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Non-Debye domain-wall-induced dielectric response in $Sr_{0.61-x}Ce_xBa_{0.39}Nb_2O_6$

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Two different non-Debye dielectric spectra are observed in a polydomain relaxor-ferroelectric $Sr_{0.61-x}Ba_{0.39}Nb_2O_6:Ce_x^{3+}$ single crystal in the vicinity of its transition temperature, $T_c \approx 320$ K. At infralow frequencies the susceptibility varies as $\chi^* \propto \omega^{-\beta}$, $\beta \approx 0.2$, and is attributed to an irreversible creep-like viscous motion of domain walls, while logarithmic dispersion due to reversible wall relaxation [T. Nattermann, Y. Shapir, and I. Vilfan, Phys. Rev. B **42**, 8577 (1990)] occurs at larger ω.

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One of the characteristic properties of ferroelectric crystals is their domain structure, which is well known to crucially determine some of their primary properties.[1] In particular, the domains have a considerable influence on the value of the complex dielectric susceptibility, $\chi^* = \chi' - i\chi''$, and related quantities.[2–4] Owing to its mesoscopic character the domain wall susceptibility $\Delta\chi_w^*$ strongly reflects the structural properties of the crystal lattice. This has become manifest, e.g., by the polydispersive behavior of χ^* in the ferroelectric multidomain phase of KH_2PO_4.[5,6]

In this crystal recently a non-Debye-type contribution to $\Delta\chi_w^*$ was discovered,[7] which bears many of the properties predicted by Nattermann *et al.*[8] In ferroics (ferromagnets or ferroelectrics) with quenched disorder $\Delta\chi_w^*$ is expected to vary as

$$\Delta\chi_w^* \propto \ln(1/\omega\tau_0)^{2/\Theta}/(1+i\omega\tau) \tag{1}$$

involving the angular frequency $\omega = 2\pi f$, microscopic relaxation times τ and $\tau_0 < \tau$ and the roughness exponent $\Theta \approx 0.83$ in $D=3$ dimensions. This law predicts a logarithmic decrease of χ' and a linear increase of χ'' at low frequencies, $\omega \ll 1/\tau$, followed by a Debye-type cutoff at $\omega > 1/\tau$. To our knowledge, both of these low-f characteristics have hitherto been observed only in KH_2PO_4 (after subtraction of several Debye-type components of unknown origin).[7] Hence, the $\ln(1/f)$ law still seems to be a rare and—sometimes—disputable event.[9] Surprisingly, an alternative low-f behavior has recently been reported on a relaxor-type single crystal of $PbFe_{1/2}Nb_{1/2}O_3$.[10] It exhibits a power-law behavior, χ', $\chi'' \propto \omega^{-\beta}$, where the decrease of χ'' with increasing ω strongly contrasts with the increase predicted by Eq. (1).

In this paper we show that these two different non-Debye responses—the irreversible and the previously described[8] reversible one—actually refer to different frequency regimes and represent complementary relaxation processes. We have measured the low-f dispersion of the uniaxial relaxor crystal $Sr_{0.61-x}Ce_xBa_{0.39}Nb_2O_6:Ce_x^{3+}$ (*SBN*:Ce,$x=0.0066$) in the vicinity of its ferroelectric transition temperature, $T_c = 320$ K, where it shows both characteristics in adjacent frequency regimes. While the $\ln(1/f)$ characteristic applies to "high" frequencies, $f > 100$ Hz, the alternative $\omega^{-\beta}$ dependence is observed in the "low"-f regime, $f < 1$ Hz. In order to understand the latter behavior, we introduce polydispersivity via a broad distribution of wall mobilities, μ_w, which describe the viscous motion of the walls[11] in the creep regime,[12] where they overcome a large number of potential walls due to a high density of pinning defects. As a characteristic of irreversibility the walls stop when switching off the field.[13] Within this concept the rapid individual Debye-type relaxation processes are averaged out on the long-time scale of a creep experiment.

