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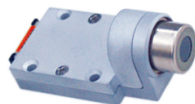
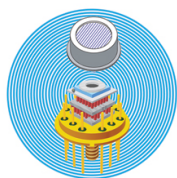
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Broadband dielectric spectroscopy of Pb-based relaxor ferroelectric (1-x)Pb(Mg_{1/3}Nb_{2/3})O₃-xPbTiO₃ with intermediate random fields

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This work is devoted to the investigation of the broad band dielectric spectra of 0.83PbMg_{1/3}Nb_{2/3}O₃-0.17PbTiO₃ (PMN-17PT) single crystals which have intermediate random fields. The necessity to understand the impact of random fields for the phase transition in heterogeneous perovskite oxides is of central importance. The thorough studies of dielectric properties revealed that the structural phase transition in PMN-17PT has a very complex dynamics. The temperature dependences of dielectric permittivity show that this material has features characteristic of polar nano regions and order-disorder phase transition dynamics. We speculate that this is the fingerprint of the phase transition in such heterogeneous perovskite oxides. *Published by AIP Publishing.*

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I. INTRODUCTION

Relaxor ferroelectrics (RFEs) are a class of disordered materials which exhibit a set of fascinating properties not only from a fundamental perspective but also for very technologically important applications. The compositions consisting of canonical relaxor and normal ferroelectric as end members of the phase diagram are of particular interest. These phase diagrams exhibit various peculiarities and interesting features. First, the gradual crossover from relaxor to normal ferroelectric is observed by the variation of the charge disorder. This crossover is caused by a structural complexity and the phase diagram has a boundary between these two distinct phases. This boundary, the morphotropic phase boundary (MPB), was identified in several systems and the main manifestation of this region in a phase diagram is the coexistence of two different structural phases. The importance of the MPB was identified through systematic studies of particular phase diagrams. Compositions in the MPB region have enhanced dielectric and electromechanical properties which are of great relevance for sensor, actuator, and transducer applications. A significant effort to explain the drastic increase of various physical properties was undertaken by the scientific community. Kutnjak *et al.* attributed such behaviour to a critical point in the temperature-electric field-composition phase diagram.¹ Other important findings concerning MPB compositions were revealed by a systematic structural investigation of lead zirconate titanate (PbZr_xTi_{1-x}O₃ - PZT) and various other lead-based systems.²⁻⁵ The X-ray and neutron diffraction studies revealed that in the vicinity of MPB lower symmetry monoclinic phase exists in lead based mixed perovskites.^{2,4,6} The polarization rotation with an application of electric field seems to be the key feature of MPB compositions and realization of

such rotations in compositionally disordered systems leads to unique piezoelectric properties.⁷⁻⁹

Ferroelectricity and related phenomena are predetermined by the lattice dynamics. Thus, the investigation of the lattice vibrations is of central importance in understanding the underlying mechanisms of ferroelectricity. There are two types of ferroelectrics: order-disorder and displacive ones. Perovskite oxides are considered to be displacive type systems and have a soft mode which softens according to Cochran law.¹⁰ Indeed, the soft mode can be observed in conventional ferroelectrics like lead titanate¹¹ and barium titanate^{12,13} but in the case of relaxors the situation is more robust. The mixed perovskites show a variety of deviations from conventional ferroelectrics which does not allow to classify them as displacive or order-disorder system unambiguously. In fact, doubts about pure soft mode behaviour in classical inorganic ferroelectrics are quite common both in theoretical¹⁴⁻¹⁷ and experimental papers.¹⁸⁻²⁰ The latter works consider the coexistence between displacive and order-disorder nature of phase transition in perovskite oxides. This coexistence can be simply explained by considering the behaviour of a 3 parameter oscillator model. The soft mode can be described by this oscillator where the frequency of soft mode varies according to Cochran law.¹⁰ Such soft modes are observed with conventional spectroscopic techniques (IR, Raman, and neutron spectroscopies). The situation gets more complicated when the oscillator is overdamped. If the resonant frequency becomes much smaller than the damping ($\omega_0 \ll 2\gamma$), the classical 3 parameter oscillator equation converges to Debye relaxation. This relaxation mode describes the order-disorder phase transitions (usually observed in organic ferroelectrics) where the system undergoes critical slowing down. So from the point of view of lattice dynamics, the gradual transition between order-disorder and displacive ferroelectrics exists. From the phenomenological point of view, this crossover is determined by the depth of thermodynamical potential.

