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On short range ordering in the perovskite lead magnesium niobate

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The structural ordering characteristics of lead magnesium niobate (PMN) and solid solutions (PMN–PT) of PMN with lead titanate have been investigated using transmission electron microscopy (TEM). It is proposed that short range, non-stoichiometric 1 : 1 ordering of the Mg and Nb cations on an F-centred superlattice generates space charges which dominate the kinetics of the ordering process and inhibit the development of long-range order. Furthermore, it is demonstrated that by introducing off-valent La^{3+} ions on to the A-site sublattice, the local charges can be at least partially-compensated and an increase in the extent of structural ordering is consequently observed.

1. Introduction

Most of the ferroelectric relaxors which crystallize with the perovskite structure and correspond to the general formula $A(B'_xB''_{1-x})O_3$ can undergo at least short-range structural ordering of the B-site cations. In the B-site order–disorder-perovskites the degree of long-range order can be varied by means of suitable thermal treatments. This has been shown to have important consequences since the dielectric properties of this class of relaxor are directly dependent on the degree of B-site order (e.g. lead scandium tantalate (PST), lead scandium niobate (PSN), lead indium niobate (PIN) [1–4]), thereby providing another variable for the tailoring of properties. In most ferroelectric relaxors, however, the degree of order is not so readily altered and often can only be brought about by modifying the bulk composition [5, 6]. In some instances, such as in lead iron niobate (PFN), even short-range order is undetectable by conventional experimental techniques and a homogeneous disorder is believed to exist [7]. Nevertheless, in relaxors which exhibit some degree of short-range order, it is reasonable to suppose that even subtle changes in the state of structural order may also affect dielectric response (in addition to any effect resulting from necessary compositional modification) particularly if the two species of B-site cations are very different in electronic character.

The ideal perovskite structure can be considered as BO_6 octahedra centred on the corners of a simple cubic lattice and linked by the sharing of oxygen ions. The A-site cations are located in the interstitial positions between these octahedra. Ordering takes place in some of the $x = 1/2$ perovskites by the diffusion of B′ and B″ cations to nearest neighbour positions on the B-site sublattice. This results in the formation of an F-centred $2a_0 \times 2a_0 \times 2a_0$ superlattice (where a_0 is the lattice parameter). This superstructure can easily be identified by the presence of superstructure reflections in X-ray and electron diffraction patterns.

The ordering characteristics of most complex $A(B'_xB''_{1-x})O_3$ perovskites can largely be understood by considering the electrostatic and mechanical forces generated, respectively, by differences in electronic charge and in ionic radii of the B′ and B″ ions. Broadly speaking, materials possessing large differences in both valence and ionic size between the B′ and B″ cations show a strong tendency for order [8]. These empirical guidelines can be used successfully to predict the degree of order that is actually observed in a large number of relaxors that have the perovskite structure. Some perovskite materials, however, do not exhibit the long-range order that is to be expected from the above considerations of electrostatic and mechanical forces. Most materials falling into this category correspond to $x \neq 1/2$ in the general perovskite formula $A(B'_xB''_{1-x})O_3$ and PMN, where $x = 1/3$, is exemplary.

By means of TEM dark field and electron diffraction techniques, the behaviour of PMN–PT [$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$] solid solutions and the effect of La substitutions in the PMN [$Pb(Mg_{1/3}Nb_{2/3})O_3$] structure have been studied in order to elucidate the special ordering characteristics of this class of perovskite relaxor.

2. Experimental procedure

Samples examined in this study included PMN, PMN + 2 wt% La_2O_3 and solid solutions corresponding to $(1 - y)$PMN–y PT with y ranging from 0.07 to 0.4.

Ceramic samples were prepared via the columbite route [9] in order to avoid formation of parasitic pyrochlore phases. Both conventionally sintered (prepared by T. R. Shrout, Pennsylvania State University, USA) and hot pressed (prepared by P. Osbond, Allen Clark Research Centre, The Plessey Co., Northants, UK) ceramic materials were examined. The hot pressed ceramic was prepared with a small excess of PbO.