SBN:Ce is known to be a random-field Ising-type ferroelectric relaxor,[14] which freezes into a nanodomain state[15] when cooling to below $T_c \approx 320$ K ($x_{Ce} = 0.0066$) in the absence of an external electric field. Dielectric response data were taken on a Czochralski-grown very pure crystal (size $0.5\times5\times5$ mm^3) with probing electric-field amplitudes of 200 V/m applied along the polar c axis. A wide frequency range, $10^{-5} < f < 10^6$ Hz, was supplied by a Solartron 1260 impedance analyzer with a 1296 dielectric interface. Different temperatures were chosen both below and above T_c and stabilized to within ± 0.01 K.

Figure 1 shows representative data of χ' (curve 1) and χ'' vs f (curve 2) taken at $T = 294$ K which illustrate the main features of the dielectric dispersion of zero-field-cooled (ZFC) *SBN*:Ce: (i) the dielectric response strongly increases below $f_{\min} \approx 25$ Hz (marked by the dotted line); (ii) neither saturation of χ' nor a peak of χ'' is observed in the infralow-frequency limit, where (iii) the magnitude of χ'' exceeds that of χ' by one order of magnitude [$\chi''(10\ \mu\text{Hz}) \simeq 1.9\times10^5$]; (iv) a plot of χ'' vs χ' is characterized by a positive curvature at frequencies $f < f_{\min}$ (Fig. 1; inset), which is opposite to the conventional Debye-type one; (v) at higher frequencies, $f > f_{\min}$, χ'' increases again in a power-law-like fashion (straight line in a log-log presentation), while χ' changes its curvature and gently bends down.

The dominating domain-wall nature of the response shown by curves 1 and 2 in Fig. 1 is evidenced by its drastic reduction when poling the sample with $E = 350$ kV/m from above T_c into a near-single domain state (curves 1′ and 2′). At a closer look it can be seen that still some response survives in the field-cooled (FC) state due to a remnant network

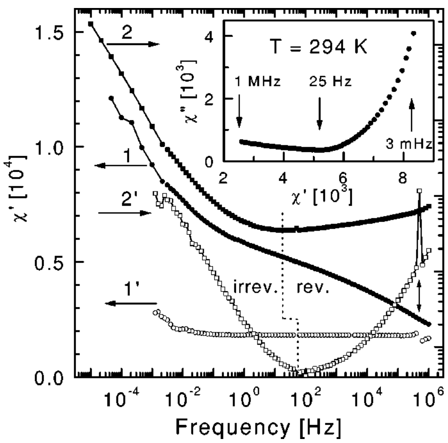

FIG. 1. Dielectric spectra of χ' and χ'' vs f of unpoled (curves 1 and 2) and poled (curves $1'$ and $2'$) SBN:Ce taken at $T=294$ K. Solid lines are guides to the eye and the vertical dotted line separates different response regimes. A piezoelectric anomaly at $f=0.5$ MHz is marked by a double arrow. The inset shows χ'' vs χ'.

of domain walls. The log-log presentation of χ'' reveals, despite the decrease by two orders of magnitude, that we still encounter the characteristics mentioned above: a symmetric increase on both sides of $f_{\min}\approx 65$ Hz (dotted line), which becomes power-law-like in the asymptotic low- and high-f regimes, respectively. An enlarged view of curve $1'$ (not shown) reveals an f dependence similar to that of curve 1, albeit diminished by at least one order of magnitude. Interestingly, a sharp piezoelectric resonance of both χ' and χ'' is observed at $f\approx 0.5$ MHz after poling. This is another tribute to the near-single domain state, which activates a piezoelectric resonance.

Let us first discuss the high-f response of both the ZFC and the FC states, which confirms many of the characteristics predicted by Eq. (1). Inspection shows that χ' decreases linearly on a linear-log scale prior to the steeper decrease at $f>10^4$ Hz, while χ'' obeys linearity on a log-log scale. Clearly, the ω prefactor strongly suppresses χ'' close to $f_{\min}$ when compared with χ'. Upon increasing f the same factor determines the positive curvature of χ'' despite the competing $\ln(1/f)$ contribution (best seen in curve $2'$). Simultaneously, χ' is bent down in a dispersion steplike fashion.