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An outstanding effort was undertaken to study the lattice dynamics in canonical relaxors. It is expected that there should be a soft mode which behaves equivalently as in conventional ferroelectrics. Unfortunately, the lattice dynamics in relaxors appeared to be much more confusing. First of all, the lowest frequency TO phonon in relaxor ferroelectrics is heavily overdamped up to wave vector q_{wf} ²¹ above which the phonon becomes underdamped. This gives rise to a well-known waterfall effect.^{21,22} This phenomenon masks the softening (if it exists at all) in the vicinity of T_{max} . The appearance of the damped region in a phonon branch correlates with the Burns temperature T_B which is considered as a temperature where polar nano regions (PNRs) appear in the material (i.e., the deviation from linear temperature dependence of refraction index). Above the Burns temperature, the softening of the lowest frequency TO mode can be observed in several systems.^{21–24} Surprisingly, the overdamping disappears at temperatures below T_{max} as well. Another overwhelming fact which was observed by inelastic neutron scattering was the softening of phonon in the Brillouin zone boundary of PMN.²⁵ This is indicative of antiferrodistortive instabilities. Apparently, this can be a signature of competing interactions and thus closely resemble the dipolar glass (DGs) systems (although DGs are considered order-disorder systems and relaxors–displacive ones²⁶). Antiferroelectric (or ferroelectric) correlations in relaxors were proposed by others as well.^{27,28}

The formation of a ferroelectric phase in these mixed perovskites is strongly affected by the (absence of) short range order. It is expected that chemically ordered regions (CORs) play a key role in relaxor physics and are responsible for local distortions of average cubic phase (i.e., rhombohedral distortions in PMN). It was shown that it is possible to control the size of CORs by particular doping. It was successfully demonstrated on PMN with lanthanum doping in the A-site.^{29,30} The latter works showed that the static polar nano regions appear in chemically ordered regions and they do not contribute to the anomaly of dielectric permittivity. With an addition of La, the increase of size of CORs was detected leading to the decrease of dielectric strength of the anomaly although the distribution of relaxation times is the same.³¹ It was concluded that the largest contribution to the permittivity comes from the dynamic PNRs which appear in the disordered matrix. This picture is in agreement with the mechanism proposed by Samara.³²

The chemical ordered regions should be affected in PMN with lead titanate doping as in previously discussed PMN:La³⁺. Indeed, the dopants lead to appearance of spontaneous ferroelectric phase transition but it might be related to the reduction of random fields with a presence of Ti⁴⁺. If the static PNRs do not contribute to the dielectric permittivity, each system should show the decrease of dielectric anomaly with the increase of the size of CORs. PMN-PT proves otherwise and the dielectric anomaly increases with the increase of PT concentration until it reaches maximum. It starts decreasing only above the MPB where a classical ferroelectric phase is reached.^{33,34} This shows that the contribution of static and dynamic PNRs is more complex than expected. It seems that the random fields are a much more

essential component in the PMN-PT system than the chemical ordered regions. The comparison of diffuse scattering between PZT and PMN revealed this importance.³⁵

Koo *et al.* did a thorough investigation on 0.8PMN-0.2PT single crystal by neutron scattering.³⁶ It was expected that the significant impact on a waterfall effect will be observed due to the addition of lead titanate. Unfortunately, the damping of the lowest TO frequencies was still observed in 0.8PMN-0.2PT. It seems that the waterfall effect is not related to PNRs because it can be observed even in classical ferroelectric system PMN-60PT.³⁷

This work is devoted to the investigation of broadband dielectric spectra of relaxor-normal ferroelectric phase transition. For that matter, the single crystal of 0.83PbMg_{1/3}Nb_{2/3}O₃-0.17PbTiO₃ was investigated, which has a phase transition from cubic to rhombohedral phase according to the literature. The crystal exhibits relaxor properties in the cubic phase and ferroelectric ones in the rhombohedral phase. This concentration is expected to have an intermediary strength of random fields. Thus, it is important to investigate this composition to bridge the knowledge of dynamics in the systems with strong and weak random fields. We would like to show that the phase transitions appearing in such intermediary systems can be considered as order-disorder type. The presence of charge disorder possibly masks the characteristic features of order-disorder phase transitions which can be observed in less complex systems which can be described by a double well potential.

Furthermore, thorough investigation was performed on the frequency dependences of modified Curie-Weiss constants and the comparison between other relaxor systems was made. Apparently, these constants exhibit pronounced frequency dependence at microwave frequencies and it seems it is universal behaviour for PMN-based relaxors.