Samples for TEM observation were mechanically polished to a thickness of $\sim 30\,\mu$m prior to ion beam thinning. Examination of the samples was carried out using a Jeol-200CX transmission electron microscope which was operated at an accelerating voltage of 200 kV. The use of 200 keV electrons enhances sample penetration, thus enabling thicker regions, more representative of the bulk, to be examined. A Hexland low temperature goniometer stage was used to vary the sample temperature within the range $-176°\mathrm{C} < T^* < 150°\mathrm{C}$ where T^* represents the temperature indicated by the thermocouple. Slight differences between the sample temperature and the temperature indicated are expected because of local heating effects from the electron beam.

3. Results

With the exception of the 0.6 PMN–0.4 PT samples, $\{h + 1/2, k + 1/2, l + 1/2\}$ superstructure reflections (F-spots) were observed in all samples for both $\langle 1\,1\,0 \rangle$ and $\langle 2\,1\,1 \rangle$ zone axis diffraction patterns. The intensities of the F-spots were assessed by comparison with the intensities of the matrix reflections. Dark field (DF) imaging using one of the F-type reflections gives regions of light contrast associated with domains of B-site structural order. Figs 1a and b show respectively a DF image formed with the $\{3/2, 3/2, 3/2\}$ reflection and the corresponding $\langle 1\,1\,0 \rangle$ zone axis diffraction pattern, obtained from undoped PMN. In Fig. 1a the ordered domains have an average size of ~ 6 nm and only small deviations in this size are present across the whole grain. The F-spots associated with these domains are indicated in Fig. 1b. As the concentration of $PbTiO_3$ is increased within the PMN–PT solid solution both the intensities of the F-spots and the sizes of associated domains diminish. Fig. 2a shows domains of about 3 nm in dimension within the 0.93 PMN–0.07 PT solid solution. Fig. 2b is the $\langle 1\,1\,0 \rangle$ electron diffraction pattern from the 0.93 PMN–0.07 PT sample, which exhibits weaker superstructure reflections than those observed in undoped PMN. The reduction in the intensities of superstructure reflections is associated with the reduction in domain size. No significant spread of domain sizes is observed. Fig. 3 shows the $\langle 1\,1\,0 \rangle$ diffraction pattern of 0.8 PMN–0.2 PT. The F-spots are significantly weaker than that in undoped PMN and it proved impossible to obtain DF images with them. In the 0.6 PMN–0.4 PT sample (Fig. 4) the F-spots are completely absent. However, when only 2 wt % of lanthanum is substituted for lead an increase in both the intensity of the F-reflections and the domain size is observed (Figs 5a and b). In most grains a range of domain sizes from 5 to 35 nm is present. However, certain grains (as in Fig. 5a) were observed to exhibit domains up to 150 nm in size. The larger ordered domains frequently exist near the grain boundaries but clusters of large domains are occasionally found in the grain interior.

The F-spots become slightly more diffuse on heating the specimens from $-176°$C through to $150°$C, but no abrupt change in intensity is observed. Undoped, hot pressed PMN samples, annealed for 7 days at 970° C in a lead-oxide-rich atmosphere do not differ markedly in microstructure from PMN samples which have not been annealed.

Zone axis diffraction patterns exposed for long periods of time reveal the presence of very weak $\{h + 1/2, k + 1/2, 0\}$ reflections (referred to as α'-spots). These reflections are strongest in the $\langle 1\,0\,0 \rangle$ zone but proved to be too weak to produce DF images. The $\{h + 1/2, k + 1/2, 0\}$ reflections in the $\langle 1\,0\,0 \rangle$ zone for undoped PMN are indicated in Fig. 6. This figure also shows the presence of weak diffuse scattering parallel to the $\langle 1\,1\,0 \rangle$ direction.