The low-f data in Fig. 1 can neither be described by a monodispersive Debye-type formalism nor by the polydispersive one, which is based on the relaxation of elastically pinned domains.[8] Satisfactory fits were obtained only when using an equation, which was empirically introduced by Park,[10] and which we complete by a conduction term,

$$\chi^{*}=\chi_{\infty}(1+1/(i\omega\tau_{eff})^{\beta})-i\sigma/\varepsilon_{0}\omega. \tag{2}$$

Here χ_∞ is the high-frequency limit of the complex susceptibility χ^*, while τ_{eff}, β, and σ are an effective relaxation time, a polydispersivity exponent, and the electric conductivity, respectively. Equation (2), which will be derived below, can be decomposed into

$$\chi'=\chi_{\infty}(1+\cos(\beta\pi/2)/(\omega\tau_{eff})^{\beta}), \tag{3}$$

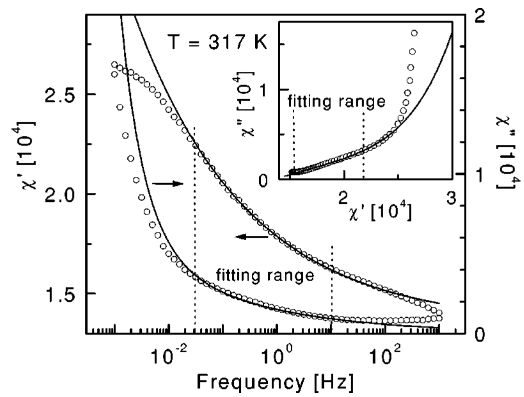

FIG. 2. Dielectric spectra of χ' and χ'' vs f of unpoled SBN:Ce taken at $T=317$ K and calculated (solid lines) with fitting parameters, which originate from best fits of χ'' vs χ' to Eqs. (3) and (4) (inset; solid line) within the range indicated by dotted lines.

$$\chi''=\chi_{\infty}\sin(\beta\pi/2)/(\omega\tau_{eff})^{\beta}+\sigma/\varepsilon_{0}\omega, \tag{4}$$

which are exemplarily fitted in Fig. 2 to a data set taken at $T=317$ K. The fitting parameters, $\chi_\infty=13\,200\pm 100$, $\tau_{eff}=29\pm 1$ s, $\beta=0.21\pm 0.01$, and $\sigma=(1.0\pm 0.2)\times 10^{-9}$ $(\Omega\ \mathrm{m})^{-1}$, have been evaluated from the χ'' vs χ' data within the range $0.3\leqslant f\leqslant 10$ Hz, which is chosen to lie between the bending point of χ' and the minimum of χ'' at low and high frequencies, respectively (inset, dotted lines; see discussion below), and then used to calculate χ'' and χ' vs f (solid lines). Within the fitting range the latter curves fit satisfactorily with the experimental data except for a small unexplained peak of χ'' at central frequencies (a similar bump marked by an arrow appears in Fig. 3). All the attributes of the low-f data as outlined above are met.

Systematic deviations are found at both sides of the fitting interval. At very low frequencies (Fig. 2) the experimental data fall below the calculated ones. This is probably due to aging of the domain state[16] as a tribute to the extremely long-time spans required for the very low-f runs (e.g., one

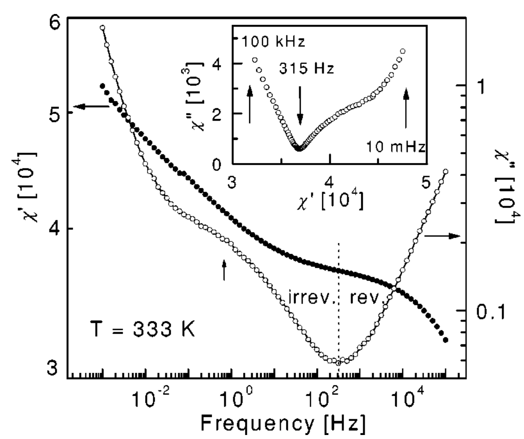

FIG. 3. Dielectric spectra of χ' and χ'' vs f of unpoled SBN:Ce taken at $T=333$ K. Solid lines are guides to eye, while the vertical dotted line separates different response regimes. An unexplained small anomaly of χ'' is marked by a vertical arrow.

