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## LETTER TO THE EDITOR

## Freezing of dipole dynamics in relaxor ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ as evidenced by dielectric spectroscopy

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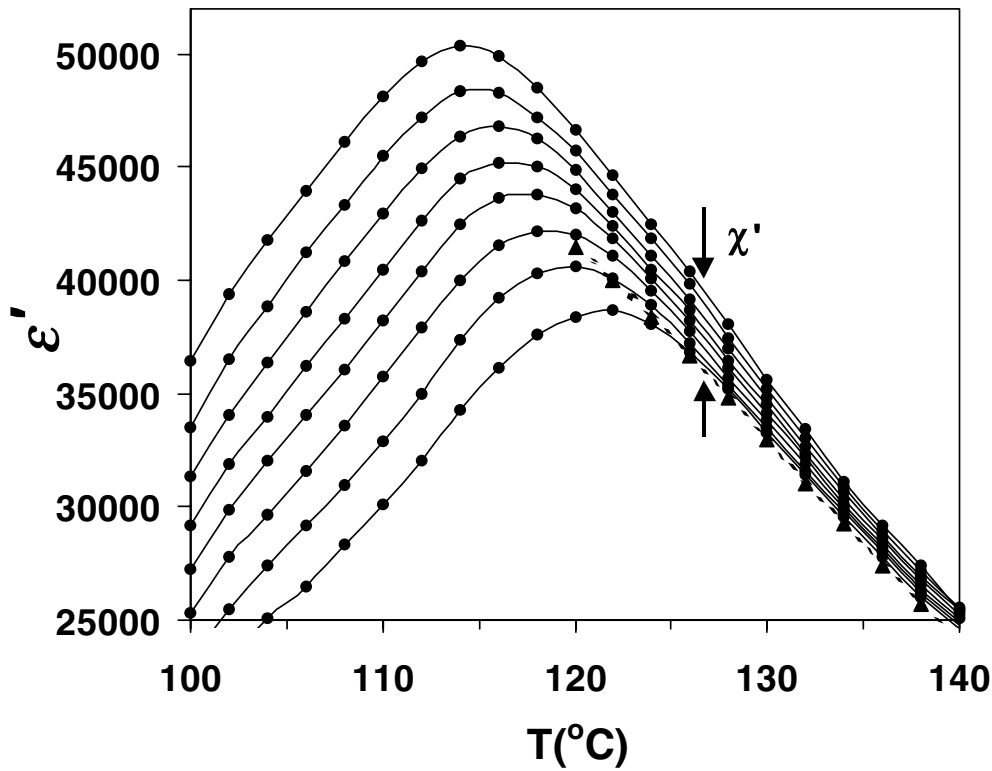
**Abstract.** Complex dielectric susceptibility ( $\chi' + j\chi''$ ) has been studied at  $f = 10^{-2}$ – $10^5$  Hz in the relaxor ferroelectric  $0.75\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--}0.25\text{PbTiO}_3$ . In addition to the well known relaxor dispersion observed at temperatures around and below the temperature of permittivity maximum  $T_m$ , a new and comparatively weak dispersion has been disclosed at  $T > T_m$ . It is described by the ‘universal relaxation law’,  $\chi'' = \cot(n\pi/2)\chi' \propto f^{n-1}$ . The temperature dependence of the exponent  $n$  follows the Vogel–Fulcher relation, indicating a process of freezing into the nonergodic state.

Relaxor ferroelectrics (or relaxors) are characterized by complex disordered crystal structure and interesting macroscopic properties relevant to advanced applications [1, 2]. Intensive fundamental investigations on relaxors have been stimulated by the discovery of a series of phenomena, which cannot be explained in terms of the conventional ferroelectric concepts. The temperature dependences of many properties, such as dielectric permittivity and lattice parameters, usually do not show any sharp anomalies, which might point to a ferroelectric phase transition. Furthermore, some of them strongly resemble the properties of orientational or dipolar glasses. In particular, the frequency dependences of the temperature  $T_m$ , at which the permittivity passes through a maximum, obeys the empirical Vogel–Fulcher law

$$f = f_0 \exp[-E_a/(T_m - T_{VF})] \quad (1)$$

where  $f$  is the measurement frequency and  $f_0$ ,  $E_a$  and  $T_{VF}$  are phenomenological parameters. It is often believed, although without solid theoretical justification, that the relation (1) is the indication of a freezing in the system at  $T_{VF}$  [3, 4]. The freezing was supposed to be associated with the transition into a nonergodic low-temperature glassy state due to random interactions between reorienting dipolar moments [3]. However, the question is still open, and it is not clear whether  $T_{VF}$  is the freezing temperature or not. One possible alternative was discussed by Tagantsev [5], who showed that the relationship (1) could be obtained as a direct consequence of gradual broadening of the spectrum with decreasing temperature and did not necessarily imply any kind of freezing. Bokov *et al* [6] studied the Vogel–Fulcher shift of  $T_m$  in  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$  in a frequency range wider than ever measured for relaxors, and found that at high frequencies the relation (1) was fulfilled with the parameter  $T_{VF}$  considerably different from the expected

