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Order and disorder in the relaxor ferroelectric perovskite $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ (PSN): comparison with simple perovskites BaTiO_3 and PbTiO_3

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Abstract. We report a structural evolution analysis of the long-range and local order and disorder of lead scandium niobate $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ (PSN) down to 10 K, using a combination of neutron and x-ray diffraction on powder and single crystals. The structure of PSN is discussed and compared with those of simple perovskite compounds BaTiO_3 and PbTiO_3 . In PSN the existence of a long-range but still disordered ferroelectric phase, different from those of simple perovskites, is evidenced. The disorder of lead and scandium/niobium atoms on short-, medium- and long-range scales is discussed in connection with the dielectric properties of these materials.

1. Introduction

A special class of ferroelectric materials is known as relaxor ferroelectrics: they possess a high dielectric constant which changes very smoothly with temperature and they display a strong frequency dispersion. Their high permittivity as well as other properties such as strong electrostriction make them suitable for industrial applications. Most of these materials are lead-based perovskite compounds with general formula $\text{PbBB}'\text{O}_3$.

Several microscopic explanations have been proposed for their unusual dielectric properties but these explanations are difficult to confirm due to a lack of structural information. However all the proposed models require, at a certain level, some kind of disorder or inhomogeneity, and from this standpoint the experimental situation is very complex. In the case of $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN), which is the most documented relaxor compound, some insights were gained when it was shown that this material remains, whatever the temperature, in a cubic paraelectric phase [1]. However this is only an average situation and there are at least three types of experimental observation which indicate microscopic deviations from the average structure.

First, it is well known that, in the $\text{PbBB}'\text{O}_3$ compounds, the disorder of the B/B' cations is required for the observation of dielectric relaxation. However, in PMN, evidence

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of nanometric non-stoichiometric charged and *ordered* regions with local composition $\text{PbMg}_{1/2}\text{Nb}_{1/2}\text{O}_3$ have been reported from electron microscopy studies [2].

A second type of observation deals with the so-called ‘cubic disorder’ of the paraelectric phase. Indeed it has been shown from neutron and x-ray diffraction data [3] that all atoms of PMN are statistically shifted from their high-symmetry cubic positions, and a comparison with a similar report in simple perovskite compounds BaTiO_3 [4] and PbTiO_3 [5] has been made. It is interesting to notice that in these ‘well known’ compounds the situation in the cubic phase is still a matter of debate. We report some new experimental factors concerning this point in this paper.

A third type of observation is related to the low-temperature order of PMN. The existence of diffuse scattering in the powder neutron diffraction patterns below 340 K was interpreted as the occurrence of local polar order inside the average paraelectric matrix [6]. The exact structure of this local polar order, which should freeze below a T_g temperature, was supposed to be rhombohedral [6]. However it is still a matter of debate whether this polar order is organized as ferroelectric nanodomains, as suggested by the existence of a long-range ferroelectric order when applying an electrical field (above a threshold value) [7] or when substituting with lead titanate PbTiO_3 (the PMN–PT system) [8,9], or as a dipole glass.

New developments in this field originated from the observation of relaxors which transform spontaneously into a ferroelectric phase as reported in $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ (PST) [10] and $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ (PSN) [11] by Setter *et al.* These materials are very interesting for the study of the relaxor effect because, due to a high-temperature order–disorder transition, ordering or disordering of B/B' cations can be obtained depending on thermal history, with corresponding drastic changes in the dielectric properties. Moreover a great sensitivity of these dielectric properties to the stoichiometry of lead cations was evidenced [11,12], introducing a new piece in the puzzle of the structural explanation of dielectric relaxation.

In this paper we report some new structural results in PSN using a combination of neutron and x-ray powder and single-crystal diffraction and diffuse scattering. We discuss separately the different types of disorder as presented above, and make some comparisons with the situation in simple perovskite compounds BaTiO_3 and PbTiO_3 .

2. Experimental details

Well crystallized powdered samples of PSN were prepared using the classical method of Swartz and Shrout [13] where the ScNbO_4 wolframite precursor is synthesized first to avoid formation of parasitic pyrochlore phases. The final product is obtained introducing a 5% excess of PbO in order to avoid lead loss. Lead vacancy samples were obtained when no special precaution was taken to avoid PbO volatility. Regarding the Sc–Nb order we followed the method of Stenger and Burggraaf [14]: disordered PSN was obtained by thermal annealing above the order–disorder transition, i.e. 1210 °C for 2 h, and by quenching afterward, whereas ordered PSN was prepared by thermal annealing at 1000 °C for 24 d. Single crystals of disordered PSN with typical sizes 1 mm × 1 mm × 1 mm were prepared using the classical flux method [15].