II. EXPERIMENTAL

Single crystals of 0.83PbMg_{1/3}Nb_{2/3}O₃-0.17PbTiO₃ (PMN-17PT) were grown by a modified Bridgman technique.³⁸ The [001] plate was investigated in a broad frequency (20 Hz–120 GHz) and temperature range (120 K–500 K). The temperature was measured with a Keithley Integra 2700 multimeter which was equipped with two types of sensors in different experimental setups: 100 Ω platinum resistor or T type thermocouple.

Several experimental techniques were implemented to cover such a broad frequency range. Measurements of capacitance and loss tangent were performed at 20 Hz–1 MHz frequencies with a HP 4824A LCR meter. The complex dielectric permittivity was extracted according to a parallel plate capacitor model.

The complex reflection coefficient from the end of coaxial line was measured at microwave frequencies from 10 MHz–1 GHz. These measurements were performed with an Agilent E8363B vector network analyser. Calculation of dielectric permittivity is based on a transmission line theory. The detailed description of the method can be found in Ref. 39.

The measurements at 8–30 GHz frequencies were conducted in two distinct custom made waveguided systems. Scalar transmission and reflection coefficients were measured with Elmika scalar network analysers. The needle-shaped sample was placed in the center of waveguide perpendicularly to the longer wall. The only excitation which can propagate in the waveguide is H_{10} which has a maximum of electric field and minimum of magnetic field in the middle of longer wall. The electric field vector was parallel to the sample. The dielectric permittivity was calculated from measured scalar transmission and reflection coefficients by solving a nonlinear set of equations. A modified Newton method was implemented to solve these equations. The background of this experimental technique can be found in the literature.^{40,41}

80–120 GHz frequency range was covered by a more sophisticated waveguide system. The sample was placed in a 6-port system. The complex reflection coefficient was measured by a custom scalar/vector network analyser produced by Elmika. The determination of dielectric permittivity was carried out by solving the same set of equations by the modified Newton method as described above. The only difference is the experimental quantities from which permittivity is obtained (i.e., reflection modulus and phase). This experimental technique was described earlier by Ivanov *et al.*⁴²

III. RESULTS AND DISCUSSION

Figure 1 represents temperature dependences of complex dielectric permittivity at different frequencies. Dielectric anomaly is associated with the ferroelectric phase transition at around 330 K from cubic to rhombohedral phase.^{6,43} Very broad dispersion above the phase transition is observed. The maximum of dielectric permittivity at different frequencies occurs at different temperatures.

However, it is important to stress that the shift of dielectric maxima is negligible at frequencies below 1 MHz. The larger shift occurs at microwave frequencies and is clearly observed in 8 and 29 GHz curves. Additional anomaly can be observed in the temperature dependence of imaginary part (Fig. 1(b)). This feature only appears at frequencies

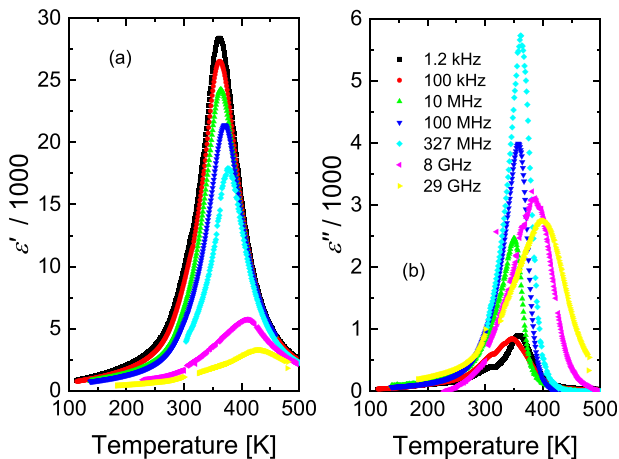


FIG. 1. Temperature dependence of complex dielectric permittivity at different frequencies of a PMN-17PT single crystal.

below 1 MHz. This anomaly can be related to the domain wall motion because it is observed in the ferroelectric phase. Another possibility is that this effect is extrinsic and related to the sample-electrode interface although we neglect this assumption because electrodes were produced with different conditions (different silver pastes with different annealing temperatures) and the same feature was observed in the experimental data. The Brillouin studies performed by Kim *et al.*⁴⁴ revealed an anomaly in the same temperature region (~ 320 K) during field-cooling/field-heating experiments. We can conclude that the anomaly we observed in the temperature dependences of dielectric permittivity is an intrinsic feature of PMN-17PT.