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**Figure 1.** Temperature dependences of the real part of dielectric permittivity ( $\epsilon'$ ) of 0.75PMN–0.25PT ceramics in the vicinity of  $\epsilon'$ -maximum at different frequencies  $f = 100, 10, 1 \text{ kHz}, 100, 10, 1, 0.1, 0.01 \text{ Hz}$  (from upper curve). The broken line with triangles represents the calculated static permittivity of the ‘conventional relaxor polarization’,  $\epsilon_\infty$ . The dielectric susceptibility ( $\chi'$ ) associated with the ‘universal’ polarization mechanism, which is the difference between  $\epsilon'$  and  $\epsilon_\infty$ , is shown by arrows.

freezing temperature. On the other hand, the experimental evidence obtained from dielectric measurements [7], neutron scattering [8] and NMR [9] supported the existence of a nonergodic glassy state in relaxors.

To understand the cooperative behaviour in relaxors, it appears rewarding to study the phenomena that are associated with many-body interactions between charges and/or dipoles. One such phenomenon is the dielectric relaxation described by the so-called ‘universal relaxation law’ [10, 11]. This law implies that both the real ( $\chi'$ ) and imaginary ( $\chi''$ ) components of complex dielectric susceptibility are given as

$$\chi'(f) = \epsilon'(f) - \epsilon_\infty \propto f^{n-1} \quad (2)$$

$$\chi''(f) = \epsilon''(f) \propto f^{n-1} \quad (3)$$

$$\chi''(f)/\chi'(f) = \cot(n\pi/2) \quad (4)$$

where  $\epsilon_\infty$  is the high-frequency limit of real permittivity  $\epsilon'$  at which the low-frequency losses described by equation (3) become negligible.

The objective of this work was to investigate the dielectric dispersion in the solid solution system  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$  (PMN–PT) to provide a better understanding of

the nature of relaxor properties. PMN–PT with low Ti concentration is known as a typical relaxor [12, 13].

Pure perovskite PMN–PT ceramics with  $x = 0.25$  were prepared by solid state reactions. The dielectric permittivity was measured as a function of frequency at different temperatures under isothermal conditions and a weak ( $0.05\text{--}0.2\text{ V mm}^{-1}$ ) ac field. A computer-controlled impedance analyser (Solartron 1260) was used for measurements in conjunction with a dielectric interface (Solartron 1296). All measurements were performed on samples freshly annealed at  $450^\circ\text{C}$ .

The temperature dependences of permittivity in the vicinity of the temperature of maximum permittivity  $T_m (= 115\text{--}122^\circ\text{C})$  show a typical relaxor behaviour (figure 1) with a strong dispersion at  $T \leq T_m$ . At higher temperatures comparatively weak dispersion was observed. This behaviour is qualitatively consistent with the results previously reported on PMN–PT [12, 13]. As in the case of other relaxors, the  $T_m(f)$  function can be fitted to the Vogel–Fulcher law (1) with  $T_{VF} = 109^\circ\text{C}$ ,  $f_0 = 9 \times 10^{11}\text{ Hz}$  and  $E_a = 200\text{ K}$  ( $0.0173\text{ eV}$ ).

In relaxor ferroelectrics the dielectric dispersion in the high-temperature slope of permittivity maximum ( $T > T_m$ ) is known to be very weak in comparison with the relaxation at  $T \leq T_m$ . Thus it was usually not considered as a meaningful property. We have found, for the first time in relaxors, that at the temperatures above  $T_m$  the dielectric dispersion in PMN–PT follows exactly the universal relaxation law (2)–(4) in a wide frequency range.