X-ray powder diffraction studies were performed at ESRF on the D2AM beam line equipped with a seven-circles goniometer ($\lambda = 1.00 \text{ \AA}$) at room temperature and also using an indoor 18 kW Rigaku rotating anode (Cu $K\alpha$ or Cu $K\beta$) with a high-resolution two-axis Bragg–Brentano goniometer, equipped with an helium cryostat or a furnace. Depending on the type of experiment (high resolution or Rietveld analysis) typical patterns were scanned through steps from 0.004 to 0.01° from 12 to 150° 2 Θ with a typical counting time of 1 up

to 120 s. Single-crystal rocking curves were also obtained with the two-axis goniometer. Data collections were performed using a Cad4 four circles (Mo $K\alpha$).

Precession patterns have been obtained at LURE with the Buerger camera ($\lambda = 1.162 \text{ \AA}$) and an image plate scanner installed on the D43 beam line facilities, using a gas stream cooler.

The neutron experiments were performed at Laboratoire Léon Brillouin using the Orphée reactor facilities (Saclay, France) on a thermal source. Powder diffraction patterns were collected on the high-resolution two-axis goniometer 3T2 ($\lambda = 1.226 \text{ \AA}$) equipped with a helium cryostat, using steps of 0.05° between 6 and $120^\circ 2\Theta$ whereas the four-circle spectrometer 6T2 ($\lambda = 0.90 \text{ \AA}$) was used for single-crystal data collections at room temperature. Structural refinements were carried out with the XND program (powder Rietveld analysis) [16] and SHELLX 93 (single-crystal analysis).

Special mention must be made of the possibility of extracting useful information from single-crystal and powder samples with neutron and x-ray diffraction when studying $ABB'O_3$ perovskite compounds (whose *average* structures are extremely simple). Structural single-crystal studies of these compounds suffer limitations from very high absorption (for x-ray) and extinction effects, pseudosymmetry and domain contaminations, as well as complicated low-temperature sample environments (i.e. below 77 K), whereas all these effects are absent from or minimized in the powder Rietveld studies. Neutron powder studies allow reliable A–O and B(B')–O distance and B thermal parameter determination; x-ray powder studies allow positioning of A and B(B') cations, but also, when special precautions are taken (constant-statistic data collection up to high Q values), reliable B parameters. These considerations have been well known since pioneering works, for instance by Hewat [17], and have been applied more recently in a very low-temperature study of $SrTiO_3$ [18]. In the study presented in this paper we tried to take complementary advantage of all these techniques (single-crystal/powder samples, x-ray/neutron diffraction).

3. Experimental results

3.1. Cationic disorder

Four types of sample have been studied, whose thermal dependences of dielectric constant are shown in figure 1. As reported in literature, disordered PSN (dis.PSN) displays a diffuse/relaxor behaviour with a high value for ϵ' , whereas ordered PSN (ord.PSN) should be a 'classical' ferroelectric compound with lower ϵ' and with no relaxation property. In fact a departure from the Curie law and a weak relaxation is also evidenced in ord.PSN (inset of figure 1(a)). A strong increase of this dielectric relaxation when lead vacancies are introduced into the structure (vac.PSN) was reported in [11], that we also observed. In order to understand the part played by the lead occupancy for the dielectric properties we have also introduced a small (6%) substitution of barium for lead. In this so-called PBSN material we have observed a maximal diffuse/relaxor effect; in particular a high value of ϵ' is still maintained, which is strongly frequency dependent. Moreover in the vicinity of room temperature, the temperature dependence is very weak, in contrast to the others types of PSN, and should allow technological applications. It is also interesting to note that a complete substitution of the Pb atoms leads to $BaSc_{1/2}Nb_{1/2}O_3$ (BSN), which remains paraelectric, whatever the temperature, with no dielectric property [19]. As already known, the temperatures T_{max} at which the maximum in the dielectric constant occurs, strongly depend on the type of sample: for ϵ' at $f = 1 \text{ kHz}$, $T_{max} = 390, 351, 357$ and 370 K for dis. PSN, ord. PSN, vac. PSN and PBSN, respectively.