The dielectric anomaly in the PMN-17PT single crystal is not as sharp as in classical 1st order phase transition; it exhibits particular “diffusivity.” Such picture reminds of organic ferroelectrics with order-disorder type phase transitions. This phase transition shows very peculiar behaviour. It is expected to observe the minimum in temperature dependence of dielectric permittivity at certain frequencies (so called critical slowing down). In the present case, such minimum was not observed.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_1}{1 + (j\omega\tau_1)^{1-\alpha_1}} + \frac{\Delta\varepsilon_2}{1 + (j\omega\tau_2)^{1-\alpha_2}}. \quad (1)$$

The absence of minimum can be explained after the analysis of dielectric spectra which are depicted in Figure 2. Solid curves represent the approximation by superposition of two empirical Cole-Cole equations (Eq. (1)) where ε_∞ is the contribution of phonons and electrons to dielectric permittivity, $\Delta\varepsilon$ is the dielectric strength, τ is the Cole-Cole relaxation time and α_1, α_2 are the parameters describing the width of dielectric spectrum. One of the components describes the broad feature of spectra which gives rise to a constant loss region at the lowest frequencies (it can be considered as a background to a main relaxation). Another component describes the main relaxation which mostly appears in microwave frequencies. The structure of all the dielectric spectra in PMN-17PT closely resembles canonical relaxors.

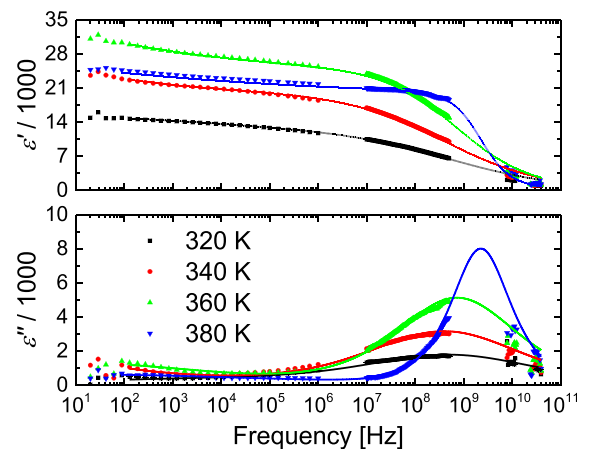


FIG. 2. Frequency dependence of complex dielectric permittivity at different temperatures for a PMN-17PT single crystal.

The distribution of relaxation times in the PMN-17PT single crystal is much broader than Debye-type relaxation. The minimum in order-disorder type systems is observed for the materials where the dielectric dispersion is close to Debye relaxation. Any broadening of the spectra is masking the minima. This can be easily shown by the modelling of 2nd order phase transition. This modelling is given in the [supplementary material](#).

The Cole-Cole relaxation time for the higher frequency process was analysed more carefully. It is well accepted that relaxor ferroelectrics undergoes freezing which is described by Vogel-Fulcher law. This freezing phenomenon manifests as the divergence of characteristic relaxation time vs. temperature. One of the key signatures of the freezing in relaxor ferroelectrics is the constant loss regime observed at low temperatures. The constant loss regime hints that the distribution of relaxation times in the system becomes infinitely broad. In our case, PMN-17PT undergoes structural phase transition from relaxor-like to normal ferroelectric one. It is difficult to discuss such a system in the framework of Vogel-Fulcher law because the long range ferroelectric order onsets at higher temperatures than the freezing supposed to appear. The parameters which are obtained by describing characteristic relaxation time by Vogel-Fulcher law have questionable physical meaning.

$$\frac{1}{\tau_{mean}} = \frac{1}{\tau_0} + \frac{1}{\tau_1} \left(\frac{T - T_C}{T_C} \right)^\beta. \quad (2)$$

The latter statements require another approach for analysing mean relaxation time in the PMN-17PT system. Thus, the order-disorder model (Eq. (2))⁴⁵ was applied for the analysis of the main relaxation process. The temperature dependence of mean relaxation time is depicted in Figure 3. The solid curve is approximation with Eq. (2). The critical slowing down model is capable of describing the mean relaxation time at a higher temperature phase. There are four fitting parameters which are represented in Table I. One of them is the phase transition temperature (Curie temperature) which correlates with the phase diagrams by Noheda *et al.* and Guo *et al.*^{6,43}

