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Probing polar nanoregions in $Sr_{0.61}Ba_{0.39}Nb_2O_6$ via second-harmonic dielectric response

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The dielectric susceptibility of pure and chromium-doped $Sr_{0.61}Ba_{0.39}Nb_2O_6$ single crystals reveals an appreciable second-harmonic component χ_2 along with the usual first- and third-order ones, χ_1 and χ_3. It is attributed to irreversible prepoling due to trapping of mobile charge carriers in the first half-cycle of the *ac* probing field. In agreement with predictions for a biased ferroelectric phase transition, the second- and third-order nonlinearity coefficients are observed to minimize at the transition temperature T_c.

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Relaxor ferroelectric materials include a large group of solid solutions with a perovskite or tungsten bronze structure. In contrast to ordinary ferroelectrics,[1] relaxors possess the following main features: (i) a significant frequency dependence of the electric permittivity, (ii) absence of both spontaneous polarization and structural macroscopic symmetry breaking, and (iii) ferroelectriclike response arising after field cooling to low temperature.[2] The archetypical perovskitelike lead-containing relaxor $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) system is known for nearly 50 years.[3]

In contrast to the cubic family related to PMN, the polarization, as an order parameter, of the strontium-barium niobate $Sr_xBa_{1-x}Nb_2O_6$ (SBN) family is a single-component vector directed along the tetragonal *c* direction, which drives the symmetry point group from $4/mmm$ to $4mm$ at the phase transition into the polar phase at low *T*.[4] Since SBN is tetragonal on the average, it belongs to the Ising model universality class rather than to the Heisenberg one as proposed for PMN-like systems.[5] Assuming the presence of quenched random fields (RF's), theory predicts the existence of a phase transition into long-range order within the RF Ising model (RFIM) universality class[6] preceded by giant critical slowing down above T_c.[7,8] Only recently, the SBN system has been found to fulfill the above necessary conditions[9] and the ferroic RFIM seems to be materialized at last.[10]

The appearance of fluctuating polar precursor clusters at temperatures $T>T_c$, which is widely accepted to be at the origin of the unusual relaxor behavior,[2,11] can be considered in a natural way as the primary signature of the polar RFIM in its fluctuation regime.[10] Acting as precursors of the spontaneous polarization, which is expected to occur below T_c, the polar clusters have been evidenced in various zero-field-cooling (ZFC) experiments comprising linear birefringence,[2,12] linear susceptibility,[13] and dynamic[14] and Brillouin light scattering.[15] After freezing into a metastable domain state at $T<T_c$, the clusters were also directly observed using high resolution piezoresponse force microscopy.[16]

A very sensitive probe of the precursor clusters is provided by optical second-harmonic (SH) generation. Although the global inversion symmetry is not broken in the paraelectric regime at $T>T_c$, an incoherent superposition of SH intensity is clearly observed up to $T\approx 1.1T_c$.[17] This principle is not applicable to low-frequency dielectric spectroscopy, where polarization waves are excited coherently. Here the superimposed SH of uncorrelated clusters are expected to interfere destructively. Hence, the dielectric second-order susceptibility χ_2 should vanish in the absence of a net polarization.[18] Surprisingly, however, this simple symmetry requirement does not seem to hold in relaxors like SBN, where an unexpectedly large SH susceptibility response is observed in the paraelectric phase. It will be shown that this phenomenon sheds some light on the nonergodic nature of the precursor cluster state and on the irreversibility of the initial poling process in a virgin sample of SBN.

Large and clear optical quality single crystals of congruently melting pure and 0.36 mole % Cr_3O_4 doped $Sr_{0.61}Ba_{0.39}Nb_2O_6$ (SBN61) were grown by the Czochralski technique. Platelet-shaped samples with typical dimensions $6\times6\times0.5$ mm^3 were cut with the polar *c*-axis normal to the large plane and polished to optical quality. In order to erase the memory of any poling history and to enhance the relaxor properties,[19] the samples were annealed without electrodes at $T=893$ K for 2 h and then slowly zero-field cooled to room temperature at a cooling rate of $\dot{T}=-4$ mK/s. Vacuum deposition of copper and subsequent gold films was used to cover the major faces with electrodes. Prior to each measurement carried out on cooling, the samples were refreshed at 420 K for 1 h in order to warrant identical conditions for all measurements and in order to eliminate possible memory effects of all previous treatments.

