 6. The observed partial 'freezing' of the polarization may be explained by the domain wall pinning effect, resulting from a disordered structure of SBN crystal [3]. In higher electric fields (accompanied by a large increase in the dc current as shown in figure 4) the polarization increases with the electric field duration. One can conclude that field-induced charge carriers may compensate the sources of random fields, giving rise to the depinning of the domain walls. This means that the regions of relaxor volume initially frozen are activated and participate in the polarization process. In this case a significant deviation from the stretched exponential law is observed. The total switched charge density $Q(t)$ calculated from $i(t)$ should be equal to twice the spontaneous polarization. As is shown in figure 7 the amount of switching polarization increases distinctly with the electric field strength and attains the value of $17.6 \pm 0.2$ $\mu$C cm$^{-2}$. It must be emphasized that this value of the polarization has been obtained only at the pulse width of 10 ms, when the switching currents were registered in a single-pulse mode. However, the full switching cannot be realized in dc pulse switching at the pulse duration of 10 ms because of the low breakdown field, being near 13 kV cm$^{-1}$. With the increase of the voltage

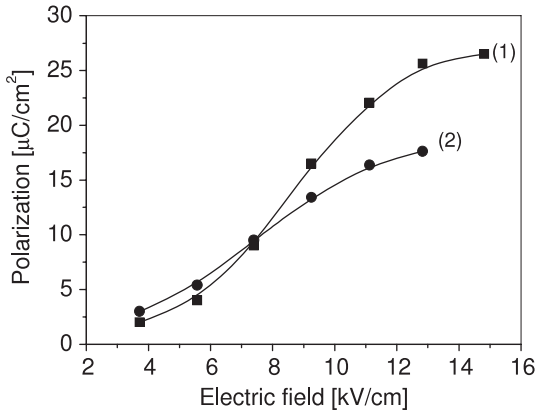


**Figure 7.** Electric field dependence of the switched polarization obtained from the $D$–$E$ hysteresis loop curve (1) and calculated under the switching current curve (after non-switching current subtraction) (2).

pulse width the saturation state of the polarization increases. The total polarization reversal in the SBN:33 crystal sample requires applying fields of the order of tens of seconds (at $E \sim 2E_c$). Thus, unlike for usual homogeneous ferroelectrics, the polarization reversal in SBN:33 crystal can occur more completely under an ac field than under a dc field, at the same pulse amplitude; see figure 7. However, this is only in the case when the switching currents are registered in a single-pulse mode. Similarly to what was observed in hysteresis loop measurements, the switched polarization increases under repeated voltage pulse cycles.

The published results show similar discrepancies of polarizations measured by various techniques. As was reported by Glass [20], the $P_s$ measured by the pulsed field technique was $25 \pm 1$ $\mu$C cm$^{-2}$ for SBN:48. The values of $P_s$ obtained from pyroelectric measurements were about 15% greater than the $P_s$ measured by the pulsed field technique. However observations of HL for SBN:25 yielded a value of $P_s = 30$ $\mu$C cm$^{-2}$ at 300 K; this was close to that obtained for the crystal sample examined, SBN:33. This value is much larger than that measured by other techniques, and is due to the high dielectric loss of the crystal at room temperature. The fact that for SBN crystal the switched charge is controlled not only by the field amplitude but also the pulse duration has great consequences. This should be reflected in the strong pulse width (or frequency) dependence of the pulse switched polarization often observed for relaxor–ferroelectric crystals, as well as SBN ceramics [13]. These results may be consistent with the observed decrease of dielectric constant and dielectric loss with increase of the frequency for SBN crystals [21].

## 4. Discussion

The changes of hysteresis loops taking place for ferroelectric crystals with ac electric fields are mainly observed for doped or irradiated crystals and are attributed usually to crystal structure defects [22]. In such crystals asymmetric hysteresis loops about $D$–$E$ axes have been observed, with a built-in internal bias field, defined as a shift of the hysteresis loop on the $E$ axis. The preferential orientation of the polarization is connected with the site-specific nature of domain nucleation and non-random distribution of domains over the crystal surface [23]. The specific features of the hysteresis loop observed for the crystal sample examined can serve as direct verification of the concept of local random fields existing due to structural disorder of the SBN crystal.

For multidomain SBN:33 crystal a non-biased hysteresis loop has been observed and the newly created (in an electric field) domains are mostly stable after the removal of the poling. This means that the polarities of the defects formed (which stabilize the domain structure during the ageing process) are more or less equally distributed over the crystal volume. So, fluctuations of the random field in SBN crystal bulk are too weak to influence entire domains or produce a macroscopic bias field, but are sufficient to stabilize the domain structure by pinning the domain walls. Such pinning centers are probably due to the charge disorder inherent to relaxor SBN [10].

For SBN:33 the domain walls can only be pinned in low external electric fields (partial freezing of the polarization as shown in figure 6). In a large $E$, the total current, the sum of the leakage current and the switching current, is high enough to compensate internal charges acting as pinning centers. This may be confirmed by the lack of a fatigue effect for SBN:33 crystal. It is generally agreed that defects, inhomogeneities, which retard the nucleation of reversed domains and pin the domain walls, are responsible for the fatigue effect [24].

The time dependence of the electric polarization is a further indication of a random-field model. The relaxation of the polarization is well described using a KWW function, often observed for a wide class of disordered systems (dielectric relaxation in glassy and polymeric materials, magnetic relaxation, relaxation of the localized electronic structures). This has been discussed in terms of models where individual elements relax independently with an appropriate wide distribution of relaxation times [19]. Therefore, the observed $P(t)$ behavior results from a superposition of many different relaxation times of relaxing domains. The spectra of the relaxation time distribution can be drawn from the experimental data, as was reported by Gladkii *et al* [4].

It must be noted that exactly the same stretched exponential relaxation polarization law was found for SBN:61 doped with cerium, by observation of nanodomains using piezoelectric force microscopy [25]. The evolution of natural and written domains revealed a very slow relaxation (of the order of minutes) into a depolarized multicluster state, and could be interpreted through the interaction between domain walls and strong pinning forces, due to the quenched random fields. The resulting polydispersivity was reflected by the small value of the stretched exponential exponent $n = 0.45$. Similarly, the same slow kinetics of relaxation was reported for a prototype relaxor $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) from field-induced linear birefringence measurements [26] and pyroelectric current measurements [27]. Remarkably, an extremely slow relaxation process (of the order of minutes or up to an hour) has been reported for a relaxor $KTaO_3$ doped with Li ions, using an optical second-harmonic generation (SHG) microscope [28]. The time evolution of the SH intensity in the low field region has been approximated using the stretched exponential law. However, the exponent determined, $n$, changed from 0.5 below the transition temperature to about 4 at lower temperature, suggesting a much more complex relaxation process in the low temperature region.

## 5. Conclusions

Our results showed that the reorientation of the polarization in SBN:33 crystal is strongly affected by a random-field environment. The fluctuations of random fields do not influence entire domains or form a macroscopic bias field, but act as pinning centers for the domain walls. The internal charge carriers are compensated by field-induced charge carriers, greatly reducing the ageing of the hysteresis loop and preventing the fatigue effect. We have shown that SBN:33 crystal exhibits a high electrical conductivity which affects the switching properties at room temperature and may be responsible for the instability of its parameters.

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