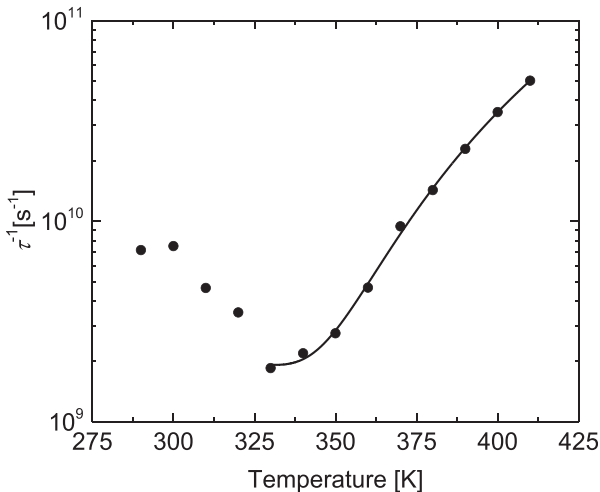


FIG. 3. Temperature dependence of inverse mean relaxation time. The solid line is approximation with a critical slowing down model.

TABLE I. Parameters obtained from the critical slowing down model.

$\frac{1}{\tau_0}$ (s ⁻¹)	$\frac{1}{\tau_1}$ (s ⁻¹)	T_C (K)	β
1.9×10^9	2.7×10^{12}	330	2.8

Parameter β for proper order-disorder type phase transitions should be equal to 1. For the PMN-17PT, this parameter is 2.8. The interpretation of such a value is related to the large random fields in PMN-PT. A similar value was obtained for the PZN-PT⁴⁵ single crystals which are known to have strong random fields.

Parameter τ_0 indicates that the minimum in the temperature dependence of dielectric permittivity should be observed in the microwave frequencies (waveguide region above 2 GHz). Unfortunately, the experiments did not show this minimum in any of the curves obtained from measurements in waveguide.

The determination of the phase transition type (order-disorder or displacive) is quite a difficult task. Order-disorder type phase transitions are mostly observed in organic ferroelectrics such as potassium dihydrogen phosphate (KDP),⁴⁶ triglycine sulphate (TGS), tris-sarcosine calcium chloride (TSCC).^{47,48} It is difficult to find systems of order-disorder type in inorganic compounds as perovskite oxides. As mentioned before there are evidence that classical ferroelectrics has a coexistence of order-disorder and displacive phase transitions.^{14-16,19} In the most of perovskites ferroelectrics, the microscopic origin of polarization is off-centering of cations. Therefore, in the temperature range far from T_C , the displacive nature is dominant. However, in the vicinity of T_C , the shallow minima of the potential (for example, the 8-site model in BaTiO₃) cause the order-disorder nature and the soft mode becomes overdamped. However, in vibrational spectroscopy, it is difficult to distinguish between overdamped soft mode and relaxation process of order-disorder nature in the vicinity of T_C .

Order-disorder and displacive models of phase transition are examined under the assumption of homogeneity. Relaxors, on the other hand, are heterogenous systems and are often considered as order-disorder systems⁴⁹ although the picture is much more complicated. In general, Mg ions favor on-centered, while Nb and Ti ions favor off-centered (ferro-active) positions. Far above the Curie temperature, Nb and Ti ions show the displacive nature, but in the vicinity of T_C the order-disorder nature according to the 8-site model is fulfilled. The charge disorder and lattice mismatch by the random occupation of three different cations may be the cause of the diffusive nature of soft mode. In addition, off-centered cations might couple to the off-center Pb ions which may also show order-disorder nature. These off-center displacements in shallow potential minima can be the origin of the fact that the minimum of dielectric permittivity near T_C is smeared as shown in the [supplementary material](#).

$$\frac{1}{\epsilon'} = \frac{1}{\epsilon_{max}} + \frac{(T - T_{max})^\gamma}{2\epsilon_{max}\delta^\gamma}. \quad (3)$$

Another important factor which was overlooked in the literature is the application of modified Curie-Weiss law