The relative intensity variation of the α'-spots with respect to composition and temperature is similar to the intensity variation observed for the F-spots. Additions of $PbTiO_3$ to the PMN–PT solid solution produces weaker α'-reflections but small La substitutions increase their intensity. No abrupt change in

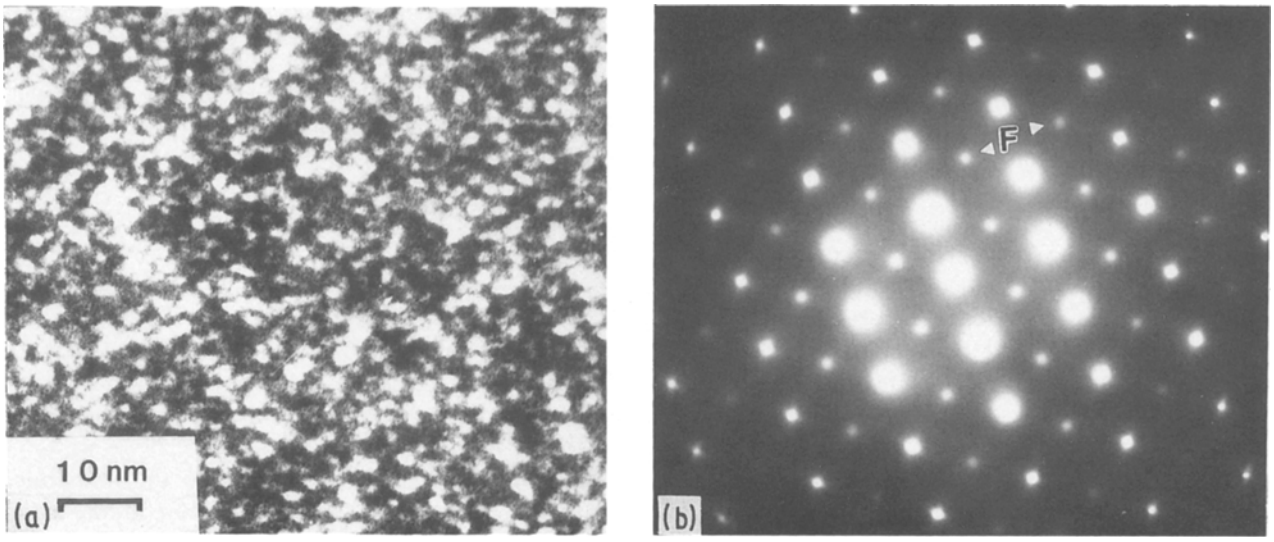

Figure 1 (a) Dark field image showing B-site ordered domains (bright areas) in undoped hot pressed PMN. (b) $\langle 1\,1\,0 \rangle$ zone axis selected area diffraction pattern taken from the grain in Fig. 1a. The F-spots are indicated.

