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Dielectric properties of high-pressure synthesized relaxor $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ ceramics

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Abstract

Single-phase perovskite $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) ceramics were synthesized from stoichiometric oxide mixtures under conditions of high pressures and temperatures. Results of dielectric studies of this material show that the high-pressure PMN ceramics consist of two phases. One of them exhibits the properties of a dipole-ordering phase with a diffuse transition and another is a relaxor–ferroelectric phase. When annealing, the high-pressure synthesized PMN ceramics acquire the features of classical relaxor PMNs. The effect of high-pressure processing on cation ordering/displacements and thereby on dielectric properties is discussed.

1. Introduction

Relaxor-ferroelectrics (relaxors) occupy a particular place among the complex oxides ($\text{AB}'_m\text{B}''_{1-m}\text{O}_3$) with promising dielectric properties. In contrast to normal ferroelectrics they are known to exhibit strong frequency dispersion of the dielectric response in the temperature range of the diffuse permittivity maximum (T_m) and no structural phase transition across T_m [1, 2].

Several approaches, which differ in their initial premises on the existence of long- or short-range dipole ordering in these systems, have been introduced to account for their physical behaviour. Smolenskii *et al* [3] originally proposed a concept of the diffuse phase transition, resulting from composition fluctuations on a microscopic scale. The complex perovskites, e.g. lead magnesium niobate ($\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ —PMN), have been considered as a mix of the regions (clusters) with a local temperature of the transition into a ferroelectric state. Burns and Dacol [4] have proved the existence of the polar regions in relaxors at higher temperatures than the dielectric permittivity maximum. Subsequently the approaches of

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superparaelectrics [1] and dipole glasses [5] were proposed where relaxor–ferroelectrics are considered as systems with large dipoles (polar clusters) being independent and interacting with each other, respectively. Both of them are based on the concept of short-range dipole ordering. Many experimental data confirmed a dipole glass state in relaxors [5, 6]. However, some facts, such as Barkhausen pulses during polarization of PMNs or an increase in the dielectric permittivity of relaxors with increasing amplitude of the applied ac field, etc, might be explained only by domain-type dynamics [7], i.e. in terms of ferroelectric long-range ordering. A spherical random bond–random field (SRBRF) model has recently been proposed [8], which incorporates the peculiar properties of both dipole glass [5] and random field [7] models. In the framework of the SRBRF model the main features of the dielectric behaviour of PMN-related relaxors have been described, in good agreement with experimental results. Nevertheless, the microscopic mechanism of the relaxor behaviour is still a matter of discussion.

In spite of a variety of descriptions of the relaxor phenomenon it is generally accepted that both a chemical disorder and competing interactions are necessary for an appearance of a relaxor state [9, 10]. In the early ‘space charge’ model by Chen *et al* [11], PMN was considered as consisting of $\text{Mg}^{2+}/\text{Nb}^{5+}$ 1:1 ordered nano-domains embedded in a Nb-rich perovskite matrix. The results obtained by Davies and Akbas [12] on modifications in the cation order in PMN-related ceramics have demonstrated that the achieved rates of B-site ordering could not be consistent with the predictions of the above model. The size and volume fraction of these ordered regions would result in an incredibly high degree of charge imbalance in the ordered systems. On the other hand, these results are in agreement with a charge balanced ‘random-layer’ model [11, 12]. In this model, ordered PMN-related perovskites are considered as 1:1 B-site ordered, with a chemical composition $\text{Pb}([\text{B}_{2/3}^{2+}\text{B}_{1/3}^{5+}]_{1/2}[\text{B}^{5+}]_{1/2})\text{O}_3$. Recent analytical electron microscopy studies [13] have revealed a strong Mg/Nb fluctuation in both the ordered and disordered domains in PMN.

Samara *et al* [14, 15] have revealed a pressure-induced ferroelectric-to-relaxor crossover in a variety of PMN-related perovskite systems. High hydrostatic pressure was found to suppress the permittivity and shift its peaks towards lower temperatures. On the other hand, as reported by Yasuda and co-workers [16], the phase transition in disordered $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ loses its relaxor features with increasing pressure and finally becomes a normal antiferroelectric (AFE). High pressure reduces the peak value of the dielectric constant and considerably increases the temperature of the dielectric peak. This phenomenon has been mainly attributed to an ordering effect of pressure in 1:1 complex perovskites. Dielectric properties of the complex perovskites are known to depend strongly on a cation ordering degree in the sublattices. For instance, $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ (PST) is a ferroelectric at the complete cation $\text{Sc}^{3+}/\text{Ta}^{5+}$ ordering and it shows relaxor properties at disordering in the perovskite B-sublattice. The cation ordering degree depends on the technology of the preparation of the samples. PST synthesized under high pressure was shown to be characterized by a high ordering degree [17].