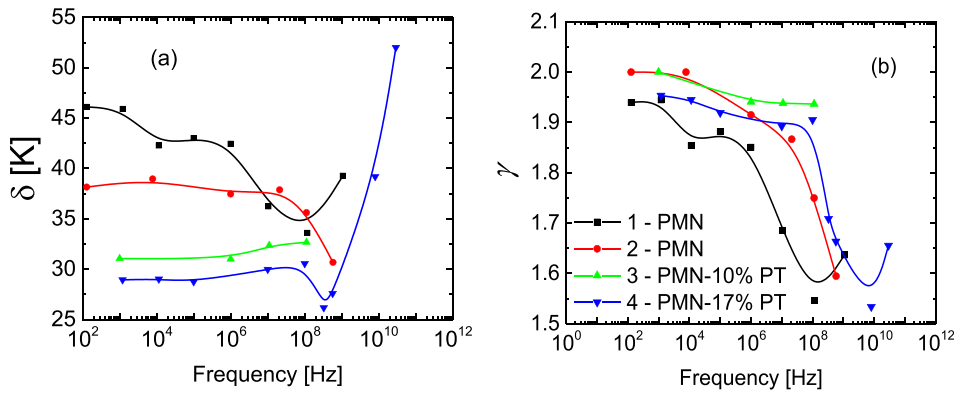


FIG. 4. Frequency dependence of modified Curie-Weiss law parameters: 1—PMN,³¹ 2—PMN,⁵⁰ 3—PMN-10%PT,⁵¹ 4—this work.

(Eq. (3)). The first application of the modified Curie-Weiss law, which was based on the distribution of phase transition temperatures, was empirically used to describe lead zirconate titanate⁵² and potassium strontium niobate.⁵³ Later on, it was used as a common equation to various perovskite ferroelectrics.⁵⁴ Usually, the literature provides the parameters obtained at certain frequencies. The broadband dielectric spectroscopy allowed us to analyse the parameters of modified Curie-Weiss law at different frequencies. The frequency dependences of modified Curie-Weiss law parameters are represented in Figure 4. These parameters are nearly frequency independent up to 100 MHz. The parameter γ (Fig. 4(b)) describes the relaxor behaviour of the system. It seems that above 100 MHz this parameter starts decreasing with the frequency. Similar behaviour can be observed in PMN and PMN-10%PT single crystals. Such dependence can indicate that the contribution of polar clusters diminishes with the increase of frequency. We speculate that this result can be related to the size of PNRs. The reason for such unusual dispersion can be related to the volume fraction of PNRs which contributes to permittivity. Very similar behaviour can be observed in other relaxor single crystals. There is a great possibility that with further increase of frequency this parameter converges to 1.0 which describes Curie-Weiss law from Landau theory. This should be tested with higher frequencies although it is a challenging and time consuming experiment to perform, but this experiment hints that it might be possible to detect this “suppressed ferroelectricity” by conventional experimental techniques.

Finally, the diffusivity parameter δ (Fig. 4(a)) decreases with the increase of PT concentration at lower frequencies. This indicates that the long range order is being enhanced by the PT concentration, because we replace Mg and Nb ions with Ti ions which decrease charge disorder. This substitution decreases the charge disorder. The opposite result was reported for the samples with a different valence (i.e., La^{3+} , W^{6+})³⁰ where the diffusivity increases with these dopants. The enhancement of CORs in such a case is achieved but it also enhances the charge disorder. This interchange makes it difficult to distinguish the impact of CORs and RFs unambiguously.

It should also be noted that measurements at different frequencies reveal different contributions to permittivity. At low frequencies, we have the contribution of all broad distribution of the relaxation times, including the lowest frequencies, which exhibit freezing according to the Vogel–Fulcher

law. This large contribution to dielectric permittivity at lower frequencies arises due to PNRs. As the frequency increases, the contribution of PNRs is less significant (as their dynamics are expected to be strongly influenced by their size). Thus, the characteristic features of order-disorder phase transition are observed due to heavily overdamped TO phonon at the zone center. Due to this reason, the parameter γ goes to 1.0 as the frequency increases. This hints that the dynamics of PNRs and the dynamics of order-disorder phase transition exist in the system simultaneously.

IV. CONCLUSIONS

The detailed studies of dielectric properties of PMN-17PT single crystals in a broad frequency range were conducted. Apparently, the phase transition in PMN-17PT has common characteristics to order-disorder and relaxor-like dynamics. This shows that we have a broad distribution of the relaxation times: low frequency part of spectrum resembles PNR-like dynamics and at high frequency part have order-disorder phase transition characteristics. This feature can particularly be attributed to the existence of the sub-lattice where random fields suppress the ferroelectric phase transition and the sub-lattice where the ferroelectric ordering takes place. This phase transition is the fingerprint of the systems with intermediate random fields.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for modelling of 2nd order phase transition which shows that the critical slowing down can be masked due to the broadening of dielectric spectra.

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¹Z. Kutnjak, J. Petzelt, and R. Blinc, *Nature* **441**, 956 (2006).