individual measurement at $f=10^{-5}$ Hz takes almost 28 h). As a rule, aging manifests itself in a decrease of both susceptibility components.[17]

At "high" frequencies, $f>f_{\min}=10$–300 Hz ($f_{\min}$ is increasing with T), the dispersion law, Eq. (2), ceases to apply because of the onset of reversible polydispersive domain-wall relaxation. As discussed above, a monotonic increase of χ'' and a $\ln(1/f)$ decrease of χ' with a steplike cutoff are encountered, again. These features are even more pronounced at $T=333$ K (Fig. 3), where the reversible domain-wall response[8] extends from about 300 to 10^6 Hz with a dispersion step centered at $f\approx 10^5$ Hz. It should be noticed that these data refer to the paraelectric relaxor state of SBN:Ce, where the response is due to cluster surfaces rather than to domain-walls.[16]

While the high-frequency dispersion regime is attributed to polarization processes due to the reversible motion of domain-walls (and their segments) experiencing restoring forces, viz., relaxation,[8] the low-frequency response is due to the irreversible viscous motion of domain-walls. They experience memory-erasing friction by averaging over numerous pinning centers in a creep process.[11,12] The latter type of motion becomes possible for at least two reasons: screening of depolarization fields by free charges in the bulk or at the surface[18] and/or pinning of the domain-walls at quenched random fields, which is believed to be due to quenched charge disorder in the special case of SBN:Ce.[14–16]

Dielectric domain response under the action of an external electric field is readily modeled by considering the average polarization, $P(t)=(2P_s/d)x(t)$, of a regular stripe domain pattern of up and down polarized regions carrying spontaneous polarization, $\pm P_s$, and having an average width d. It arises from a sideways motion of walls perpendicular to the field direction, x. Starting with $P(0)=0$ at $x(0)=0$, the favorable domains enhance their total width by an amount $2x$ until reaching (in principle) the limit $P=P_s$ when $x\rightarrow d/2$. By assuming viscous motion of the walls[11] one obtains the rate equation

$$\dot{P}(t)=(2P_s/d)\mu_w E(t), \tag{5}$$

where the wall velocity $\dot{x}(t)=\mu_w E(t)$ involves the wall mobility μ_w and the driving field $E(t)$. Assuming constant mobility at sufficiently weak fields and disregarding the depinning threshold[11,12] one finds a linear time dependence of the polarization in a constant field, $P(t)=(2\mu_w P_s/d)Et$, while a harmonic time dependence, $E(t)=E_0\exp(i\omega t)$, yields

$$P(t)=[(2\mu_w P_s/i\omega\varepsilon_0 d)+\chi_\infty]\varepsilon_0 E_0\exp(i\omega t). \tag{6}$$

Here the second term refers to "instantaneous" response processes due to reversible domain-wall rearrangements occurring on shorter-time scales (see above).

The above relations are expected to hold in the limit of small displacements x, before the walls are stopped either by depolarizing fields (in conventional ferroelectrics[1]) or by new domain conformations under the constraint of strong random fields (in disordered ferroelectrics[13]). Weak periodic fields thus probe a linear ac susceptibility

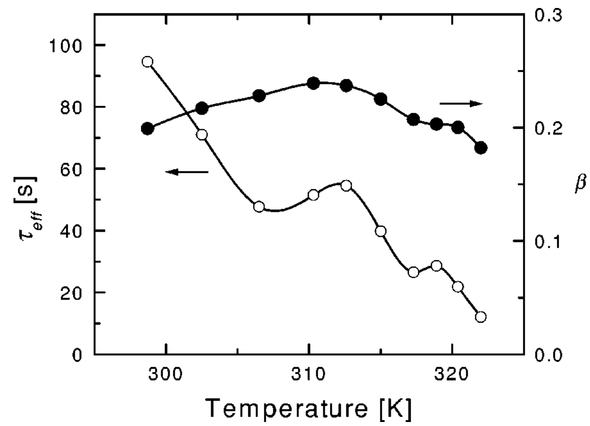

FIG. 4. Temperature dependencies of the characteristic relaxation time τ_{eff} and of the exponent β. Solid lines are guides to the eye.