Two types of measurements have been carried out. First, the linear susceptibility was measured using a Solartron 1260 impedance analyzer with a 1296 dielectric interface in the frequency range of $10^{-2}\leqslant f\leqslant 10^2$ Hz using a weak probing *ac* electric field with amplitude $E_0=200$ V/m. Second, the linear and nonlinear components of the electric susceptibility which appear in the expansion of the polarization *P* with respect to the electric field *E* referring to the polar *c* axis,[18]

$$P=\epsilon_0(\chi_1E+\chi_2E^2-\chi_3E^3\pm\cdots), \qquad (1)$$

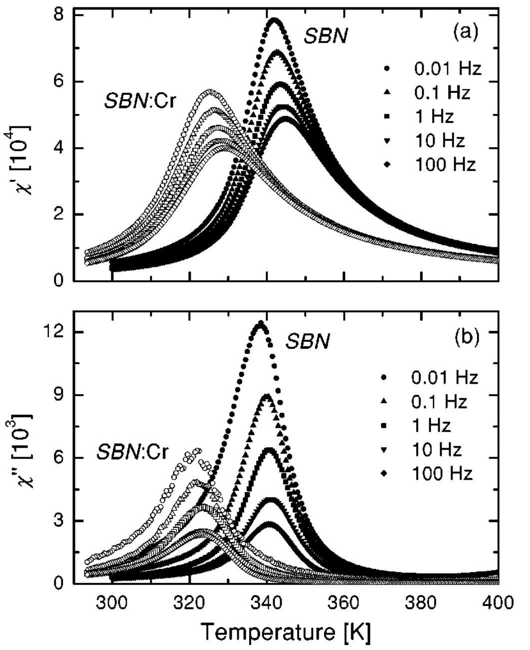

FIG. 1. Temperature dependences of the real (a) and the imaginary part (b) of the linear dielectric susceptibility of SBN61 and SBN61:0.36% Cr taken on ZFC in the frequency range of $10^{-2} \leqslant f \leqslant 10^{2}$ Hz at an oscillation level $E_0 = 200$ V/m.

were measured simultaneously at several selected frequencies between 1 Hz and 10 kHz. This procedure significantly reduces noise in the subsequent computation of the relevant nonlinearity coefficients. Here χ_1, χ_2, and χ_3 are the first-, second-, and third-order susceptibilities, respectively. Two basically different set-ups have been used in our experiments. In "setup 1" the pure SBN61 sample was connected to a low-loss standard capacitor in series, and the voltage across the standard capacitor was picked up and analyzed by using a HP35665 A Dynamic Signal Analyzer. In "set-up 2" the chromium doped SBN61 sample was connected to a low-noise current preamplifier SR570 (Stanford Research Systems) in series, and the displacement current thus obtained was elaborated by a computer using fast Fourier transformation. A probing field as low as $E_0 = 15$ kV/m was chosen for all nonlinear experiments in order to avoid contributions of higher than third order in Eq. (1), and the cooling rates were typically $\dot{T} = -1$ mK/s for all kind of measurements.

Linear susceptibility data measured on cooling in the sub-Hertz and Hertz limit are presented in Fig. 1. At a first glance one notices differences in the peak temperatures of the susceptibility of both the real [Fig. 1(a)] and the imaginary [Fig. 1(b)] parts for pure and Cr-doped SBN61, respectively. The observed shifts are due to the increase of quenched charge disorder[10] owing to the replacement of Nb^{5+} by Cr^{3+}. Closer inspection shows that both samples display large frequency dispersion in the ordered ferroelectric state. Remarkably, the losses [Fig. 1(b)] increase with decreasing frequency, thus demonstrating a new dispersion region ascribed to a domain-wall contribution to the dielectric response.[20] It is observed to survive in the paraelectric phase, thus indicating the presence of slowly relaxing polar regions. This particular behavior of the susceptibility is absent in the case of the prototypical PMN system.[1]

