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## FAST TRACK COMMUNICATION

# Quasi-ferroelectric state in $\text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ relaxor: dielectric spectroscopy evidence

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Online at [stacks.iop.org/JPhysCM/19/092001](http://stacks.iop.org/JPhysCM/19/092001)**Abstract**

The dielectric spectroscopy of perovskite  $\text{Ba}(\text{Ti}_{0.675}\text{Zr}_{0.325})\text{O}_3$  (BTZ<sub>325</sub>) relaxor ceramics is performed in a wide frequency range of  $10^{-2}$ – $10^6$  Hz. In contrast to other known relaxors, where the dipole dynamics is subject to non-Arrhenius slowing-down and freezing upon cooling so that the cubic ergodic relaxor phase transforms into a cluster dipolar-glass phase or a ferroelectric phase, none of these transformations are observed in BTZ<sub>325</sub>. In the course of cooling from the ergodic relaxor phase the characteristic time and the spectral width of the main relaxation process first increase rapidly in a Vogel–Fulcher manner, but then become almost temperature independent below the temperature of permittivity maximum, indicating the onset of the state which we call quasi-ferroelectric. The properties and the origin of this state are discussed.

Relaxor ferroelectrics (or relaxors) are crystalline materials widely studied in recent years due to their remarkable properties and wide prospects of practical applications (see [1] and [2] for a review). The determinative property of relaxors is the extraordinary large, diffuse and frequency-dispersive maximum in the temperature ( $T$ ) dependence of dielectric permittivity ( $\epsilon$ ). This maximum is believed to originate from the polarization of nanosize regions inside which permanent ferroelectric-like order exists, i.e. the polar nanoregions (PNRs). The relaxor behaviour has been studied elaborately in lead-containing crystals with perovskite-type structure, such as  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN) and  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$  (PMN–PT). The evolution of the high-temperature cubic ergodic relaxor phase upon cooling is known to occur in one of two ways. In some relaxors (e.g. in PMN–PT with large  $x$ ) the ergodic phase transforms into a ferroelectric (and thus nonergodic) phase at a Curie temperature which is usually several degrees below the temperature of the permittivity maximum,  $T_m$ . At low temperatures the crystal reveals all major characteristics of the ferroelectric (FE) phase, including polar (in most cases rhombohedral) symmetry and pronounced FE properties (polarization hysteresis loops, piezo- and pyroelectric effects, etc). In some others, the

canonical relaxors (e.g. PMN), the structure remains macroscopically cubic (nonpolar) but a glassy nonergodic relaxor phase appears. The ergodicity becomes broken because of the dipolar interactions, which lead to a cluster glass state where the dipole moments of PNRs are frozen in random directions. The FE phase can typically appear in the temperature range of the nonergodic relaxor phase after application of a strong enough external electric field.

Freezing of dipole dynamics can be effectively probed by means of dielectric spectroscopy. In the canonical relaxors the characteristic relaxation time ( $\tau$ ) of the main (so-called conventional relaxor) relaxation process contributing to the  $\varepsilon(T)$  peak upon cooling tends to infinity at a non-zero temperature  $T_f$ , following the Vogel–Fulcher (VF) law,

$$\tau = \tau_0 \exp[E_\tau/(T - T_f)], \quad (1)$$

where  $\tau_0$  and  $E_\tau$  are the parameters and  $T_f$  (which is significantly lower than  $T_m$ ) can be considered as the freezing temperature [3–5].

In the present work we discover a new type of relaxor behaviour. In the perovskite  $\text{Ba}(\text{Ti}_{0.675}\text{Zr}_{0.325})\text{O}_3$  (BTZ<sub>325</sub>) solid solution which was shown to be relaxor with a cubic structure (space group  $Pm\bar{3}m$ ) down to low temperatures (similar to canonical relaxors) [6–9], the dielectric dipole dynamics is, however, found not to be subject to any critical slowing-down and glassy freezing. This implies that in contrast to other known relaxors the low-temperature state in BTZ<sub>325</sub> is neither dipolar glass nor FE. Nevertheless, such a state is nonergodic, and it can be considered as a quasi-ferroelectric state.

The relative dielectric permittivity ( $\varepsilon^* = \varepsilon' - i\varepsilon''$ ) of the BTZ<sub>325</sub> ceramics with sputtered gold electrodes was measured as a function of frequency ( $f$ ) and temperature upon slow cooling using an impedance analyser (Novocontrol turnkey dielectric spectrometer Concept 20). Details on specimen preparation and measurement technique were given in [9].