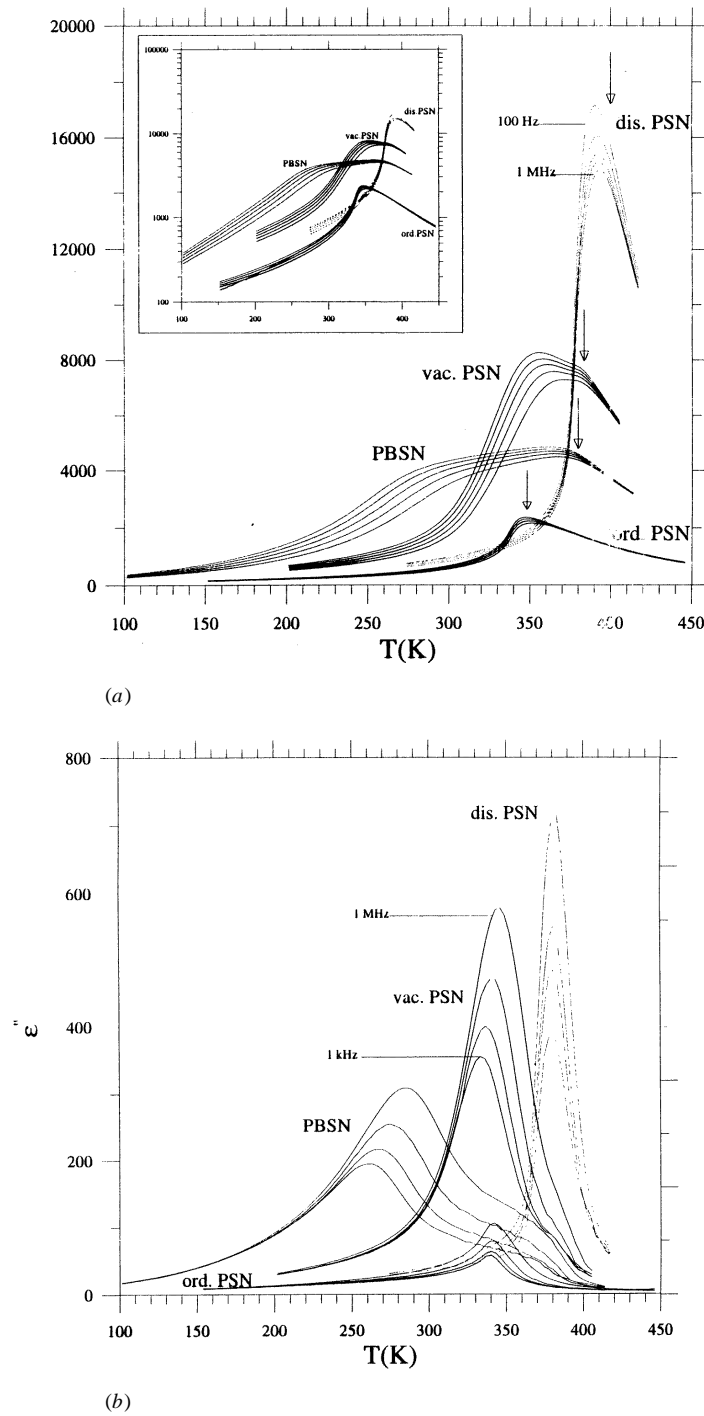


Figure 1. Dielectric constant versus temperature in ordered PSN (ord. PSN), in disordered PSN (dis. PSN), in PSN with vacancies (vac. PSN) and in PSN with a 6% substitution of barium (PBSN), measured at $f = 10^2, 10^3, 10^4, 10^5$ and 10^6 Hz: (a) the real part (log scale in inset); arrows are the critical temperature deduced from x-ray measurement (see the text); (b) the imaginary part.

The order/disorder of scandium and niobium atoms has been characterized using powder synchrotron radiation in the four types of PSN compound and using neutron diffraction on a disordered single crystal. The degree of order is traditionally measured using the superstructure peaks associated to the Sc–Nb ordering along the [111] direction by an S coefficient, which is the ratio of the integrated intensities of $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ and $(1\ 0\ 0)$ peaks divided by the same ratio calculated for a perfect ordered sample. In our samples S varies from zero (dis. and vac. PSN), to 55% for PBSN, up to 92% for ord. PSN. However the study of ordered samples reveals that the superstructure peaks have about ten times the width of the corresponding Bragg peaks (figure 2), which means that the ordering of Sc–Nb cations remains only short ranged, with a typical length of coherence of ≈ 200 Å. No temperature dependence of the intensity of the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ peaks was observed between 470 K and room temperature. The disordered PSN shows no noticeable superstructure peaks in the powdered samples but the neutron study of a single crystal reveals for high counting time a weak and broad superstructure $(\frac{3}{2} \frac{3}{2} \frac{3}{2})$ peak with an associated length of coherence of ≈ 40 Å; in the same experiment $(\frac{1}{2} \frac{1}{2} 0)$ and $(\frac{1}{2} 0 0)$ peaks were not observed.