The frequency dependences (log-log plots) of the imaginary component of susceptibility  $\chi'' = \varepsilon''$  measured at several temperatures around and above  $T_m$  are shown in figure 2(a). In a wide frequency range depending on temperature, the relations described by equation (3) were observed with  $n$  smaller than but close to 1. At high temperatures and low frequencies the exponent  $n$  changes and the universal behaviour with  $n = 0.2$  can be observed. At temperatures around  $T_m$  one can observe the increase of  $\varepsilon''$  with frequency in the high frequency range, indicating one more relaxation process. Similar dispersion was usually observed in other relaxors, therefore we call it the ‘conventional relaxor dispersion’. It moves to lower frequencies with decreasing temperature.

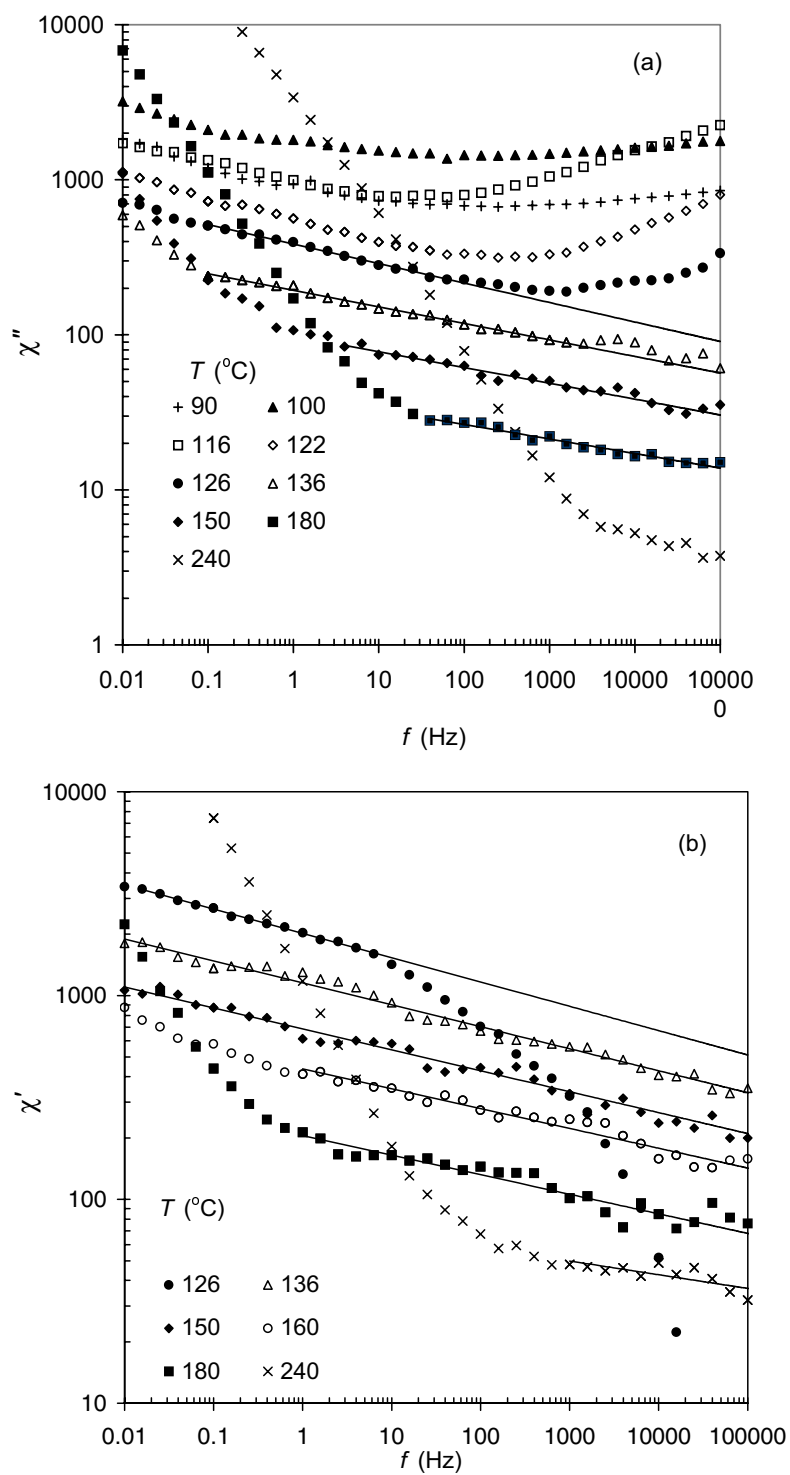
To determine the real part of susceptibility  $\chi'$  resulting from the polarization mechanism responsible for the ‘universal’ relaxation, we used the customary procedure [10, 11]. By subtracting the suitable values of  $\varepsilon_\infty$  from  $\varepsilon'$ , we obtained at each temperature the  $\chi'(f)$  dependences that are described by power law (2) with the same exponents  $n$  as for the  $\chi''(f)$  dependences (figure 2(b)). The low-frequency and conventional relaxor dispersions are also clearly observable in the  $\chi'(f)$  dependences as in the case of  $\chi''(f)$ . An alternative way to calculate  $\chi'(f)$  is to use equation (4). The  $\chi'$  values, calculated by these two methods, showed a good agreement. The comparative results for the frequency  $1\text{ Hz}$  are shown in figure 3. This agreement testifies the validity of the universal law (2)–(4) for the observed dielectric relaxation process.