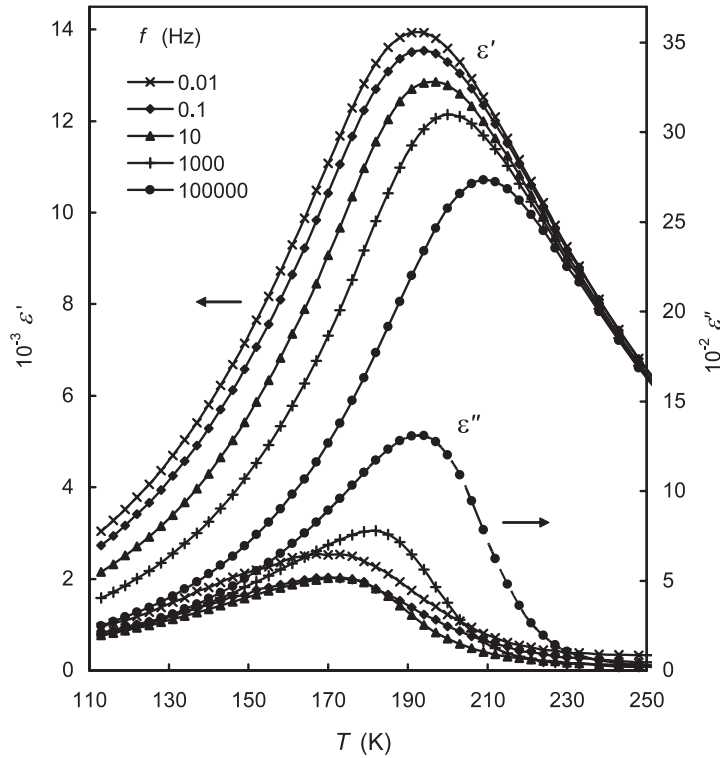
The diffuse peaks in the temperature dependences of  $\varepsilon'$  and  $\varepsilon''$  found in BTZ<sub>325</sub> (see figure 1) are characteristic of relaxors. As shown previously [8, 9], both the real and imaginary peak temperatures follow the VF relation  $f = f_m \exp[E_a/(T_m - T_{VF})]$ . However, it should be underlined that this fact does not necessarily imply the freezing of the dielectric spectrum, i.e. the divergence of  $\tau$  according to equation (1). To confirm equation (1) in classical relaxors, the dielectric spectra have been properly analysed [3–5]. In the present work we apply to BTZ<sub>325</sub> ceramics the method of analysis developed in [5].

Figure 2 shows the frequency dependences of  $\varepsilon^*$  at selected temperatures around  $T_m$ . At relatively high  $T$  the spectra are qualitatively the same as we observed at  $T > T_m$  in other relaxors PMN [5] and PMNT [10–12] in the same frequency range, i.e. two relaxation processes exist. The so-called universal relaxor (UR) process gives the dominating contribution to the loss at low frequencies while the conventional relaxor (CR) relaxation becomes more important at high  $f$ . Accordingly, we use the sum of the two terms to describe analytically the frequency dispersion of permittivity:

$$\varepsilon^*(f) = \chi_U^*(f) + \chi_R^*(f) + \varepsilon_\infty, \quad (2)$$

where the complex susceptibilities  $\chi_U^*$  and  $\chi_R^*$  refer to the UR and CR polarizations, respectively, and the third, frequency-independent term represents the contribution arising from electronic and phonon polarization and (if any) from other high-frequency relaxation processes with losses negligible at the measurement frequency. The nonlinear least-square fitting of the experimental data to equation (2) is carried out at several fixed temperatures in the same way as described in [5]. Very good fitting can be obtained when the same dispersion formulae are used as in the case of PMN and PMNT, namely the Curie–von Schweidler (fractional power) law,