$$\Delta\chi_w^*=\chi_\infty(1+1/i\omega\tau_i), \tag{7}$$

with $\chi_\infty/\tau_i\equiv(2\mu_w P_s/\varepsilon_0 d)$. The "relaxation" time τ_i denotes the time in which the interface contribution to the polarization equals that achieved instantaneously, $\Delta P=\varepsilon_0\chi_\infty E$.

Since the electric fields used in our experiments are well below the coercive field, $E_c\approx 150$ kV/m,[19] we have to account for the nonlinearity of v vs E in the creep regime, where thermal excitation enables viscous motion below the depinning threshold $E_{crit}\approx E_c$.[12] Approximating this regime roughly by $v\propto E^\delta$, $\delta>1$, Eq. (7) may be modified phenomenologically by introducing an exponent $\beta<1$,

$$\Delta\chi_w^*=\chi_\infty(1+1/(i\omega\tau_{eff})^\beta), \tag{8}$$

similarly as used in the case of polydispersive Debye-type relaxation.[20] Here τ_{eff} denotes an effective relaxation time. When finally taking into account the finite electric conductivity σ as experienced in the very low-f limit of real samples (see below) one arrives at Eq. (2).

In the case of $\sigma=0$ a linear relationship, $\chi''/(\chi'-\chi_\infty)=\tan(\pi\beta/2)$, is predicted by Eqs. (3)–(4). This was observed in the low-f dispersion of $PbFe_{1/2}Nb_{1/2}O_3$,[10] and also applies to SBN:Ce at moderately low frequencies (Fig. 1; inset). In case of monodispersivity ($\beta=1$) constant values, $\chi'=\chi_\infty$, are expected, while χ'' should vary as $1/f$. In reality, however, small and virtually T-independent polydispersivity exponents, $\beta\approx 0.2$ (Fig. 4), hint at a wide spectrum of mobilities due to the nonlinearity of v vs E. A further origin of polydispersivity may reside in the broad domain size distribution, which is well known in the case of SBN:Ce from piezoelectric force microscopy.[15] On the other hand, as shown in Fig. 4, the parameter τ_{eff} decreases from 100 to 10 s when approaching the phase-transition region within a temperature interval of only 20 K. As expected for creeplike motion[12] the irreversible response speeds up on heating owing to thermally activated processes. Simultaneously E_{crit} tends to decrease and the ferroelectric domains convert into random-field stabilized clusters with softened walls.[16] For the same reason also the value of χ_∞ increases drastically on heating as indicated, e.g., by the values of $\chi'(f_{\min})$ in Figs. 1–3. On the other hand, the electric dark conductivity, $\sigma \approx 10^{-9}\ (\Omega\ \mathrm{m})^{-1}$, is virtually temperature independent owing to its origin in deep donors in SBN:Ce.[21]

In conclusion, the susceptibility due to both irreversible and reversible domain-wall response has been observed in the domain state of zero-field-cooled SBN:Ce in different frequency regimes. Different theoretical descriptions based on creeplike wall motion and polydispersive wall relaxation, respectively, have been employed. Very probably both frequency ranges are linked by a dynamical phase transition as predicted very recently for the hysteretic dynamics of ferroic domain-walls.[22] At a given frequency ω and temperature T and below a threshold field amplitude, $E<E_{\omega}$, the walls do not exhibit any macroscopic motion, since their segments oscillate between metastable states with close energies giving rise to dissipation as described previously.[8] Similarly, a transition is also expected when keeping E fixed, but increasing the frequency to $\omega>\omega_{\min}$ as in the present experiments. It remains a task for the future to transform the theory of dynamic hysteresis, P vs E at variant ω and T,[22] into the frequency domain, χ^* vs ω at variant E and T, and to compare it with the present phenomenological theory.

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