²B. Noheda, J. A. Gonzalo, L. E. Cross, R. Guo, S.-E. Park, D. E. Cox, and G. Shirane, *Phys. Rev. B* **61**, 8687 (2000).

³B. Noheda, D. E. Cox, G. Shirane, R. Guo, B. Jones, and L. E. Cross, *Phys. Rev. B* **63**, 014103 (2000).

⁴Z.-G. Ye, B. Noheda, M. Dong, D. Cox, and G. Shirane, *Phys. Rev. B* **64**, 184114 (2001).

⁵J.-M. Kiat, Y. Uesu, B. Dkhil, M. Matsuda, C. Malibert, and G. Calvarin, *Phys. Rev. B* **65**, 064106 (2002).

- ⁶B. Noheda, D. E. Cox, G. Shirane, J. Gao, and Z.-G. Ye, *Phys. Rev. B* **66**, 054104 (2002).
- ⁷H. Fu and R. E. Cohen, *Nature* **403**, 281 (2000).
- ⁸Z. Kutnjak, R. Blinc, and Y. Ishibashi, *Phys. Rev. B* **76**, 104102 (2007).
- ⁹M. Ahart, M. Somayazulu, R. E. Cohen, P. Ganesh, P. Dera, H. Mao, R. J. Hemley, Y. Ren, P. Liermann, and Z. Wu, *Nature* **451**, 545 (2008).
- ¹⁰W. Cochran, *Adv. Phys.* **9**, 387 (1960).
- ¹¹G. Shirane, J. D. Axe, J. Harada, and J. P. Remeika, *Phys. Rev. B* **2**, 155 (1970).
- ¹²G. Shirane, B. C. Frazer, V. J. Minkiewicz, J. A. Leake, and A. Linz, *Phys. Rev. Lett.* **19**, 234 (1967).
- ¹³Y. Luspjn, J. L. Servoin, and F. Gervais, *J. Phys. C: Solid State Phys.* **13**, 3761 (1980).
- ¹⁴E. A. Stern, *Phys. Rev. Lett.* **93**, 037601 (2004).
- ¹⁵R. Pirc and R. Blinc, *Phys. Rev. B* **70**, 134107 (2004).
- ¹⁶A. Bussmann-Holder, H. Beige, and G. Völkel, *Phys. Rev. B* **79**, 184111 (2009).
- ¹⁷M. Stachiotti, A. Dobry, R. Migoni, and A. Bussmann-Holder, *Phys. Rev. B* **47**, 2473 (1993).
- ¹⁸J. Hlinka, T. Ostapchuk, D. Nuzhnyy, J. Petzelt, P. Kuzel, C. Kadlec, P. Vanek, I. Ponomareva, and L. Bellaiche, *Phys. Rev. Lett.* **101**, 167402 (2008).
- ¹⁹B. Zalar, V. V. Laguta, and R. Blinc, *Phys. Rev. Lett.* **90**, 037601 (2003).
- ²⁰R. Blinc, B. Zalar, V. V. Laguta, and M. Itoh, *Phys. Rev. Lett.* **94**, 147601 (2005).
- ²¹P. M. Gehring, S. Wakimoto, Z.-G. Ye, and G. Shirane, *Phys. Rev. Lett.* **87**, 277601 (2001).
- ²²P. M. Gehring, S.-E. Park, and G. Shirane, *Phys. Rev. Lett.* **84**, 5216 (2000).
- ²³S. B. Vakhruhev and S. M. Shapiro, *Phys. Rev. B* **66**, 214101 (2002).
- ²⁴V. Bovtun, S. Kamba, A. Pashkin, M. Savinov, P. Samoukhina, J. Petzelt, I. P. Bykov, and M. D. Glinchuk, *Ferroelectrics* **298**, 23 (2004).
- ²⁵I. P. Swainson, C. Stock, P. M. Gehring, G. Xu, K. Hirota, Y. Qiu, H. Luo, X. Zhao, J.-F. Li, and D. Viehland, *Phys. Rev. B* **79**, 224301 (2009).
- ²⁶J. Banys, R. Grigalaitis, A. Mikonis, J. Macutkevicius, and P. Keburis, *Phys. Status Solidi C* **6**, 2725 (2009).
- ²⁷N. Takesue, Y. Fujii, M. Ichihara, and H. Chen, *Phys. Rev. Lett.* **82**, 3709 (1999).
- ²⁸T. Steilmann, B. J. Maier, M. Gospodinov, U. Bismayer, and B. Mihailova, *J. Phys.: Condens. Matter* **26**, 175401 (2014).