The present work reports on high-pressure synthesis and dielectric characterization of the perovskite $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics. Single-phase perovskite PMN ceramics were synthesized directly from a stoichiometric oxide mixture without preparing an intermediate columbite phase [18]. Features of their dielectric response and its evolution on annealing were analysed in terms of areas with different cation ordering degrees, whose dielectric characteristics are affected by high pressure in different ways.

2. Experimental procedure

The PMN ceramics were prepared directly from an oxide mixture. High quality PbO , MgO and Nb_2O_5 powders were mixed in the proper ratio and ball-milled in ethanol for 1 h.

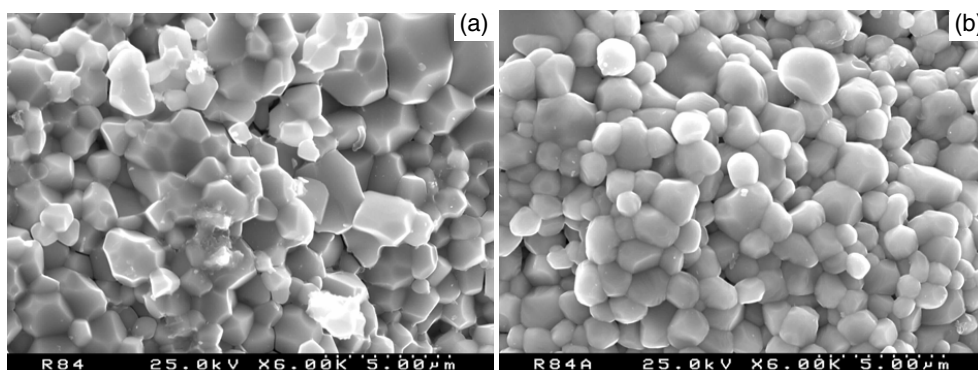


Figure 1. Microstructure of the fractured surface of the high-pressure synthesized PMN ceramics annealed for 2 h at 700 (a) and 1150 K (b).

The dried mixture was then pressed into pellets 4.5 mm in diameter and about 4 mm in height. High-pressure and high-temperature treatment of the samples was performed in an anvil press DO-138A with a press capacity up to 6300 kN. Single-phase PMN ceramics were synthesized at 5 GPa and 1400 K. The processing time did not exceed 5 min.

Phase identification and determination of the crystal lattice parameters of the compounds were carried out by x-ray diffraction (XRD) using Cu $K\alpha$ radiation and a DRON-3M diffractometer. The microstructure of the fractured surface of the ceramics was studied by scanning electron microscopy (SEM, Hitachi S-4100).

As-synthesized PMN samples were polished to obtain discs of 0.4–0.5 mm thickness and then electroded with a silver paste, followed by annealing at 700 K. Measurements of dielectric permittivity and loss tangent were carried out on samples annealed at several temperatures between 700 and 1100 K. Permittivity and loss were measured as a function of temperature at frequencies of 0.1, 1, 10 kHz and 1 MHz using E7-12 and E7-14 LCR meters on cooling from 500 to 77 K.

3. Results and analysis

The structure of the high-pressure synthesized PMN was found to be cubic perovskite with the lattice parameter $a = 4.048 \pm 0.001 \text{ \AA}$ at room temperature. It is essentially close to the value reported previously for PMN ceramics prepared by the conventional mixed-oxide route [19]. SEM observations of the high-pressure PMN ceramics revealed a dense small-grain microstructure (figure 1(a)). In order to check the temperature stability of the high-pressure prepared ceramics, XRD analysis of samples annealed at different temperatures was carried out. The perovskite PMN phase was found to remain at normal pressures up to 1150 K. Figure 1(b) shows the PMN microstructure after annealing at 1150 K for 2 h. Some evolution of the grains are observed, such as surface melting and no traces of a second phase. When heating above this temperature, the appearance of a pyrochlore phase was detected. The high-pressure synthesized PMN ceramics were characterized by narrow diffraction lines with $K\alpha_1$ and $K\alpha_2$ doublets well separated. An annealing at temperatures below the perovskite phase decomposition did not lead to any modification of the diffraction line profiles.