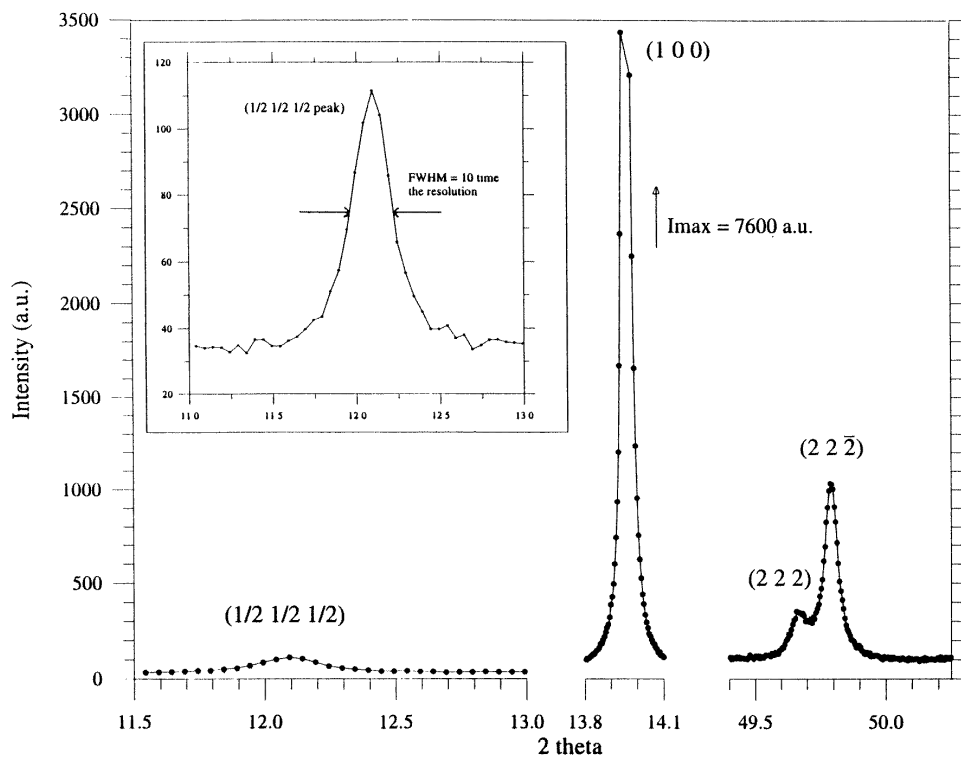


Figure 2. Selected parts of the synchrotron powder pattern of ordered PSN at room temperature.

3.2. Cubic disorder

The so-called ‘cubic disorder’ of the ABO_3 simple perovskites is still a matter of debate. It started from diffraction observations by Itoh *et al* [4] in $BaTiO_3$ and diffusion observations by Comes *et al* in $KNbO_3$ [21]. Itoh introduced disordered shifts of the Ba and Ti atoms

from their special positions of the cubic phase of BaTiO₃ which allowed an improvement of structure refinements, in a temperature range close to the critical temperature T_c . However the gain obtained on the R agreement factor is extremely small (some 10^{-3} on the R factor, for instance 1.506 instead of 1.512 for shifts of the Ti atoms) and could result in our opinion as well from correlations between different parameters, for example between B factors and absorption/extinction factors. Later these observations were extended to the cubic phase of PbTiO₃ by Nelmes *et al* [5] who used both anharmonic and disordered treatments of their data, with significant improvement of refinements and corresponding decrease in the abnormally high value of the lead B thermal parameter. However these latter observations were surprising as lead titanate had previously been considered to be a ‘textbook’ displacive system. On the other hand the observation of a diffuse scattering network in the cubic phase of KNbO₃ [21] revealed a high-temperature disorder and showed the appearance of long-range correlations during the successive ferroelectric transitions. Recent synchrotron experiments have also pointed out the importance of the competition between order–disorder and displacive mechanisms [22, 23].

This set of experiments showed that the shifts from the cubic special positions in these simple perovskite compounds should be essentially dynamic and result from cross-over from displacive to order–disorder regime, as the temperature reaches T_c from above. In this case one experimental interesting point is that the associated atomic slowing down could be evidenced from pure diffraction experiments by careful treatments of the scattered intensity.

Table 1. Neutron Rietveld refinement results, B (Å²) of the cubic phase of BaTiO₃, PbTiO₃, PSN and BSN.

	BaTiO ₃ 400 K	PbTiO ₃ 765 K	PSN 523 K	BSN 300 K
A:Ba/Pb	0.50(3)	3.04(6)	4.33(4)	1.00(4)
B:Ti/Sc/Nb	0.54(5)	1.42(4)	0.84(3)	0.78(4)
O $\beta_{11} = \beta_{22}$	0.0103(3)	0.032(4)	0.043(5)	0.020(2)
β_{33}	0.0098(4)	0.018(3)	0.014(3)	0.023(4)
B_{eq}	0.66(5)	1.73(5)	2.20(8)	1.43(6)

In the case of relaxor PMN the same type of disordered shift as in BaTiO₃ was observed at high temperatures [1, 3], but with no conclusion regarding its static or dynamic nature.