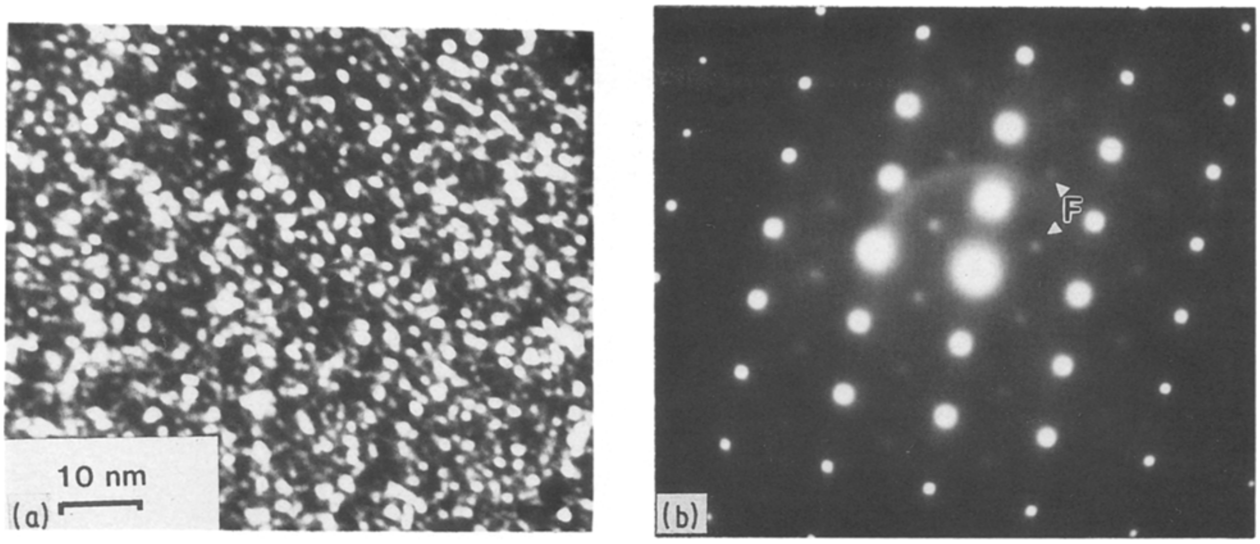

Figure 2 (a) Dark field image showing B-site ordered domains in conventionally sintered 0.93 PMN–0.07 PT. (b) ⟨1 1 0⟩ selected area diffraction pattern taken from Fig. 2a.

intensity of the α'-reflections is observed in the temperature range $-176°\mathrm{C} < T < 150°\mathrm{C}$.

4. Discussion

4.1. Ordering

The presence of F-spots indicates that an F-centred $2a_0 \times 2a_0 \times 2a_0$ superlattice exists in all samples with the exception of the 0.6 PMN–0.4 PT sample. Since the intensities of the F-spots do not change significantly with temperature it can be concluded that they are not associated specifically with either the ferroelectric phase or with tilting of the oxygen octahedra [10] but are chemical in origin.

The F-centred superstructure in PMN has previously been identified using high resolution [11] and dark field [12] imaging techniques. On the basis of X-ray data it has also been pointed out that a number of $x = 1/3$ and other $x = 1/2$ perovskites can order stoichiometrically provided the appropriate superlattice can develop [13, 14]. However, the ordering schemes proposed for such systems necessarily generate particular superlattice reflections. These superlattice reflections were not present within electron diffraction patterns observed in the current study.

We believe that our results demonstrate that non-stoichiometric 1 : 1 ordering of Mg and Nb cations takes place on an F-centred $2a_0 \times 2a_0 \times 2a_0$ superlattice in the PMN system. For the $x = 1/2$ materials such as PST, it is interesting to note that a charge imbalance which would accompany a non-stoichiometry between B-site cations would be reduced by the diffusion of these cations to alternate B-sites. In the case of a perovskite where $x \neq 1/2$, as in PMN (where $x = 1/3$ in the ideal compound), the implications of 1 : 1 order are less straightforward. In this case, the nucleation and growth of ordered domains implies the outward diffusion of B″ (excess) ion species into the circumferential zones which become enriched in element B″ (Nb in PMN). Thus in the absence of compensating charge effects, large electric fields would be generated in the lattice between ordered and disordered regions (with effective positive and negative charge respectively). These charge effects would become more severe as the ordered regions increase in

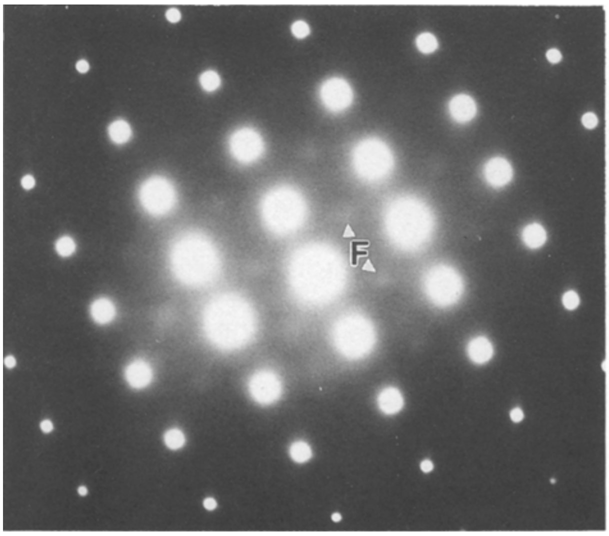

Figure 3 ⟨1 1 0⟩ selected area diffraction pattern from hot pressed 0.8 PMN–0.2 PT.