Dielectric studies of the high-pressure PMN ceramics revealed that both real (ϵ') and imaginary (ϵ'') parts of the dielectric permittivity change strongly when annealing at elevated temperatures. The temperature dependence of the dielectric response for PMN samples

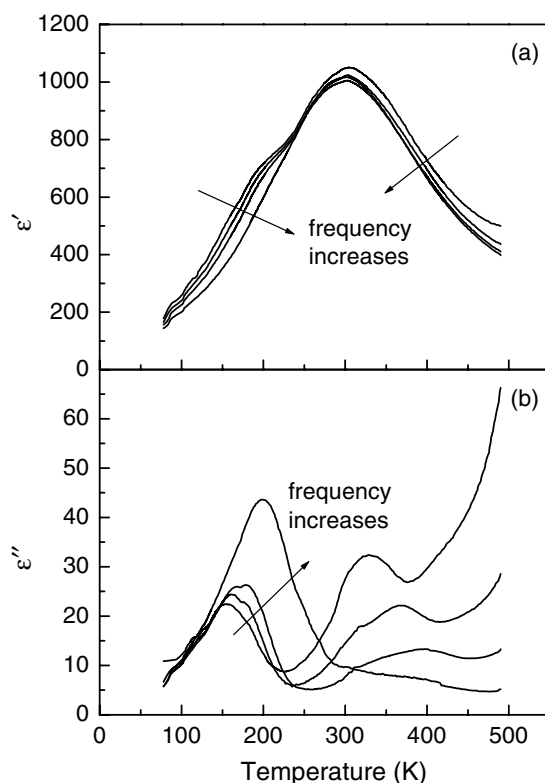


Figure 2. Temperature dependence of the real— ϵ' (a) and imaginary— ϵ'' (b) parts of the dielectric permittivity at 0.1, 1, 10 kHz and 1 MHz for high-pressure PMN ceramics annealed at 700 K.

annealed at 700 K is shown in figure 2. One can see two particular temperature regions corresponding to different behaviours of ϵ' and ϵ'' above and below 250 K, respectively. In the high-temperature range a diffuse maximum of ϵ' is observed at about 300 K (T'_m). Its position does not depend on the frequency of the applied electrical field (10^2 – 10^6 Hz). The $\epsilon''(T)$ curves in this range also exhibit a broad maximum (at T''_m). It should be noted that some dispersion of ϵ' and ϵ'' is observed near T'_m and T''_m , respectively. This appears to result from a contribution of the dielectric response related to lattice defects, which are formed during high-pressure synthesis. This assumption is proved by an increase of the dielectric loss with temperature, which is especially evident at low frequencies (see figure 2(b)). If the contribution of defects to ϵ'' is taken into account, the position of the maximum, T''_m , is nearly frequency-independent. Therefore, the behaviour of the PMN dielectric response near T'_m corresponds to the characteristic features of the diffuse ferroelectric phase transition, namely a broad maximum of $\epsilon'(T)$ and the absence of frequency dispersion.

In contrast, in the temperature region below 250 K both real and imaginary parts of the PMN dielectric permittivity demonstrate a frequency-dependent behaviour. An anomaly of $\epsilon'(T)$ looks like a shoulder in the curves and $\epsilon''(T)$ exhibits a maximum in the temperature range 150–200 K, which shifts towards a higher temperature with increasing frequency of the applied field. The behaviour of the dielectric response of the high-pressure synthesized PMN ceramics in this temperature range is similar to a relaxor-ferroelectric. Its imaginary part was

Table 1. Parameters of the $\varepsilon''(T)$ fitting with the Vogel–Fulcher equation.

High-pressure synthesized PMN ceramics	T_{VF} (K)	f_0 (Hz)	E_A (eV)
Annealed at 700 K for 2 h	90	4.09×10^{11}	0.121
Annealed at 1100 K for 2 h	209	3.11×10^{12}	0.084

found to follow the empirical Vogel–Fulcher equation [9]:

$$f = f_0 \exp \left\{ - \frac{E_A}{k(T_m'' - T_{VF})} \right\}, \quad (1)$$

where f is the frequency of the applied field and the adjustable parameters, T_{VF} , f_0 and E_A , are the Vogel–Fulcher freezing temperature, a pre-exponential factor (characteristic frequency) and activation energy, respectively. Parameters of the $\varepsilon''(T)$ fitting with equation (1) for the material under study are summarized in table 1.