We have performed an investigation of this problem in the cubic phase of the four types of PSN compound, using neutron and x-ray powder refinement, and made also for the sake of comparison a reinvestigation of this problem in the cubic phase of BaTiO₃ and PbTiO₃, using the same procedure†. Moreover in order to understand the part played by the Pb or Ba atoms we have also studied the totally barium based perovskite BaSc_{1/2}Nb_{1/2}O₃ (BSN), which remains cubic whatever the temperature, with no dielectric property (as observed in [19] and during this study).

The results of the standard neutron Rietveld analysis of the different cubic phases of BaTiO₃, PbTiO₃, dis. PSN and BSN are shown in table 1. Two main comments can be made.

† During this study we also performed 10 K and 300 K neutron structure refinements of the tetragonal phase of lead titanate as well as high-resolution x-ray experiments; we observed no structural modification from the tetragonal phase; in particular no orthorhombic distortion (reported by some authors [24]) could be evidenced.

(i) In both barium perovskite compounds, all atoms have a normal B thermal factor; moreover whereas anisotropic factors are symmetry allowed for the oxygen atoms they retain a quasi-isotropic value.

(ii) In the lead based perovskite compounds, whereas the Ti/Sc/Nb cations have normal B values, the Pb atoms display an abnormally high value, as well as the O atoms, for which strong anisotropy is also observed; the same results (not shown) are also observed in the other PSN compounds.

These anomalous high B values are an indication of (static or dynamic) disorder in the lead compounds, as a disordered split atoms treatment of these data can show. Indeed, in PbTiO_3 at $T = 765$ K, i.e. just above T_c , and in PSN at $T = 450$ K, i.e. well above T_{max} , shifts of the lead atom from its special position along simple cubic directions result in a realistic minimum in the R agreement versus shift amplitude curve (figure 3). These shifts have a value of ≈ 0.25 Å, for which normal B values are recovered (1.6 Å² for PbTiO_3 and 2.1 Å² for dis. PSN)[†]. On the other hand no minimum is evidenced for the Ti/Sc/Nb atoms, which is coherent with the observation of normal B values, nor for the oxygen atoms, for which high B values are obtained[‡]. At higher temperatures the two compounds behave differently: in PbTiO_3 the minimum disappears (figure 3(a)) whereas it is retained for PSN.

In the case of barium based perovskite BaTiO_3 and BSN, no significant minimum could be found for any atom at any temperature, which, again, is coherent with the observation of normal B values.

3.3. Polar order/disorder

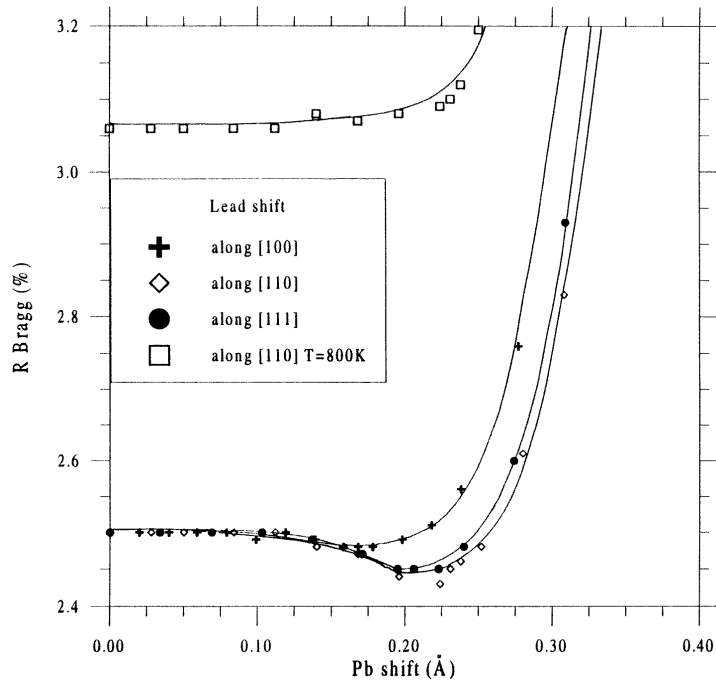
3.3.1. Phase transitions. Disordered PSN was the first relaxor compound with PST for which a polar ferroelectric phase was reported [10, 11]. However the dielectric properties of PSN are drastically dependent on the order/disorder of cations and it was not clear whether all types of PSN compound have a long-range polar phase. We have thus performed high-resolution x-ray experiments on the four types of PSN compound, which show that all these compounds have a low-temperature rhombohedral ferroelectric phase. In particular, clear rhombohedral splitting could be evidenced at room temperature for the ordered compound ($S = 92\%$) (figure 2). In figure 4 the temperature dependence of some FWHMs is plotted, indicating critical temperatures T_c of 400(5), 350(2), 365(3) and 375(3) K for dis. PSN, ord. PSN, vac. PSN and PBSN, respectively.

The rhombohedral phase appears through a weak first-order transition with a very small jump in the lattice constants (inset of figure 4), which is hardly detectable in powdered samples.