To determine whether the universal dynamic response observed in PMNT75/25 is a true bulk phenomenon, we have studied the dimensional effects. Samples with different electrode areas ( $0.8$  and  $0.06\text{ cm}^2$ ) and different interelectrode distances ( $0.12$  and  $1\text{ cm}$ ) were examined. Very similar results were obtained in all cases, confirming the bulk universal relaxation behaviour. To study the possible aging effects we performed the measurements under different mean cooling rates (from  $0.1$  to  $10\text{ K h}^{-1}$ ). No temporal change of  $n$  was observed.

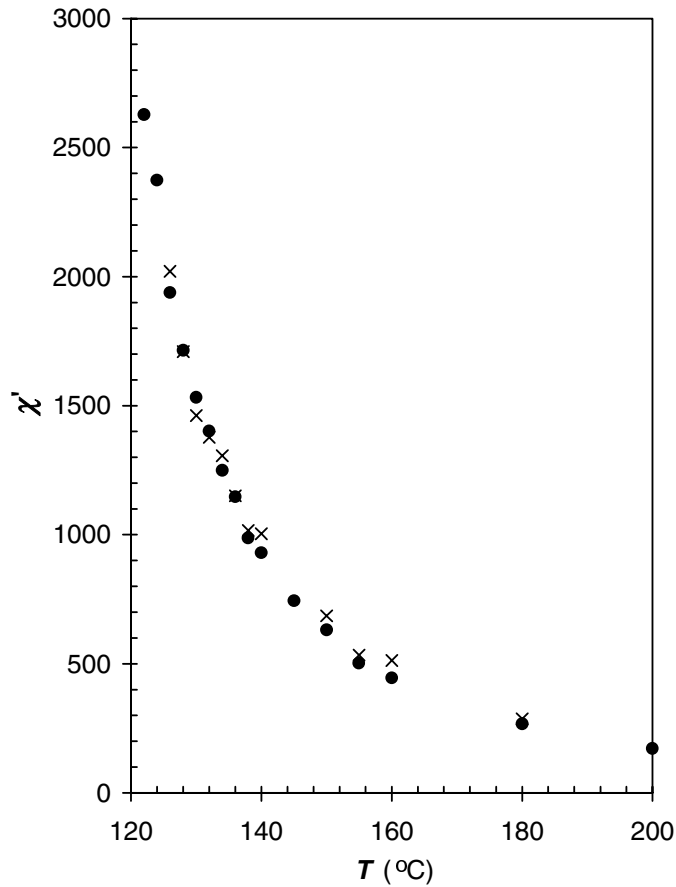
It is found in figure 4 that when the temperature approaches  $T_m$  from  $T > T_m$ , the values of the universal exponent  $n$  vary according to the Vogel–Fulcher law:

$$n = n_0 \exp[-N/(T - T_f)]. \quad (5)$$

The best-fit values of  $n_0$ ,  $N$  and  $T_f$  are  $0.909 \pm 0.001$ ,  $(0.37 \pm 0.05)\text{ K}$  and  $(113.1 \pm 1.2)^\circ\text{C}$ ,



**Figure 2.** Frequency dependences of the imaginary (a) and real (b) parts of dielectric susceptibility at temperatures around and above  $T_m$ . Solid lines represent least-squares fitting to equations (2) and (3).



**Figure 3.** Real part of dielectric susceptibility ( $\chi'$ ) associated with the 'universal' polarization mechanism. The values of  $\chi'$  were calculated at 1 Hz using equation (4) (dots) and equation (2) (crosses) with the same exponents  $n$  which was determined from  $\chi''(f)$  plots using equation (3).