The Vogel–Fulcher law was supposed [5] to indicate a glass-like state in a system. Tagantsev [20] has shown this law does not necessary imply freezing of the relaxation time spectrum but could be related to its gradual broadening upon cooling without infinite increase. However, it was revealed later [21] that there is a freezing of the spectra at a non-zero temperature, at least for PMN.

The Vogel–Fulcher temperature, T_{VF} , is considered as the extrapolated temperature where the characteristic relaxation time diverges. It differs from the freezing temperature (T_f) of the polar regions determined as a temperature of appearance of the dipolar glass state. Since at T_f the longest relaxation time diverges, $T_f > T_{VF}$ in any cases. However, T_{VF} is suitable for estimating roughly the freezing temperature. The activation energy, E_A , corresponds to the height of the highest potential barrier of a relaxing species at temperatures far above T_{VF} . Regarding the pre-exponential factor, f_0 , it is more convenient to consider the reciprocal value, $\tau_0 = 1/f_0$. This parameter is the lowest relaxation time and is believed to relate to the smallest polar regions in a relaxor system [22].

The dielectric response of high-pressure PMN ceramics air-annealed at 900–1100 K is shown as a function of temperature in figure 3. There is evolution in both the $\varepsilon'(T)$ and $\varepsilon''(T)$ dependences in comparison with those of PMN annealed at 700 K (see figure 2). As the annealing temperature increases, the low-temperature frequency-dependent anomaly shifts towards higher temperatures, while the diffuse dielectric maximum shifts to the opposite side. After treatment at 900 K both anomalies were revealed to combine into a single dielectric maximum. Peak values of both the real and imaginary parts of the permittivity rise with further increases in the annealing temperature. It is clear from figure 3 that the high-pressure PMN annealed at 1100 K exhibited solely relaxor behaviour. Moreover, its dielectric properties were found to correspond to PMN ceramics obtained by a conventional ceramic route [18]. The shape of the $\varepsilon'(T)$ and $\varepsilon''(T)$ curves, their peak values as well as T_m' and T_m'' at each particular frequency nearly coincided with those of the well-known PMN. Fitting ε'' with equation (1) gave the parameters close to the T_f , f_0 and E_A values for this relaxor-ferroelectric material [5].

Taking into account the above-mentioned physical meaning of the Vogel–Fulcher fitting parameters, it is possible to estimate the dielectric evolution of the PMN ceramics when annealing. It has been proposed [22] that the distribution of relaxation times in the relaxor phase is to be controlled by the size distribution of the polar regions. Values of the lowest relaxation time, τ_0 , were evaluated to be 10^{-12} and 10^{-13} s for samples annealed at 700 and 1100 K, respectively. These correspond to the smallest polar regions, which are bigger than a unit cell size (with $\tau_0 \sim 10^{-14}$ s, that is, of the order of the reciprocal optical phonon frequency) [23]. It is clear that the size of the smallest regions does not characterize a distribution of these regions.

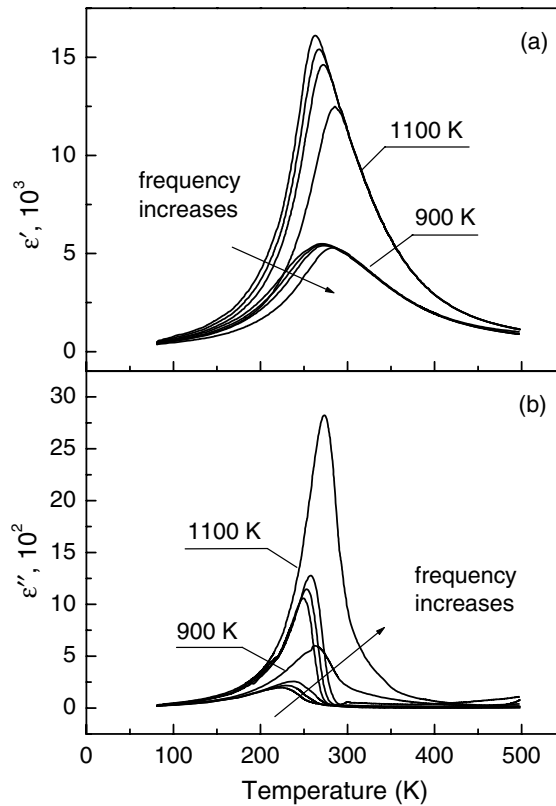


Figure 3. Temperature dependence of real (a) and imaginary (b) parts of the dielectric permittivity at 0.1, 1, 10 kHz and 1 MHz for PMN ceramics annealed at 900 and 1100 K.