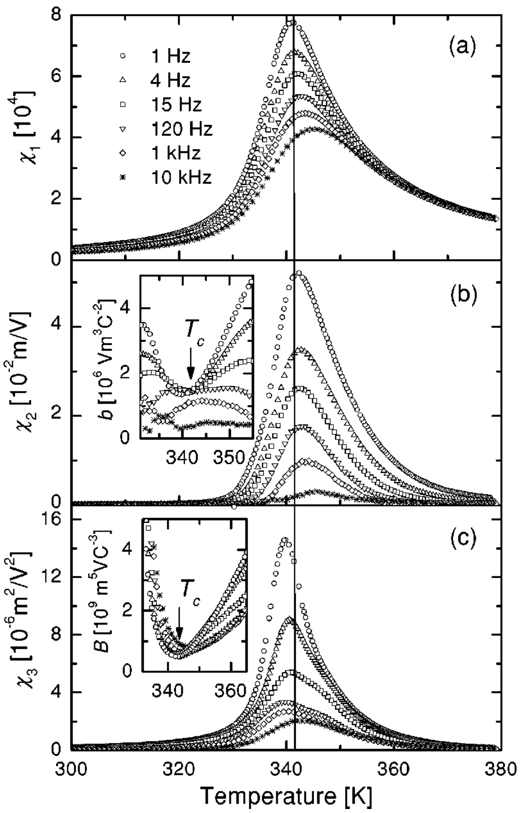

FIG. 2. Temperature dependences of the electric susceptibilities χ_1 (a), χ_2 (b), and χ_3 (c) taken on ZFC on a pure SBN61 single crystal. The insets to (b) and (c) display the temperature dependences of the appropriate nonlinearity coefficients b and B, respectively; (a) indicates the frequencies within the range $10^{0} \leqslant f \leqslant 10^{4}$ Hz and applies to (b) and (c) as well.

Figure 2 presents temperature dependences of the electric susceptibilities χ_1 (a), χ_2 (b), and χ_3 (c) taken on ZFC in the frequency range of $10^{0} \leqslant f \leqslant 10^{4}$ Hz using setup 1. In addition to already published results on χ_1 and χ_3 (Ref. 13), the second-harmonic response in dielectric susceptibility is unexpectedly large [Fig. 2(b)]. In contrast to χ_1 and χ_3, the peaks of χ_2 are strongly asymmetric relative to the peak temperature T_{m}. The SH susceptibility is much more significant in the paraelectric part of the curve than in the ferroelectric one. Similar results were obtained on the SBN61:Cr sample by using setup 2. As shown in Fig. 3, the relative peak heights $(\chi_2/\chi_1)[T_m]$ are four times larger than those observed on pure SBN (Fig. 2). This is a clear hint at the relaxor typical precursor clusters, which are more active in the doped than in pure SBN61 owing to the enhanced concentration of pinning centers.

In order to explain the occurrence of a SH susceptibility in the paraelectric regime, $T > T_c$, globally broken inversion symmetry has to be verified. We have to stress that any memory of previous poling procedures was erased in the samples used in this study by an initial annealing at high temperatures, $T = 893$ K. It is well known that strong repoling occurs in SBN61 and SBN61:Cr on cooling, if the