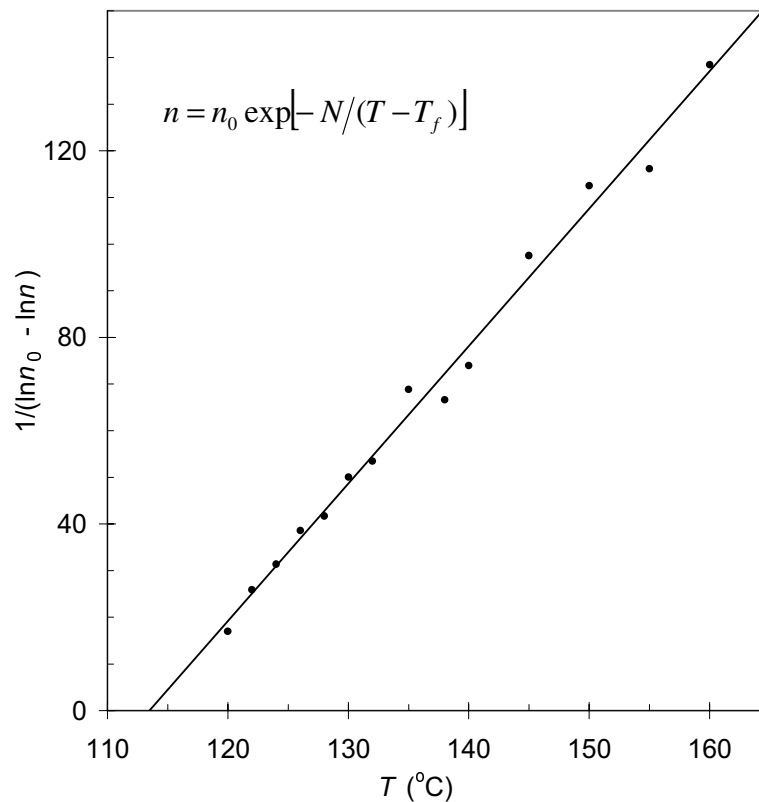
respectively.

The fulfillment of the relation (5) implies that the exponent  $n$  becomes zero at  $T = T_f$ . To interpret this result it is useful to discuss the problem in terms of the time-domain response of the system. The Fourier transform of the fractional power law (2) and (3) gives another fractional power law,  $i(t) \propto t^{-n}$ , which describes the time dependence of the relaxation current after a sudden removal of the polarizing field [10]. This time behaviour is known as the Curie–von Schweidler law. The case of  $n = 0$  corresponds to time-independent current. As the steady state polarization of the system,  $P = \int_0^\infty i(t) dt$ , is finite, the discharge current  $i$  must be zero in this case, thus  $P$  does not change with time. This indicates a freezing in the system at  $T_f$ .

The frequency independent part of the permittivity  $\varepsilon_\infty$  was found to follow the relation

$$1/\varepsilon_\infty = A + B(T - T_A)^2 \quad (6)$$

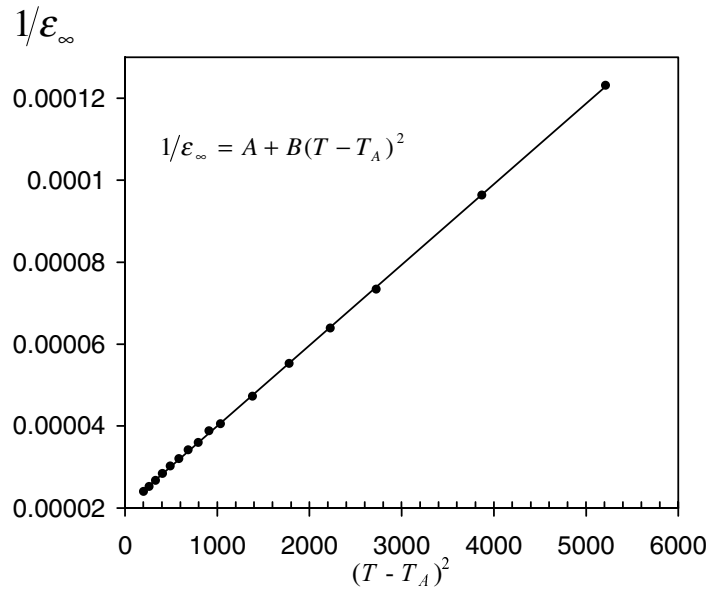
at all temperatures where the values of  $\varepsilon_\infty$  can be measured (figure 5). The parameters  $A$ ,  $B$  and  $T_A$  were determined by the least-squares fitting to be  $A = 2.03 \times 10^{-5}$ ,  $B = 1.97 \times 10^{-8} \text{ K}^{-2}$  and  $T_A = 110^\circ\text{C}$ , respectively.