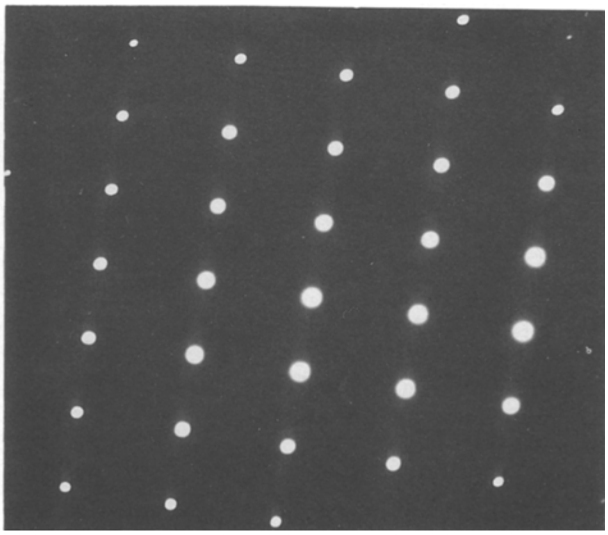

Figure 4 ⟨1 1 0⟩ selected area diffraction pattern from conventionally sintered 0.6 PMN–0.4 PT. The F-spots are absent.

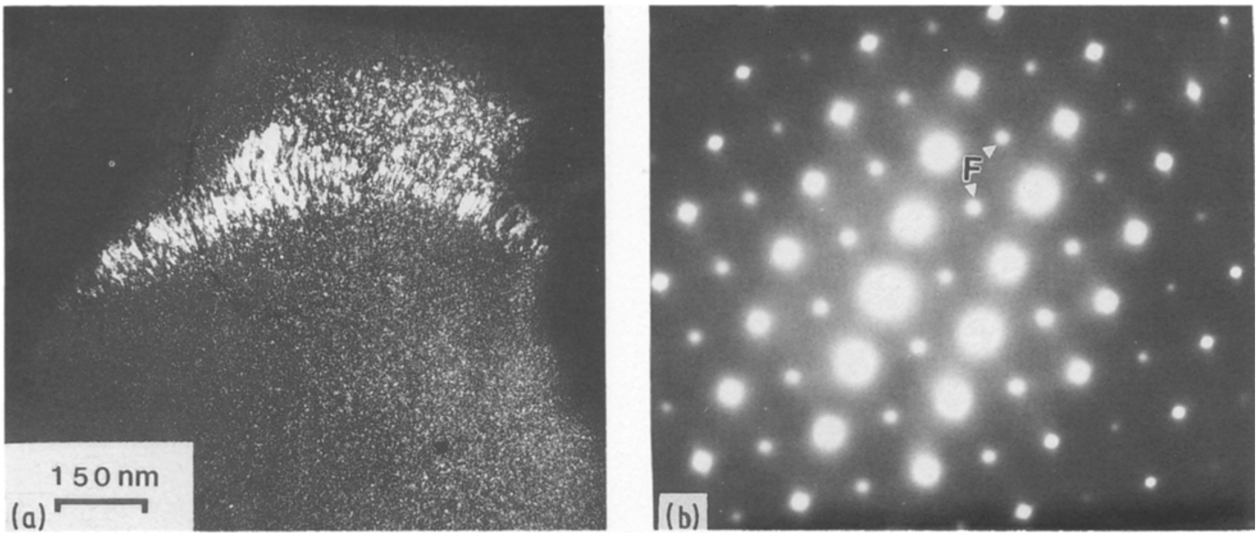

Figure 5 (a) Dark field image showing the influence of grain boundaries on the sizes of B-site ordered domains in hot pressed PMN + 2 wt % La_2O_3. Domains ranging from 5 to 150 nm in dimensions are present. (b) ⟨1 1 0⟩ selected area diffraction pattern taken from Fig. 5a.