From the common consideration of the nature of relaxors [9, 24] one can assume there is not too large a variation in the polar region size. It should also be noted that polar regions are believed not to change considerably in size as the temperature decreases down to T_f [9]. All these allow us to suppose that larger (on average) polar regions exist in ceramics annealed at 700 K than in those treated at 1100 K. That appears also to be the reason why the former has a higher E_A value in comparison with the latter. The main feature of the $\epsilon''(T)$ frequency-dependent behaviour of the PMN ceramics annealed at 700 K is an appreciably lower T_{VF} (table 1). Even though the $\epsilon''(T)$ peak in these is located in a lower temperature range (compare figures 2 and 3), their T_{VF} is shifted down by a wider temperature interval with respect to the peak at each measured frequency. For instance, the difference $T_m''(1 \text{ kHz}) - T_{VF}$ was found to be 73 K in these as against 44 K in ceramics annealed at 1100 K. It means that the freezing process in PMN annealed at 700 K is relatively slowed down. This fact is apparently related to the difference in the size distribution of the polar regions and the interaction between them.

Figure 4 shows the dielectric permittivity characteristics of high-pressure PMN ceramics as a function of annealing temperature. As can be seen, peak values of ϵ'' measured for a range of relaxor behaviours increase on annealing. T_m'' values corresponding to these peaks also increase when approaching saturation. It is known that the frequency shift of the dielectric peak defined by $\Delta T_m = T_m(10^6 \text{ Hz}) - T_m(10^2 \text{ Hz})$ can serve as a measure of the dispersion and diffuseness of a phase transition [25]. However, it concerns mainly that real part of the permittivity,

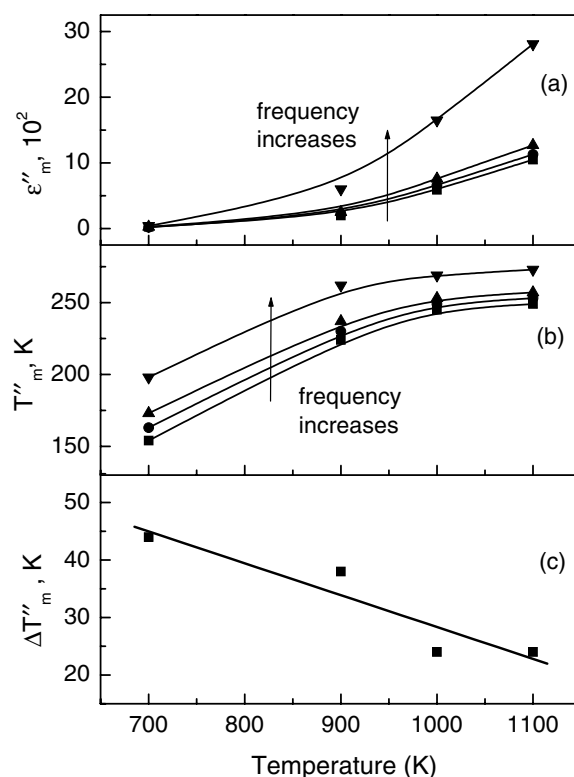


Figure 4. Value of ε'' at maximum (a), temperature of the maximum (b) and the value $\Delta T''_m = T''_m(10^6 \text{ Hz}) - T''_m(10^2 \text{ Hz})$ (c) for high-pressure PMN ceramics at frequencies of 0.1, 1, 10 kHz and 1 MHz as a function of annealing temperature.

$\varepsilon'(T)$. In our case $\Delta T'_m$ was difficult to determine since the frequency-dependent region initially appeared as a shoulder in the $\varepsilon'(T)$ curve (figure 2(a)). It was also shown [25] that, unlike $\Delta T'_m$, the temperature range estimated for ε'' ($\Delta T''_m$) is less sensitive to compositional and processing variations when prepared by the conventional ceramic route since these do not strongly affect the basic loss mechanism in relaxors. Nevertheless, $\Delta T''_m$ of high-pressure PMN ceramics is seen from figure 4 to decrease almost two times after thermal treatment. These features of the material under study seem to be a consequence of high-pressure synthesis.

4. Discussion

While analysing the experimental data presented above for the PMN ceramics, the peculiar conditions of high-pressure processing should be taken into account, namely synthesis in a closed volume and a high reaction rate followed by fast cooling (quenching). A closed reaction volume prevents evaporation of the volatile lead oxide during the treatment. Due to a high rate of chemical reaction the ceramics obtained have small crystal grain sizes (see figure 1). As a result of fast cooling of the system after synthesis point defects of the crystal lattice might be formed. On the other hand, high pressure is known to promote B-site cation ordering.