$$\chi_U'(f) = \chi_{U1} f^{n-1} = \tan(n\pi/2) \chi_U''(f), \quad (3)$$

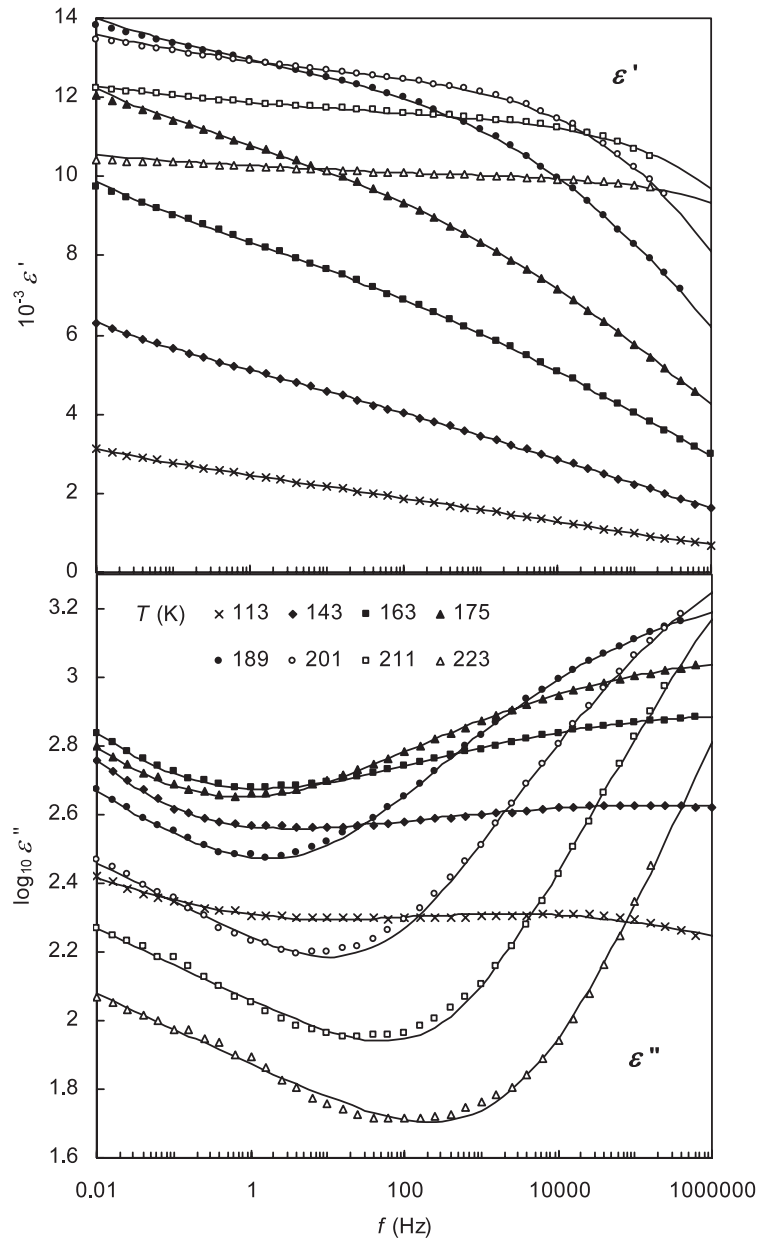


**Figure 1.** Temperature dependences of the real and imaginary parts of permittivity in  $\text{Ba}(\text{Ti}_{0.675}\text{Zr}_{0.325})\text{O}_3$  ceramics.

for the UR relaxation, and the Kohlrausch–Williams–Watts (KWW) law for the CR relaxation. The CR susceptibility  $\chi_R^*$  is calculated as the Fourier transform of the time derivative of the KWW (stretched exponential) function,  $\exp[-(t/\tau_{\text{KWW}})^\beta]$  (see [5] for details). The parameters  $\chi_{U1}$ ,  $n$ ,  $\chi_{R0} \equiv \chi_R'(f=0)$ ,  $\tau_{\text{KWW}}$ ,  $\beta$  and  $\varepsilon_\infty$  are considered the adjustable ones. The fitting results for selected temperatures are shown in figure 2.

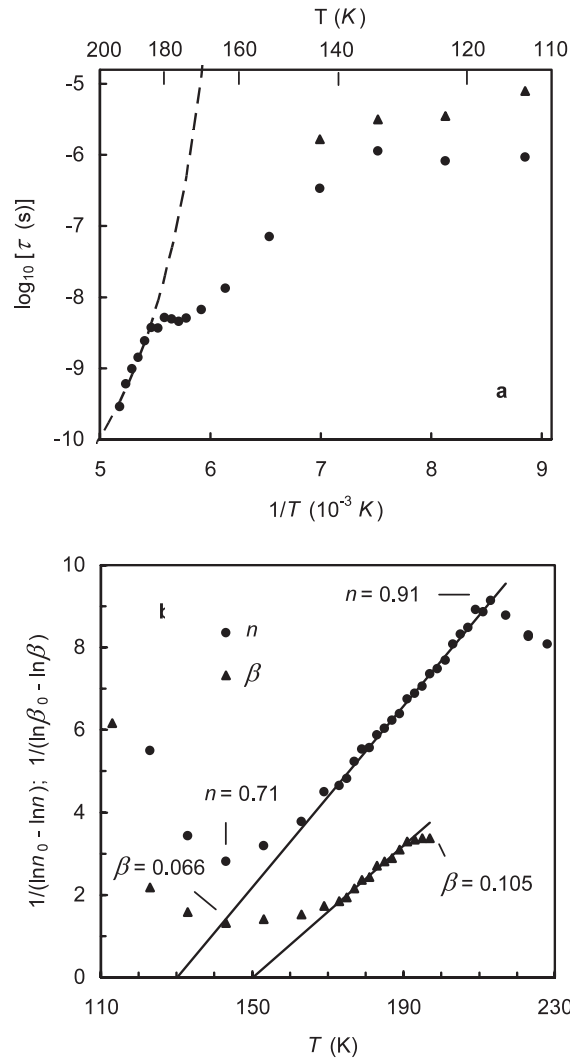
Note that although fitting is adequate at all frequencies and temperatures studied, it yields negative values of  $\varepsilon_\infty$ . This means that the experimental data significantly deviate from the KWW trend at frequencies higher than the highest measurement frequency, and as a result the dielectric strength ( $=\chi_{R0}$ ) of CR relaxation appears to be smaller than the value prescribed by the KWW formula. One can expect this effect at relatively small values of  $\tau$  and  $\beta$ . Indeed, the stretched exponent diverges at  $t \rightarrow 0$  and thus is unable to describe the relaxation at very short times, or in the frequency domain at frequencies significantly higher than the attempt frequency of dipole motion (which is of the order of the phonon frequency,  $\sim 10^{13}$  Hz in our case). Consequently, the KWW  $\varepsilon''(f)$  peak should necessarily be cut off at  $f \sim 10^{13}$  Hz. If  $f_{\text{KWW}} \equiv (2\pi\tau_{\text{KWW}})^{-1}$  is close to this cutting frequency and  $\beta$  is small, i.e. the  $\varepsilon''(f)$  peak is wide (as in the case of BTZ), the area under the curve becomes significantly reduced. On the other hand, according to the Kramers–Kronig relation, this area determines the value of dielectric strength, which is therefore also reduced.