size. In this case one may anticipate that an equilibrium domain size will be reached when the driving forces for B cation ordering (electrostatic and mechanical) are balanced by forces tending to disorder B-site cations (from the interactions between local space charges generated by the expansion of non-stoichiometrically ordered regions). In the case where space charges can be compensated by lattice defects, an equilibrium size of ordered domains is also anticipated when the space charges become too large to be compensated by existing defects. These views are supported by the observation that an equilibrium size for ordered domains of 6 nm is found in undoped PMN even after prolonged annealing. Exaggerated growth of ordered domains at grain boundaries has been reported in PST [15] and PSN [16] annealed ceramics. The existence of enhanced vacancy concentrations [17] which facilitate cation diffusion near grain boundaries was invoked to explain this phenomenon. No such effect has been found in PMN or 0.93 PMN–0.07 PT samples.

From considerations of ionic radii it is generally accepted that Ti ions occupy B-sites in PMN–PT solid solutions. It is not believed, however, that Ti ions are directly involved with the ordering process. Consideration of the possible 1 : 1 ordering of Mg and Ti ions yields an average B-site valency of + 3 and is therefore electrostatically less favourable than Mg : Nb order. Nb : Ti ion order is unlikely since the degree of order would be expected to increase with increasing $PbTiO_3$ content. Since a progressive decrease in B-site order is observed with increasing $PbTiO_3$ content it is possible that Ti ions 'dilute' the electrostatic and mechanical interactions which exist between Mg and Nb cations thus reducing their tendency to order.

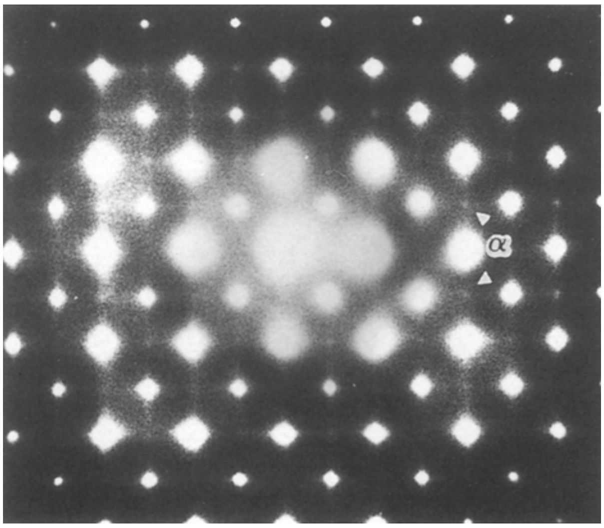

Figure 6 ⟨1 0 0⟩ selected area diffraction pattern of undoped hot pressed PMN. Weak α′-spots are indicated.

It is interesting to note that small substitutions of lanthanum oxide to PMN promote the formation of larger ordered domains and a non-uniformity of domain size. We believe that La^{3+} ions, which probably occupy Pb^{2+}/A-sites, aid in reducing the charge inbalance generated by non-stoichiometric ordering although the exact mechanism for this process is presently unclear. The associated lead vacancies may also relax bonding constraints thereby enhancing diffusion and facilitating ordering. The anomalously large ordered domains frequently observed near grain boundaries in La-doped PMN suggests that charge heterogeneity is no longer the limiting factor on domain size, as in PMN and PMN–PT systems, but that the kinetics of ordering is then governed by the usual factors constraining diffusion. Alternatively, the non-uniformity of domain sizes observed could be attributed to the segregation of La ions to the grain boundaries or to improper mixing during processing. Clusters of large ordered domains sometimes found in grain interiors also imply that a non-uniform distribution of La ions exists within these regions.