- ²⁹X. Long, A. A. Bokov, Z.-G. Ye, W. Qu, and X. Tan, *J. Phys.: Condens. Matter* **20**, 015210 (2008).
- ³⁰X. Zhao, W. Qu, X. Tan, A. A. Bokov, and Z.-G. Ye, *Phys. Rev. B* **79**, 144101 (2009).
- ³¹D. Jablonskas, R. Grigalaitis, J. Banys, A. A. Bokov, and Z.-G. Ye, *Appl. Phys. Lett.* **107**, 142905 (2015).
- ³²G. A. Samara, *J. Phys.: Condens. Matter* **15**, R367 (2003).
- ³³S. W. Choi, R. T. R. ShROUT, S. J. Jang, and A. S. Bhalla, *Ferroelectrics* **100**, 29 (1989).
- ³⁴K. Katayama, M. Abe, T. Akiba, and H. Yanagida, *J. Eur. Ceram. Soc.* **5**, 183 (1989).
- ³⁵D. Phelan, C. Stock, J. A. Rodriguez-Rivera, S. Chi, J. Leão, X. Long, Y. Xie, A. A. Bokov, Z.-G. Ye, P. Ganesh, and P. M. Gehring, *Proc. Natl. Acad. Sci. U.S.A.* **111**, 1754 (2014).
- ³⁶T. Y. Koo, P. M. Gehring, G. Shirane, V. Kiryukhin, S.-G. Lee, and S.-W. Cheong, *Phys. Rev. B* **65**, 144113 (2002).
- ³⁷C. Stock, D. Ellis, I. P. Swainson, G. Xu, H. Hiraka, Z. Zhong, H. Luo, X. Zhao, D. Viehland, R. J. Birgeneau, and G. Shirane, *Phys. Rev. B* **73**, 064107 (2006).
- ³⁸H. Luo, G. Xu, H. Xu, P. Wang, and Z. Yin, *Jpn. J. Appl. Phys., Part 1* **39**, 5581 (2000).
- ³⁹J. Banys, S. Lapinskas, S. Rudys, S. Greicius, and R. Grigalaitis, *Ferroelectrics* **414**, 64 (2011).
- ⁴⁰J. Grigas, *Microwave Dielectric Spectroscopy of Ferroelectrics and Related Materials* (CRC Press, 1996).
- ⁴¹J. Grigas, A. Brilingas, and V. Kalesinskas, *Ferroelectrics* **107**, 61 (1990).
- ⁴²M. Ivanov, J. Banys, S. Rudys, and R. Grigalaitis, *Ferroelectrics* **367**, 229 (2008).
- ⁴³Y. Guo, H. Luo, D. Ling, H. Xu, T. He, and Z. Yin, *J. Phys.: Condens. Matter* **15**, L77 (2003).
- ⁴⁴T. H. Kim, S. Kojima, and J.-H. Ko, *Curr. Appl. Phys.* **14**, 1643 (2014).
- ⁴⁵S. Kojima and S. Tsukada, *Ferroelectrics* **405**, 32 (2010).
- ⁴⁶P. S. Peercy, *Phys. Rev. Lett.* **31**, 379 (1973).
- ⁴⁷G. V. Kozlov, A. A. Volkov, J. F. Scott, G. E. Feldkamp, and J. Petzelt, *Phys. Rev. B* **28**, 255 (1983).
- ⁴⁸R. Mackeviciute, M. Ivanov, J. Banys, N. Novak, Z. Kutnjak, M. Wencka, and J. F. Scott, *J. Phys.: Condens. Matter* **25**, 212201 (2013).
- ⁴⁹R. Blinc, in *Ferro-Antiferroelectricity*, edited by N. S. Dalal and A. Bussmann-Holder (Springer, Berlin, Heidelberg, 2007), pp. 51–67.
- ⁵⁰R. Grigalaitis, J. Banys, A. Kania, and A. Slodczyk, *J. Phys. IV Proc.* **128**, 127 (2005).
- ⁵¹R. Grigalaitis, J. Banys, A. Brilingas, J. Grigas, A. Kania, and A. Slodczyk, *Ferroelectrics* **339**, 21 (2006).
- ⁵²H. T. Martirena and J. C. Burfoot, *Ferroelectrics* **7**, 151 (1974).
- ⁵³R. Clarke and J. C. Burfoot, *Ferroelectrics* **8**, 505 (1974).
- ⁵⁴K. Uchino and S. Nomura, *Ferroelectrics* **44**, 55 (1982).