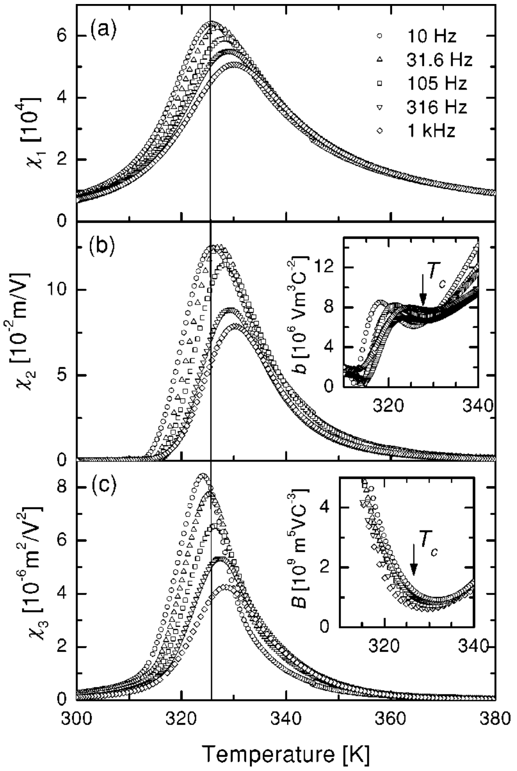

FIG. 3. Same as in Fig. 2, while replacing SBN61 by SBN61:0.36% Cr.

samples were annealed at a temperature no higher than about T_c+100 K.[21] In order to exclude this "trivial" source of symmetry breaking, complete absence of the pyroelectric current was confirmed upon reheating in the case of the SBN61:Cr sample. Hence, the situation encountered here rather involves the nonergodic dynamics of the polar precursor clusters in the vicinity of T_c. Its presence is clearly indicated by the appearance of hysteresis in periodic P vs E cycles and of dielectric losses, χ'' vs T, above T_c [Fig. 1(b)]. Remarkably, both χ'' [Fig. 1(b)] and χ_2 [Figs. 2(b) and 3(b)] increase in a very similar way as the frequency decreases. Obviously, both the phase shift between polarization and field, i.e. χ'', and the symmetry-breaking internal polarization, i.e., χ_2, are based on similar slow processes.

It is well known[20] that the linear dielectric response of SBN is strongly determined by domain wall ($T<T_c$) and cluster surface pinning ($T>T_c$), respectively, due to quenched RF's. It gives rise to a conduction-type response $\chi''\propto f^{-\beta}$ with $\beta<1$. On the other hand, the field-induced domain wall and cluster surface motions, respectively, have a retroactive effect onto the charge distribution in the crystal. While the ionic charges are not displaced at moderate temperatures $T\approx T_c$, a redistribution of the mobile charge carriers inherent to SBN is known to take place upon poling.[22] Let us now assume that the very first half-cycle of the external field activates the motion of free charges and that a certain percentage of these carriers becomes trapped in deep local potential wells. As a consequence, a new internal field distribution arises, which biases the *ac* field in forthcoming periods. It should be noticed that a similar *first half-cycle* process was proposed to explain a dielectric second-harmonic response in the dipolar glass $\mathrm{KTa}_{1-x}\mathrm{Nb}_x\mathrm{O}_3$ ($x=0.009$).[23] Similarly, Taylor and Damjanovic observed that the state of a thin film of $\mathrm{Pb(Zr,Ti)O_3}$ is severely modified during the first dielectric hysteresis cycles while increasing the field amplitude E_0.[24] Hence, odd harmonics may arise in the lattice potential, which enable spurious dielectric second-harmonic generation (SHG).[25]

Under this field the mobile polar clusters are partially ordered, forming a net polarization P_0 of the sample, and give rise to the second-harmonic polarization response. The abrupt decrease of χ_2 in the ordered state at $T\approx T_\mathrm{c}-10$ K [Figs. 2(b) and 3(b)] is due to the onset of spontaneous polarization with a multitude of up- and down-oriented ferroelectric domains. They gradually make the system macroscopically centrosymmetriclike. The mobile polar clusters are freezing into a metastable domain state and thus lose their dynamic properties. The *dc* field produced by the trapped charges, however, is not strong enough to overcome the coercive field. That is why it cannot produce any poled state, and the second-harmonic component in the polarization response virtually vanishes in the ferroelectric state.