The temperature dependences of the relaxation parameters obtained from the fitting are presented in figures 3 and 4. The first striking difference between  $\text{BTZ}_{325}$  and the prototypical relaxor PMN is the behaviour of the parameters of the CR (i.e. the main) dielectric contribution.



**Figure 2.** Frequency dependences of the real and imaginary parts of permittivity in  $\text{Ba}(\text{Ti}_{0.675}\text{Zr}_{0.325})\text{O}_3$  at selected temperatures. Experimental data are shown by dots; solid lines represent the fitting to equation (2).

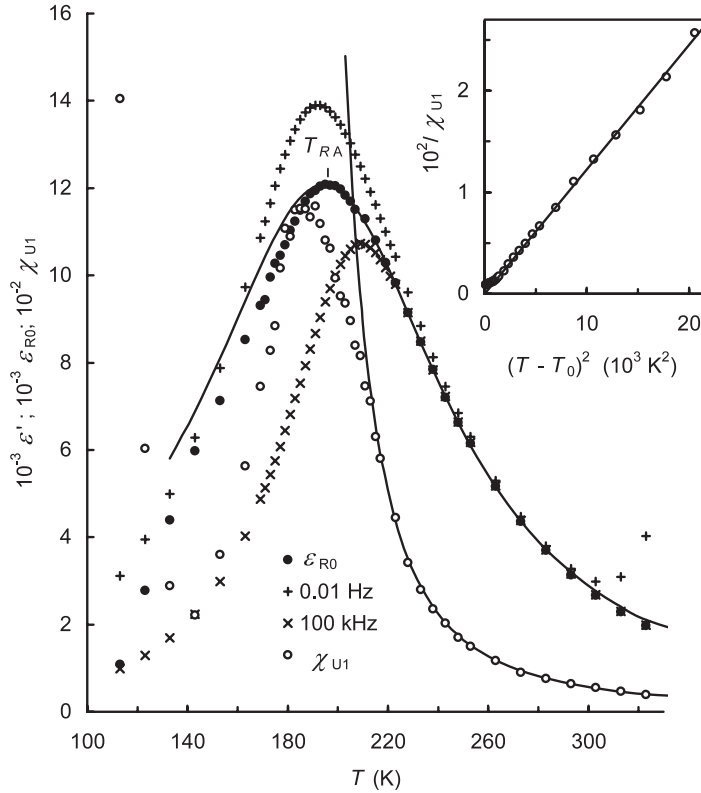
In PMN,  $\tau_{\text{KWW}}$  [5] as well as the longest relaxation time in the CR spectrum [3, 4] and the most probable relaxation time [13] follow the VF relation (1) in the range from  $10^{-12}$  s up to the largest value of  $10^3$  s attainable in experiment, signalling an effective freezing of the CR dipole subsystem at  $T_f \neq 0$  into a glassy nonergodic state. In  $\text{BTZ}_{325}$  (see figure 3(a)), after an interval of sharp increase,  $\tau_{\text{KWW}}$  grows more slowly on cooling and then (below 140 K)



**Figure 3.** Temperature dependences of (a) CR relaxation parameters  $\tau_{\text{KWW}}$  (dots) and  $\tau_{\text{mp}}$  (triangles), and (b) CR relaxation parameter  $\beta$  (triangles) and UR exponent  $n$  (dots) in  $\text{Ba}(\text{Ti}_{0.675}\text{Zr}_{0.325})\text{O}_3$ . Solid lines are the fits to equations (4) and (5) with the parameters  $T_\beta = 150 \pm 6 \text{ K}$ ,  $T_n = 131 \pm 5 \text{ K}$ ,  $\beta_0 = 0.141 \pm 0.012$ ,  $n_0 = 1.01 \pm 0.02$ ,  $E_\beta = 12 \pm 5 \text{ K}$  and  $E_n = 9 \pm 2 \text{ K}$ . The dashed line represents the trend of equation (1) with  $\tau \equiv \tau_{\text{KWW}}$  and the parameters  $T_f = T_\beta$ ,  $\tau_0 = 8 \times 10^{-14} \text{ s}$  and  $E_\tau = 360 \text{ K}$ .

becomes saturated. Though the behaviour is definitely non-Arrhenius at all temperatures, it is not possible to check reliably whether or not the VF relation (1) holds in the high-temperature range (because the experimentally available data interval is too narrow). However, if the value of  $T_f$  is fixed at  $\sim T_\beta$  (the VF temperature defined in equation (4), see below for details) the high-temperature data can be fitted to equation (1) (dashed line in figure 3(a)) with the values of other parameters being reasonable for relaxors.