The origin of α′-spots observed in the current study is presently uncertain. α′-spots have previously been reported to be present within electron diffraction patterns of PST [15]. Since the intensities of α′-spots in PMN do not change significantly with temperature it is likely that they are chemical in origin. Furthermore, since the intensities of the α′-spots reduce with $PbTiO_3$ additions and increase with La substitutions, it is likely that their intensity is related to the extent of structural order. However, we note that the intensity dependence of the α'-spots with temperature is different for PMN and PST systems. It is therefore possible that the origin of the α'-spots in these two systems is different.

4.2. Electrical properties

Ordering may be anticipated to change either or both the amplitudes of compositional fluctuations and the sizes of the chemically distinct regions with which the broad phase transitions of relaxors have been associated [18, 19]. However, TEM studies have so far failed to reveal the mechanism by which the degree of order modifies the dielectric characteristics. No strong interactions are observed between macro-ferroelectric domains and the antiphase boundaries which define the ordered domains [15, 20]. This supports the view that the process of structural ordering influences the diffuse nature of relaxor paraelectric–ferroelectric (PE–FE) phase transitions only indirectly. However, the relationship between ordered domains and the micro-polar domains, which can be observed in unpoled relaxors [21, 22], is still ambiguous. Studies of the order–disorder relaxors, for which $x = 1/2$, has shown that an increase in the degree of structural order is associated with a less diffuse PE–FE phase transition and a reduction in frequency dispersion. Such observations therefore fit into the existing framework for relaxor behaviour. However, it has been shown that phase transitions exhibited by PMN become less diffuse and less frequency dependent (i.e. the relaxor tends to "normal" ferroelectric behaviour) with increasing $PbTiO_3$ content [23]. The present study illustrates that the size of ordered domains is reduced with increasing $PbTiO_3$ additions. There does therefore seem to be a basic antagonism in the relationship between stoichiometric order in $x = 1/2$ materials, non-stoichiometric 1 : 1 order in $x = 1/3$ materials and the corresponding trends in dielectric properties. In brief, an increase in order in the $x = 1/2$ relaxors reduces chemical inhomogeneity and therefore favours more "normal" dielectric behaviour. An increase in non-stoichiometric order in $x = 1/3$ relaxors promotes space charge fluctuations and the corresponding dielectric data shows an enhancement of the relaxor characteristics. In the latter case it is possible that some interaction may exist between the dipoles formed in the FE state and any uncompensated fluctuations in charge. Alternatively, it is apparent that the complete or partial compensation of charge fluctuations would involve significant alteration of the local defect chemistry. This suggests that although only small ordered domains may be able to form in relaxors like PMN, they may have a more significant effect on the dielectric permittivity as compared to the effect of a similar degree of order in a $x = 1/2$ relaxor. It is interesting to note however, that both systems appear to follow a common trend in that more "normal" ferroelectric behaviour is favoured as charge fluctuations are reduced. This is necessarily the result of a reduction in the variation between local B-site chemistry and bulk stoichiometry. We therefore suggest that the possibility of charge heterogeneity should be further investigated in relation to the influence of order on the dielectric behaviour of relaxors.

5. Conclusions

Using TEM techniques the ordering characteristics of PMN and PMN–PT solid solutions have been investigated. The restricted dimensions of the ordered domains which are observed in these systems are believed to be the result of charge fluctuations which develop as Mg and Nb ions order on alternate B-lattice sites. The ordering process is arrested when the space charges become too large to be accommodated by the structure or when the lattice is no longer able to compensate for such charges with existing lattice defects. A reduction in the ability to order is observed on adding $PbTiO_3$ to the PMN–PT solid solution. Ti ions are believed to 'dilute' the forces responsible for the ordering process. Substitution of off-valence La^{3+} ions on the Pb^{2+} sublattice enhance order by aiding in the charge compensating mechanisms. It is suggested that charge fluctuations which occur in relaxor materials affect both ordering and dielectric behaviour.

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