**Figure 4.** Temperature dependence of the universal relaxation exponent  $n$ . The solid line represents the least-squares fitting to equation (5).

Therefore, the dielectric relaxation behaviour found in 0.75PMN–0.25PT ceramics at temperatures around and above  $T_m$  suggests three relaxation processes associated with different polarization mechanisms. The first one is found at extremely low frequencies. Such a low-frequency dispersion was observed in many materials and is usually explained by the relaxation of slowly mobile ionic and/or electronic charges [10, 11]. It has no relation to the ferroelectric properties. The second polarization process can be described by the universal relaxation law (2)–(4). It provides a comparatively small contribution  $\chi'$  to the total permittivity  $\varepsilon'$ . The temperature evolution of the dispersion associated with this process indicates a freezing of dipole dynamics in the system at the Vogel–Fulcher temperature  $T_f$ . The third mechanism is related to the conventional relaxor polarization. It provides the main contribution to the extremely high permittivity in the vicinity of  $T_m$ , and is also responsible for the conventional relaxor dispersion, which was observed in relaxors around and below  $T_m$ . The value of  $\varepsilon_\infty$  calculated from equation (2) is the static permittivity of the conventional relaxor polarization. Figure 1 illustrates the relation between  $\varepsilon'$ ,  $\varepsilon_\infty$  and  $\chi'$ .

The conventional relaxor dispersion contributes to the frequency shift of the temperature  $T_m$ , which can be described by the Vogel–Fulcher law (1). At high frequencies where the effect of ‘universal’ relaxation is comparatively small, the relaxor contribution is dominating. However, the Vogel–Fulcher fitting of  $T_m$  does not necessarily mean any freezing at  $T_{VF}$ . We have demonstrated that at temperatures well above  $T_A$ ,  $\varepsilon_\infty$  follows the relation (6). Thus a



**Figure 5.** Reverse dielectric permittivity  $1/\epsilon_\infty$  as a function of  $(T - T_A)^2$  at  $T > T_A$ . The solid line represents the least-squares fitting to equation (6).

maximum of static permittivity related to the conventional relaxor polarization can naturally be expected at temperatures close to  $T_A$ . Such a maximum is implied in the phenomenological approach relating the Vogel–Fulcher shift of temperature  $T_m$  to the wide and smooth spectrum of relaxation times, which broadens with decreasing temperature without any freezing-related singularity [5, 14]. According to this approach the Vogel–Fulcher temperature  $T_{VF}$  should coincide with  $T_A$ . Our results on PMN–PT have confirmed this coincidence experimentally with  $T_{VF} = 109^\circ\text{C}$  and  $T_A = 110^\circ\text{C}$ .

The conclusion about freezing has been drawn irrespective of any particular models of relaxation. The possible microscopic mechanisms are discussed as follows.

According to the structural glass models [3, 9], the nonergodic glassy state appears as a result of the freezing of thermally activated and reorientational dipolar moments of the nanoclusters, which are known to exist in relaxors. The reorientation of dipoles and the motion of the cluster interphase boundaries may contribute to the dielectric response of relaxor ferroelectrics. Based on the above analysis, we suggest that the susceptibility  $\chi'$  is related to the reorientation of dipolar moments of the nanoclusters, while the conventional relaxor polarization results predominantly from the vibration of polar cluster boundaries. A more detailed discussion on these issues will be given elsewhere [15].

In conclusion we have suggested the following interpretations of the dielectric relaxation in relaxor ferroelectrics. The Vogel–Fulcher behaviour of  $T_m$  associated with the conventional relaxor dielectric dispersion seems to result from a specific distribution of relaxation times (of the polar cluster boundaries), rather than from any freezing. On the other hand, the polarization of polar clusters gives rise only to a comparatively small addition to the magnitude of permittivity. It is this polarization that is related to the universal relaxation behaviour (2)–(4) discovered in PMN–PT at  $T \geq T_m$ . At temperatures high enough, the interactions between polar clusters are negligible. Upon cooling, the interactions become enhanced because of the growing number and correlation length of polar clusters. Upon further cooling, the dipolar



moments freeze at  $T_f$  as a result of the critical slowing-down of dipole dynamics. The freezing manifests itself by the Vogel–Fulcher-type temperature dependence of the universal relaxation exponent  $n$ , as described by equation (5). The final state below  $T_f$  can be a nonergodic glassy one.

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