The deviation from the VF law and the temperature independence of  $\tau_{\text{KWW}}$  at low temperatures suggest that the CR relaxation spectrum does not freeze. It can also be understood in a simpler way without using the sophisticated fitting procedure. The CR and UR losses are relatively separated in frequency at all temperatures (see figure 2(b)) so that the most probable relaxation time ( $\tau_{\text{mp}}$ ), i.e. the standard characteristic of relaxation, can be easily determined for the CR contribution from the position of the  $\epsilon''(f)$  maximum. At high temperatures this maximum is located above the largest measurement frequency, but moves down on cooling and can be clearly seen at  $T < 150 \text{ K}$  in the range of  $10^4$ – $10^6 \text{ Hz}$ . As one can see in figure 3(a),



**Figure 4.** Temperature dependences of the permittivity  $\epsilon'$  measured in  $\text{Ba}(\text{Ti}_{0.675}\text{Zr}_{0.325})\text{O}_3$  at  $10^{-2}$  and  $10^5$  Hz (crosses) and the static CR permittivity,  $\epsilon_{R0} = \chi_{R0} + \epsilon_{\infty}$  (filled circles), and UR susceptibility,  $\chi_{U1} \equiv \chi'_{U1}$  (1 Hz) (open circles), derived from fitting. Solid lines are the fits to equations (6) and (7) with the parameters  $T_{RA} = 194$  K,  $\epsilon_{RA} = 12 \times 10^3$ ,  $\delta_R = 41.8$  K,  $T_0 = 180$  K and  $C_U = 8.2 \times 10^5$  K<sup>2</sup>. The inset shows  $1/\chi_{U1}$  as a function of  $(T - T_0)^2$ .

the values of  $\tau_{mp}$  are larger than  $\tau_{KWW}$  (as they should be in the case of KWW relaxation) and follow a similar temperature dependence without any sign of freezing.

The situation is perhaps possible (though never observed experimentally) in which  $\tau_{KWW}$  is weakly temperature dependent, but the spectrum anomalously broadens on cooling so that the longest relaxation time ( $\tau_{max}$ ) diverges at  $T \neq 0$ ; i.e., only part of the spectrum related to certain relaxation mechanism freezes. The values of  $\tau_{max}$  in classical relaxors (including PMN) were determined from the onset of frequency dispersion on  $\epsilon'(T)$  curves using the condition that  $\tau_{max} = 1/(2\pi f)$  when  $\epsilon'(f, T)$  deviates from its low-frequency limit [4]. In fact, only the CR relaxation mechanism was analysed in that work, which was understandable because of the negligible value of  $\chi'_U$  as compared to the total measured  $\epsilon'$ , especially at high frequencies (frequencies up to 200 MHz were used). Unfortunately, this method works only at comparatively high temperatures, namely higher than  $T_m$  for the lowest measurement frequency (190 K in our case). Therefore, it is impossible to test it for  $\text{BTZ}_{325}$  in the most interesting low-temperature range, where  $\tau_{max}$  is expected to be non-divergent. As for the temperatures above 190 K, we found, using this method, that  $\tau_{max}$  increases upon cooling in a VF-like manner (i.e. similar to  $\tau_{KWW}$ ) but the VF parameters could not be reliably determined due to the undesirable  $\chi'_U$  contribution, which appears to be significantly higher than in PMN

(compare figure 4 for BTZ and figure 1 in [5] for PMN), making it impossible to measure  $\tau_{\max}$  precisely.

Alternatively,  $\tau_{\max}$  can be estimated if  $\tau_{\text{KWW}}$  and  $\beta$  are known. The KWW parameter  $\beta$  determines the width of the relaxation spectrum: it is equal to unity in the case of single relaxation time (Debye relaxation) and becomes smaller when the spectrum expands. As shown in figure 3(b),  $\beta$  in BTZ, and the UR relaxation parameter  $n$ , first decrease with decreasing  $T$  according to the VF-type relations,

$$\beta = \beta_0 \exp[-E_\beta/(T - T_\beta)], \quad (4)$$

$$n = n_0 \exp[-E_n/(T - T_n)], \quad (5)$$

(this behaviour was also observed in PMN, see [5]). If equations (4) and (5) persisted down to the lowest temperatures, they would indicate a singular broadening of the CR spectrum at  $T_\beta$  and a freezing of the UR spectrum at  $T_n$  [5, 11], respectively. However, below  $\sim 170$  K both relations are violated and the parameters even increase upon further cooling. At high temperatures equation (5) becomes no longer valid either and  $n$  decreases with increasing  $T$  from 0.905 at 213 K to 0.84 at 270 K and then remains unchanged (not shown in figure 3). The observed low-temperature behaviour of  $\beta$  means that  $\tau_{\max}$  for the CR dielectric contribution does not decrease upon cooling below 140 K and the whole CR relaxation spectrum remains unfrozen.

The possibility found in the present work of a freezing-free relaxation accompanied by the fulfilment of the VF law for  $T_m$  was theoretically predicted [14], but it has never been experimentally verified in canonical relaxors. The conditions necessary for such a kind of behaviour are a maximum in the temperature dependence of static permittivity and a gradual broadening of the dielectric spectrum upon cooling. Both these conditions are satisfied for the CR dielectric contribution of BTZ<sub>325</sub> in the temperature range around  $T_m$ .