The empirical equation (1) can be deduced from a free-energy expansion

$$\tilde{F}(\tilde{P})=\frac{1}{2}\tilde{A}\tilde{P}^2+\frac{1}{4}\tilde{B}\tilde{P}^4-\tilde{E}\tilde{P}, \tag{2}$$

where $\tilde{A}=\tilde{\alpha}(T/T_\mathrm{c}-1)$ with $\tilde{\alpha}>0$ and $\tilde{B}>0$ are the usual coefficients referring to even powers of the scalar order parameter $\tilde{P}$, and $\tilde{E}$ is the apparent electrical field. Now we assume that the system is polarized by an internal bias polarization P_0. Then any change of the free energy is determined by the shifted variable $P=\tilde{P}-P_0$. Insertion into Eq. (2) yields the modified free energy

$$\begin{aligned}F(P)&=\frac{1}{2}\tilde{A}(P+P_0)^2+\frac{1}{4}\tilde{B}(P+P_0)^4-\tilde{E}(P+P_0)\\&=F_0+aP+\frac{1}{2}AP^2+\frac{1}{3}bP^3+\frac{1}{4}BP^4-\tilde{E}P,\end{aligned} \tag{3}$$

where $F_0=\frac{1}{2}\tilde{A}P_0^2+\frac{1}{4}\tilde{B}P_0^4-\tilde{E}P_0$, $a=\tilde{A}P_0+\tilde{B}P_0^3$, $A=\tilde{A}+3\tilde{B}P_0^2$, $b=3\tilde{B}P_0$, and $B=\tilde{B}$. Apart from the modified second-order coefficient A and a shift of the equilibrium by $F(0)=F_0$, the appearance of odd order coefficients, a and b, is noticed. The equilibrium condition $(\partial F/\partial P)_{\tilde{E}}=0$ then yields the equation of state $\tilde{E}=a+AP+bP^2+BP^3$, where $a=\tilde{E}(P=0)$ is the internal field. Hence we obtain the modified equation of state involving the external electric field $E=\tilde{E}-\tilde{E}(P=0)$ in the form

$$E=AP+bP^2+BP^3, \tag{4}$$

which can be inverted into Eq. (1) by assuming that Eq. (4) represents the beginning of a converging infinite series expansion. The coefficients appearing in Eq. (4) are easily shown to be given by $A=(\varepsilon_0\chi_1)^{-1}$, $b=-\varepsilon_0^{-2}\chi_2\chi_1^{-3}$, and $B=\varepsilon_0^{-3}\chi_1^{-5}(\chi_1\chi_3+2\chi_2^2)$, where χ_1, χ_2 and χ_3 are the experimentally determined linear and nonlinear susceptibilities as given by Eq. (1). While the second term in the coefficient B is only a small correction with respect to that already published,[13] a novel SH coefficient b is recognized to occur in the paraelectric state of SBN.

The insets to Figs. 2(b,c) and 3(b,c) show the temperature dependences of the two non-linearity coefficients b and B, respectively, in the vicinity of the phase transition point. It is well known[26] that the behavior of the nonlinear polarization response is a key issue distinguishing between long-range ferroic order and dipolar glass behavior. As discussed previously,[13] the appearance of a minimum of B at T_c is a clear hint at the ferroelectric nature of the relaxor transition in SBN and rules out a glassy scenario like that applied to PMN.[27] Remarkably, the novel coefficient b also minimizes at T_c, thus corroborating the predicted proportionality between b and B [Eq. (3)]. It remains to be shown that b is also proportional to the background polarization $P_0 = b/3B$, which turns out to be roughly constant at $T > T_c$ and in the order 10^{-3} Cm^{-2} when inserting the experimental data of b and B [Figs. 2(b,c) and 3(b,c)]. Preliminary pyroelectric current measurements being capable of resolving $\delta P \approx 10^{-4}$ C/m^2 did not show, within errors, any release of charges when heating the sample up to $T_c + 100$ K. This seems to indicate an anomalous temperature stability of P_0, which might be explained by the immobilization of the field-inducing charge carriers in their deep trapping levels.

In summary, large SH contributions to the dielectric susceptibility of SBN61 and SBN61:Cr have been observed after high-temperature depoling and ZFC. They are proposed to originate from a bias polarization arising after applying the *ac* probing field by deep level trapping of mobile charge carriers. Very probably similar mechanisms may apply also to other systems with dielectric SH generation of hitherto unknown origin (e.g., D-BP-BPI, where specific properties of an underlying three-state Potts model were invoked,[28] and SBN61, where the appearance of dielectric SHG was directly interpreted to signify the existence of polar clusters[29]).

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