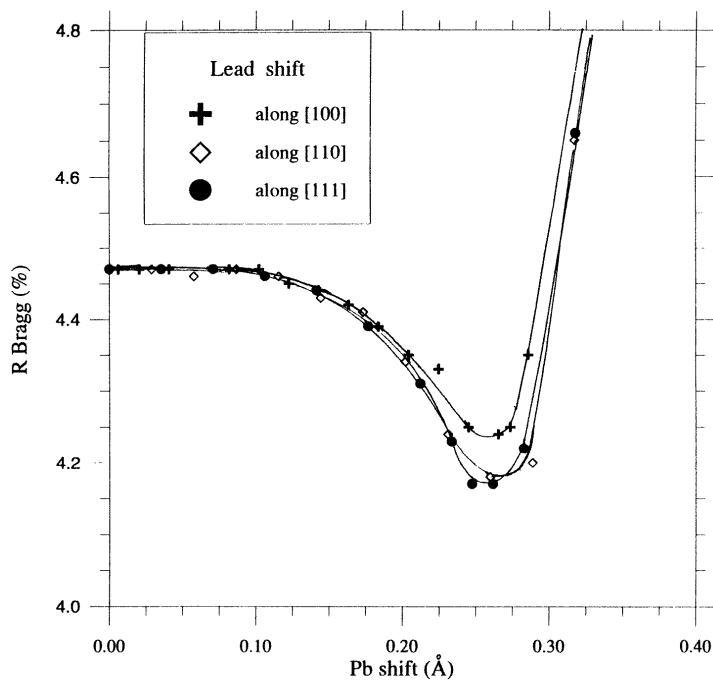
3.3.2. Polar structure and disorder. The polar structure of disordered PSN has already been reported by Knight and Baba-Kishi at $T = 200$ K [25]. We have performed a comparative

[†] In our opinion no information can realistically be extracted concerning a possible anisotropy of these disorders because the different minima have close values. The absolute minimum is obtained for the $\langle 110 \rangle$ directions but any other directions display such a minimum (for instance we have tested the general $\langle 123 \rangle$ direction which works as well). This absolute minimum in the $\langle 110 \rangle$ direction probably results from the fact that this direction is the most degenerate one in cubic symmetry and thus gives a better description of the anomalous high isotropic B factor of the lead atoms than any less degenerate direction.

[‡] The high anisotropic B values associated with the oxygen atoms could not be modelled by similar static shifts; possibly anharmonic treatments should be performed. However it is most probable that some (at least partially dynamic) shifts do exist also for these atoms but are more difficult to evidence. Hewat [26] reported such observations on B thermal parameters in simple perovskites, associated with low-frequency modes of oxygen movements.



(a)



(b)

Figure 3. Agreement factor R_B of x-ray Rietveld analysis versus disordered shift amplitude, for the lead atom: (a) in cubic PbTiO_3 at $T = T_c + 2\text{ K} = 765\text{ K}$ and $T_c + 37\text{ K} = 800\text{ K}$; (b) in cubic dis. PSN at $T = 450\text{ K}$, i.e. well above the T_{max} temperatures.