The static CR contribution,  $\varepsilon_{R0} = \chi_{R0} + \varepsilon_\infty$ , is compared with the experimentally determined  $\varepsilon'$  in figure 4. The  $\varepsilon_{R0}(T)$  curve is fitted to the Lorentz-type relation

$$\varepsilon_{RA}/\varepsilon_{R0} = 1 + (T - T_{RA})^2/(2\delta_R^2). \quad (6)$$

At  $T > T_m$  and comparatively high frequencies, where  $\varepsilon_{R0} \cong \varepsilon'$ , this relation is known to be characteristic of relaxors [5, 15] and confirmed also in BTZ<sub>325</sub> [9]. At  $T \cong T_m$  and below, the temperature behaviour of  $\varepsilon_{R0}$  in relaxors is not well studied, because the deviation of the measured  $\varepsilon'(T)$  from the  $\varepsilon_{R0}(T)$  trend takes place due to large CR dispersion. Therefore, some efforts, e.g. fitting of dielectric spectra in the same way as performed in the present work, are required to determine  $\varepsilon_{R0}(T)$ . As one can see in figure 4,  $\varepsilon_{R0}(T)$  in BTZ<sub>325</sub> follows equation (6) not only at  $T > T_m$  but also at  $T \cong T_m$ . At lower temperatures a small deviation is observed.

The temperature dependences of the real and imaginary parts of UR contribution at all frequencies show a quadratic critical behaviour following the relation

$$1/\chi_U = (T - T_0)^2/C_U, \quad (7)$$

where  $T_0$  and  $C_U$  are the frequency-dependent parameters. This is presented in figure 4 for a selected frequency of 1 Hz. The critical behaviour of the susceptibility is indicative of an FE phase transition and in PMN-PT, where equation (7) also holds for the UR susceptibility in the ergodic relaxor phase [10, 12], the low-temperature phase is indeed FE. However, BTZ<sub>325</sub> is not ferroelectric at low  $T$ .

The BTZ<sub>325</sub> ceramics studied in this work possess the basic characteristics of the relaxors. The peak of  $\varepsilon'(T)$  is very large and diffuse, with a strong dispersion on the low-temperature side and the VF shift of  $T_m$ . Below  $T_m$ , the symmetry of the structure remains cubic. This is confirmed by x-ray diffraction data [6] and by the fact that Raman spectra do not show any



change in width or frequency of the lines upon cooling through  $T_m$  and below, indicating the absence of a structural phase transition [16]. Besides, the existence of PNRs at  $T \gg T_m$  was evidenced by Raman spectroscopy [16], heat capacity measurements (anomaly at  $T \gg T_m$ ) [17] and dielectric study (strong nonlinearity and deviation from the Curie–Weiss law) [7, 9]. In canonical relaxors, flipping of the PNRs dipole moments is believed to freeze out, giving rise to the freezing of the CR dielectric response (divergence of  $\tau_{KWW}$  and vanishing of  $\beta$ ) so that the KWW susceptibility does not contribute to the measured permittivity at  $T < T_f$ .<sup>3</sup> However, our analysis clearly demonstrates that the CR dielectric relaxation dynamics in BTZ<sub>325</sub> remains active down to low  $T$ . The small, nearly  $T$ -independent (below 140 K) value of  $\tau_{KWW} \approx 10^{-6}$  s and the increasing value of  $\beta$  on cooling imply that the dipoles have enough time to reach equilibrium during the period of a typical experiment and thus the CR dipole subsystem shows the behaviour characteristic of an *ergodic* state. Note that in the PMN relaxor crystals, freezing (non-ergodicity) has been found not only for the CR dipole subsystem but also for the UR subsystem based on the fact that  $n \rightarrow 0$  according to equation (5), when  $T \rightarrow T_f$ . In BTZ<sub>325</sub>, equation (5) is not valid at low temperature, thus there is no freezing of the dipoles responsible for the UR relaxation either. However, some other experiments hint at the non-ergodicity of the low- $T$  state in Zr-rich BTZ. In particular, the pyroelectric current in poled samples and the FE-type hysteresis loops are observed [7, 16], which implies the possibility for the material to exist in different long-living (polar) states at the same temperature, i.e. non-ergodicity.

To interpret the results we suggest that, similar to the PMN and PMN–PT relaxors [5, 18], the CR and UR relaxations in BTZ originate from the flipping of the PNR dipole moments between the allowed directions and from the reorientations of the dipole moments of some individual unit cells inside PNRs, respectively. The size and number of PNRs in relaxors are known to increase upon cooling starting from a temperature much higher than  $T_m$  [2, 19]; therefore, the static CR susceptibility  $\chi_{R0}$ , which is determined by the number and (average) dipole moment of PNRs, also increases. Accordingly, the increase of  $\varepsilon_{R0} = \chi_{R0} + \varepsilon_{\infty}$  is observed (see figure 4). The characteristic time of PNR dipolar relaxation is expected to be dependent on their size, the (frustrated) interactions among them and the local random electric and elastic fields present due to quenched disorder in the crystal structure. In PMN such a kind of dependence leads to anomalous broadening of the relaxation spectrum, deviation from the Arrhenius behaviour and VF freezing of the dipole dynamics ( $\tau_{KWW} \rightarrow \infty$ ,  $\beta \rightarrow 0$  and  $n \rightarrow 0$  when  $T \rightarrow T_f$ ) so that the subsystem of PNR dipole moments forms the glassy state (according to the majority of existing theoretical models, e.g. spherical random bond-random field model [20]). In BTZ<sub>325</sub>, as we have experimentally shown above, the deviation from the Arrhenius law also takes place and the behaviour at  $T \sim T_m$  and at higher temperatures resembles the behaviour in the classical relaxors, suggesting a significant role of PNR correlations. However, the VF freezing does not happen at low temperatures, possibly for the following reasons. After the gradual growth upon cooling, the size of *some* PNRs increases *abruptly*<sup>4</sup>. This may be due to the merging of neighbouring PNRs into larger ones or/and due to the thermally activated critical nucleation and growth of the regions of ferroelectric phase, as described in the kinetic model of phase transitions in disordered crystals [21]. Since the activation energy of the PNR dipole moment flipping is roughly proportional to the volume of PNR [1] and the relaxation time depends on the energy exponentially, at temperatures close to  $T_f$  even a comparatively small growth of PNR can lead to a huge increase in the relaxation time. Therefore, the dipole moments of those PNRs whose size has increased abruptly can no