The dielectric behaviour described above of the high-pressure synthesized PMN allows us to conclude that there are at least two kinds of dipole order transformations in this compound. The low temperature transition is a typical relaxor crossover accompanied by strong frequency

dispersion of the dielectric permittivity. Another one (at higher temperature) represents a diffuse ferroelectric phase transition characterized by the frequency-independent broad maximum of ϵ' . Thus, below the low-temperature transition a mixed (relaxor (R) and a dipole long-order) state appears to be present in high-pressure synthesized PMN. This two-phase state apparently is due to some compositional heterogeneity in PMN synthesized under high-pressure and temperature conditions. It was possible because of the characteristic features of the method, namely high reaction rate and fast cooling (quenching). Due to these, mechanical stresses and defects of the crystal lattice could arise in the ceramics during synthesis and quenching. Hence, in this sense, the high-pressure synthesized ceramics are not in equilibrium.

As already mentioned in the introduction, there are strong compositional fluctuations in PMN even prepared by the conventional ceramic route. High pressure is known to favour a regular atomic order; nevertheless, areas of slightly different composition and ordering degree might arise in the process of fast high-pressure synthesis. Let us identify the virtual regions of R- and dipole long-order phase with areas of the largest and smallest compositional fluctuations, respectively.

Recent high-pressure investigations of PMN by Raman spectroscopy [26] have revealed the fundamental pressure-induced changes in this relaxor material. One of them was attributed to the restoring of B-cations towards the centre of the BO_6 octahedra. Pressure (or compressive mechanical stress) suppresses the B-cation shifts that apparently result in the reduction of the dielectric constant and a decrease in the transition temperature. Although Pb^{2+} displacements are believed to be dominant in the origin of anomalous polar properties of lead-based perovskites, a polar 'active' B-cation (Nb^{5+} in PMN) plays an important role in dipole coupling [25]. It seems this restoring of the B-cation can be expressed in terms of a decrease in the correlation length for dipolar interactions with pressure [14]. Another pressure-induced change in the Raman spectrum of PMN [26] was interpreted as related to a modification of the type of Pb^{2+} displacement from parallel to antiparallel. Such antiparallel (AFE-type) displacements of Pb^{2+} were recently revealed [27] by high-resolution electron microscopy in PMN. The latest x-ray diffuse scattering study [28] clearly shows that high pressure suppresses the displacement disorder and promotes AFE long-range order in PMN. Regarding the material under study, pressure is expected to induce AFE Pb^{2+} displacements predominantly in the most compositionally regular regions of PMN. It seems reasonable that such antiparallel shifts are easier to induce in those particular volumes having a more regular cation arrangement.

Thus, high pressure is believed to reduce polarization in the relaxor regions and increase it in those regions of antiparallel cation displacements. The first effect leads to decreasing the temperature of the relaxor crossover according to that observed in PMN and related systems [14, 15]. Second, one should increase the temperature of the AFE transition, as it took place in antiferroelectrics under pressure [10, 16]. In both cases, however, their dielectric permittivity is expected to be reduced by high pressure. One can imagine that, after high-pressure synthesis followed by quenching, different areas of the PMN are under different effects of mechanical stresses. It is equivalent to being under different pressures and, therefore, the observed transition is diffuse. When annealing, most of these defects disappear and stresses are released, leading to solely relaxor behaviour of the ceramics.

5. Conclusions

The high-pressure/high-temperature synthesis method allows preparation of single-phase perovskite ceramics of PMN composition directly from a stoichiometric oxide mixture. These high-pressure PMN ceramics are non-equilibrium. There are areas of compositional fluctuations, with regions of higher and lower ordering degree being under different mechanical

stresses. High pressure is believed to induce antiparallel (AFE-type) displacements of Pb^{2+} in those areas of lowest compositional fluctuations and, at the same time, it suppresses B-cation shifts in the whole volume. Thus high pressure causes a double effect in PMN: it decreases the transition temperature in the more disordered areas and increases it in areas of the antiparallel Pb^{2+} displacements. In terms of the observed dielectric behaviour the PMN ceramics exhibit two kinds of dipole ordering transformations when the temperature decreases, namely a diffuse (AFE) phase transition and frequency-dependent (relaxor) crossover. An annealing of this high-pressure synthesized material leads to solely relaxor behaviour being typical of well-known PMN prepared by the conventional ceramic route.

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