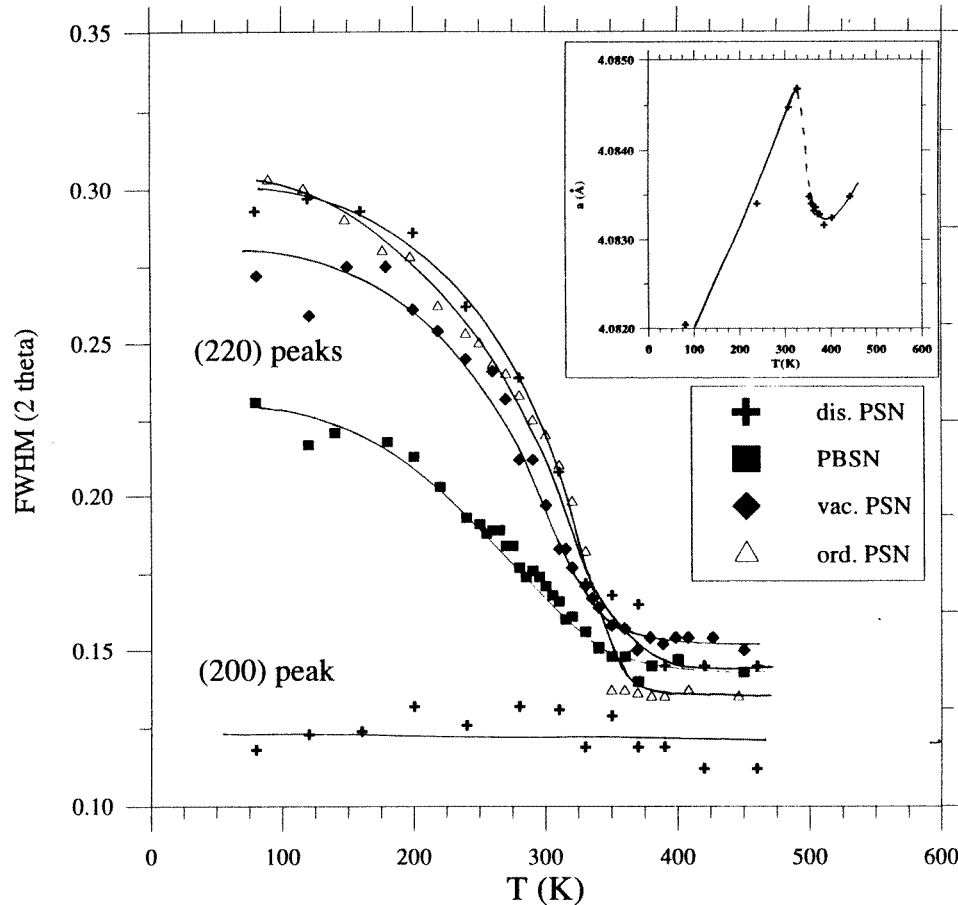


Figure 4. X-ray FWHM of some Bragg peaks versus temperature; the inset is the pseudocubic a lattice parameter versus temperature in a PSN single crystal.

study of the four types of PSN compound at 10 and 300 K, as well as a structural evolution of the disordered compound, by performing a Rietveld neutron and x-ray analysis at different temperatures and a neutron single-crystal study at room temperature. In table 2 the 10 K powder neutron results are summarized. The oxygen cuboctahedron environment of the lead atom and the oxygen octahedron environment of the scandium/niobium atoms are shown in figure 5, with a schematic picture of the polar shifts. The low-temperature phase is satisfactorily refined using the $R3m$ rhombohedral space group. This phase is characterized by cooperative shifts of lead and scandium/niobium atoms in the same direction along the threefold axis $[111]$ of the high-temperature phase, which becomes the polar axis. A small distortion of the oxygen octahedra is also observed (in the xxz position of the O atoms, z is weakly different from $x - 0.5$): the two oxygen triangles of the octahedron (shaded in figure 5) have two slightly different areas, but remain parallel with a common threefold axis.

In table 3 bond distances and ferroelectric shifts δ (as represented in figure 5) are reported for 10 and 300 K and in the cubic phase at 450 K. During the cubic to rhombohedral

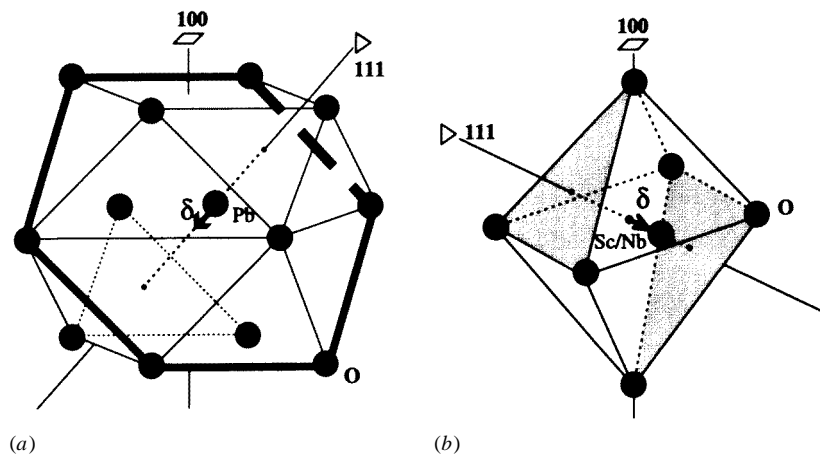


Figure 5. The two types of cation environments in the cubic perovskite structure, with the corresponding shifts in the rhombohedral ferroelectric phase: (a) the cuboctahedron environment of the lead atom; (b) octahedron environment of the scandium/niobium atom.

Table 2. Neutron Rietveld analysis of different PSNs at 10 K; the lead atom is taken as the origin.