<sup>3</sup> The dielectric response of canonical relaxors at  $T < T_f$  is dominated by the relaxation of PNR boundaries, which is characterized by frequency-independent loss [13].

<sup>4</sup> In principle, the abrupt increase of PNR size in a certain temperature interval is in agreement with a number of experiments and seems to be characteristic of relaxors, see e.g. [19].

longer be reoriented by thermal motion and thus do not contribute to the dielectric relaxation<sup>5</sup>. This mechanism leads to a decrease in the concentration of dynamic PNRs and thereby to the decrease of  $\chi_{R0}$ . At  $T < T_{RA}$  this effect overwhelms the effects of emergence and gradual growth of PNRs and a maximum in the  $\chi_{R0}(T)$  curve appears (figure 4). Decreasing the concentration of dynamic PNRs should also lead to a decrease of the interactions among them and thus to decreasing  $\tau_{KWW}$  and increasing  $\beta$  (deviation from VF laws at  $T < T_{RA}$ ). Besides, abrupt growth is expected for the largest PNRs [21], i.e. those having the largest relaxation time. Their exclusion from the ensemble of dynamic PNRs additionally promotes the decrease in  $\tau_{KWW}$ . As the UR contribution is also related to PNRs, the decrease of the dynamic PNR number leads to a  $\chi'_{U}(T)$  maximum and to an increase of  $n$  on cooling. In this way, the  $T$  dependences of the relaxation parameters are explained.

This explanation implies that the type of nonergodicity in BTZ<sub>325</sub> is different from that in canonical relaxors (e.g. PMN), where the nonergodicity is related to the VF freezing due to frustrated dipolar interactions and formation of a cluster dipolar-glass state. In BTZ two interpenetrating sets of PNRs are suggested to exist in the low-temperature state, i.e. static (large) PNRs and dynamic (small) PNRs. The interactions among dynamic PNRs are weak and they behave like ergodic species. The nonergodicity is associated with the incapability of the static PNRs to be thermally reoriented because of their comparatively large size. Application of a strong enough external electric field (poling) can bring them to different configurations with close energies (similar to normal FE domains), i.e. the state is nonergodic. On the other hand, the macroscopic symmetry of the non-poled crystal remains cubic, i.e. the state is not FE. It can be called a quasi-ferroelectric state.

We note that the existence of a comparatively large number of static polar regions at  $T \sim T_m$  is also confirmed by the fact that significant piezoresponse is observed in poled BTZ at temperatures several dozens of degrees higher than  $T_m$  [22]. In poled PMN the piezoresponse vanishes on heating at  $T \ll T_m$  [23]. Presumably, the formation of static (large) PNRs in PMN is hindered by local random electric fields caused by the disordered Mg<sup>2+</sup> and Nb<sup>5+</sup> ions. In BTZ these fields should be much smaller because the valences of the disordered ions Ti<sup>4+</sup> and Zr<sup>4+</sup> are the same. However, the PNRs in BTZ are still unable to become macroscopic FE domains. Thus, some other mechanism restricting the PNR growth exists. Furthermore, this mechanism works even in the presence of strong external electric field (according to reference [6] the symmetry of BTZ, determined from x-ray diffraction, remains cubic after poling). It can be related [6] to the existence of the nanometer-size Zr-rich regions which was suggested based on the high-pressure Raman study [24] and confirmed by EXAFS experiments [25]. Spontaneous polarization in such a kind of region is impossible (pure BaZrO<sub>3</sub> is not FE), thus PNRs located beside them cannot grow. Therefore, the quasi-ferroelectric state in BTZ<sub>325</sub> can be considered as a mixture of the randomly distributed static and dynamic polar nanoregions and the non-polar Zr-rich nanoregions.

Our conclusion on the absence of glassy freezing in BTZ is in agreement with our preliminary dielectric investigations [9], as well as with the recent measurements of the thermal properties of this material [26]. Freezing should lead to an anomalous decrease of entropy and, consequently, to an anomaly in the temperature dependence of heat capacity. Such a kind of anomaly was theoretically derived [27] in the framework of the random bond–random field model for spherical glasses [20] and was indeed observed in PMN [27]. It was experimentally found [27] that in PMN the entropy related to the thermal motion of PNRs vanishes on cooling

<sup>5</sup> To illustrate this process, consider two dynamic PNRs having the activation energy of  $360 \text{ K} = E_{\tau}$ . At the temperature of  $165 \text{ K} < T_m$  their relaxation time can be estimated from equation (1) with the parameters listed in the caption of figure 3 and equals  $2 \times 10^{-3} \text{ s}$ . After merging of these two PNRs, the activation energy of the new PNR is equal to  $2E_{\tau}$  and the relaxation time to  $5 \times 10^7 \text{ s}$ , i.e. it is effectively frozen.

at the same temperature  $T_f$ , which is derived as the freezing temperature from the dielectric relaxation experiments [5]. However, in BTZ<sub>35</sub> the anomaly of the heat capacity around  $T_m$  is not observed [26], which implies that freezing is absent (in [17] a very small anomaly, much smaller than in PMN, was reported, which can be related to the change of dynamic PNR number discussed above).

Concerning the relation between the structure and properties of the quasi-ferroelectric phase, it is interesting to note that the Neumann's principle is seemingly not satisfied here. According to this principle, the point group of a crystal structure must be a subgroup of the symmetry group of any macroscopic physical property [28]. As revealed in the x-ray diffraction experiment (i.e. the conventional method for crystal symmetry determination), the symmetry of BTZ with large Zr content does not change after poling and remains centric ( $m3m$ ) [6]. The Neumann's principle prohibits piezo-, pyro- and ferroelectric properties in this case. However, as mentioned above, these properties have been observed in experiments. The paradox can be understood by taking into account nanoscale inhomogeneities of quasi-ferroelectric structure in which the ferroelectric regions separated by non-polar Zr-rich regions are too small to be detected from the profiles of the x-ray diffraction peaks.

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## References

- [1] Cross L E 1987 *Ferroelectrics* **76** 241
- [2] Bokov A A and Ye Z-G 2006 *J. Mater. Sci.* **41** 31
- [3] Levstik A, Kutnjak Z, Filipic C and Pirc R 1998 *Phys. Rev. B* **57** 11204
- [4] Glazounov A E and Tagantsev A K 1998 *Appl. Phys. Lett.* **73** 856
- [5] Bokov A A and Ye Z-G 2006 *Phys. Rev. B* **74** 132102
- [6] Sciau Ph, Calvarin G and Ravez J 2000 *Solid State Commun.* **113** 77
- [7] Yu Z, Ang C, Guo R and Bhalla A S 2002 *J. Appl. Phys.* **92** 2655
- [8] Simon A, Ravez J and Maglione M 2004 *J. Phys.: Condens. Matter* **16** 936
- [9] Bokov A A, Maglione M, Simon A and Ye Z-G 2006 *Ferroelectrics* **337** 169
- [10] Bokov A A and Ye Z-G 2000 *Appl. Phys. Lett.* **77** 1888
- [11] Bokov A A and Ye Z-G 2000 *J. Phys.: Condens. Matter* **12** L541
- [12] Bokov A A and Ye Z-G 2002 *Phys. Rev. B* **65** 144112
- [13] Bovtun V, Kamba S, Pashkin A, Savinov M, Samoukhina P, Petzelt J, Bykov I and Glinchuk M D 2004 *Ferroelectrics* **298** 23
- [14] Tagantsev A K 1994 *Phys. Rev. Lett.* **72** 1100
- [15] Bokov A A, Bing Y-H, Chen W, Ye Z-G, Bogatina S A, Raevski I P, Raevskaya S I and Sahkar E V 2003 *Phys. Rev. B* **68** 052102
- [16] Farhi R, El Marssi M, Simon A and Ravez J 1999 *Eur. Phys. J. B* **9** 599
- [17] Gorev M V, Bondarev V S, Flerov I N, Sciau P and Savariault J M 2005 *Phys. Solid State* **47** 2304
- [18] Bokov A A and Ye Z-G 2002 *Phys. Rev. B* **66** 064103
- [19] Xu G, Shirane G, Copley J R D and Gehring P 2004 *Phys. Rev. B* **69** 064112
- [20] Pirc R and Blinc R 1999 *Phys. Rev. B* **60** 13470
- [21] Bokov A A 1994 *Phys. Solid State* **36** 19
- [22] Smolenskii G A, Tarutin N P and Grudtsin N P 1954 *Zh. Tekh. Fiz.* **24** 1584 (in Russian)
- [23] Ayazbaev T, Zaitseva N V, Isupov V A, Pronin I P and Shaplygina T A 1996 *Phys. Solid State* **38** 115
- [24] Kreisel J, Bouvier P, Maglione M, Dkhil B and Simon A 2004 *Phys. Rev. B* **69** 092104
- [25] Laulhe C, Hippert F, Kreisel J, Maglione M, Simon A, Hazemann L and Nassif V 2006 *Phys. Rev. B* **74** 014106
- [26] Nagasawa M, Kawaji H, Tojo T and Atake T 2006 *Phys. Rev. B* **74** 132101
- [27] Gorev M V, Flerov I N, Bondarev V S and Sciau Ph 2003 *J. Exp. Theor. Phys.* **96** 531
- [28] Nye J F 1964 *Physical Properties of Crystals, Their Representation by Tensors and Matrices* (Oxford: Clarendon)