	dis. PSN	vac. PSN	ord. PSN	PBSN
Lattice parameters				
$a(\text{\AA}), \alpha(^{\circ})$	4.0791(8), 89.86(3)	4.0818(7), 89.85(2)	4.0797(11), 89.85(4)	4.0811(10), 89.91(6)
Position of Pb				
xxx	0	0	0	0
$B_{pb} (\text{\AA}^2)$	1.76(5)	2.01(4)	1.62(6)	2.23(8)
Position of O				
xx	0.5537(6)	0.5580(3)	0.5514(8)	0.5406(11)
z	0.0410(7)	0.0450(4)	0.0390(10)	0.0311(13)
$B_{eq} (\text{\AA}^2)$	1.47(5)	1.26(7)	1.81(6)	1.75(5)
Position of Sc/Nb				
xxx	0.5333(3)	0.5318(2)	0.5335(3)	0.5317(3)
$B_{eq} (\text{\AA}^2)$	0.54(3)	0.53(3)	0.43(5)	0.42(5)
R_{wp} (%)	5.17	4.15	7.13	6.87
R_{exp} (%)	3.4	3.2	4.6	4.5
Gof	1.50	1.30	1.56	1.51
R_B (%)	2.8	2.7	4.2	3.4

transition, the cubic 12-fold degenerate Pb–O distance inside the oxygen cuboctahedron splits into one three fold degenerate short distance (with the O atoms of one triangle-shaped face), one six fold degenerate medium distance (with the O atom hexagon) and one three fold degenerate long distance (with the O atoms of the second triangle-shaped face); the cubic six fold degenerate Sc/Nb–O distance inside the oxygen octahedron splits into two three fold degenerate distances (with the two O atom triangles).

The 10 K structure is characterized by large shifts of the lead atoms, larger than those of the Sc/Nb atoms (δ values in table 3). All the different PSN compounds have almost the same low-temperature structure, but PBSN displays Sc/Nb δ shifts almost equal to zero. At 300 K only the lead atoms are strongly off their cubic positions. Table 4 displays the structural evolution of disordered PSN and a comparison with the rhombohedral ferroelectric

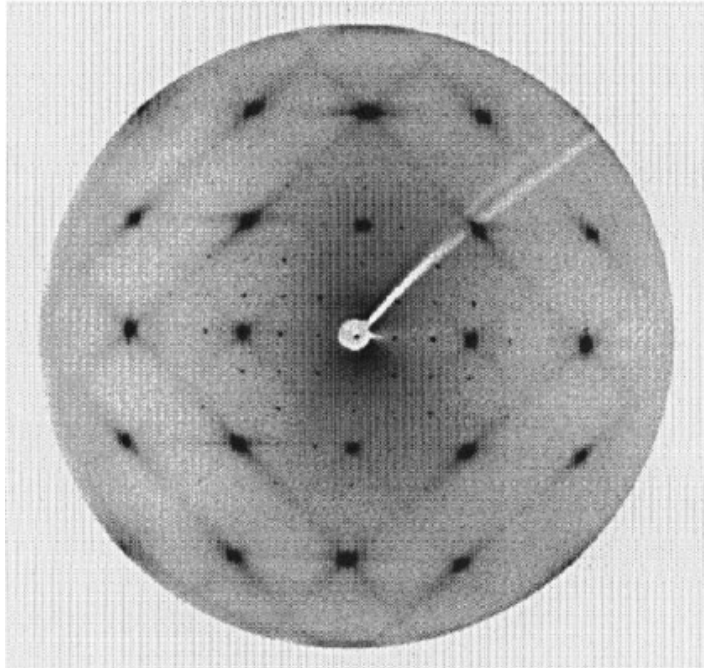
Table 3. Bond distances and ferroelectric shifts δ (as represented in figure 5) at 10 and 300 K and in the cubic phase at 450 K.

	dis. PSN	vac. PSN	ord. PSN	PBSN
10 K				
Pb–O	2.55(1)	2.56(1)	2.57(2)	2.66(2)
	2.91(1)	2.91(1)	2.91(1)	2.90(1)
	3.23(2)	3.23(1)	3.22(1)	3.13(2)
Sc/Nb–O	1.99(1)	1.99(2)	2.00(2)	2.04(2)
	2.10(1)	2.10(1)	2.09(1)	2.04(2)
δ_{Pb-O} (Å)	0.39(5)	0.38(5)	0.36(4)	0.29(6)
$\delta_{Sc/Nb-O}$ (Å)	0.16(6)	0.16(5)	0.14(6)	0.04(5)
300 K				
Pb–O	2.64(3)	2.63(3)	2.62(2)	2.73(3)
	2.89(2)	2.90(3)	2.90(3)	2.89(2)
	3.13(3)	3.15(2)	3.16(3)	3.05(2)
Sc/Nb–O	2.02(3)	2.02(2)	2.03(2)	2.02(3)
	2.06(2)	2.07(3)	2.05(2)	2.06(2)
δ_{Pb-O} (Å)	0.28(4)	0.30(5)	0.30(6)	0.18(5)
$\delta_{Sc/Nb-O}$ (Å)	0.07(6)	0.08(4)	0.08(4)	0.01(5)
450 K				
Pb–O	2.89(1)	2.89(1)	2.89(2)	2.89(2)
Sc/Nb–O	2.04(1)	2.04(1)	2.04(2)	2.04(1)
δ_{Pb-O} (Å)	0	0	0	0
$\delta_{Sc/Nb-O}$ (Å)	0	0	0	0

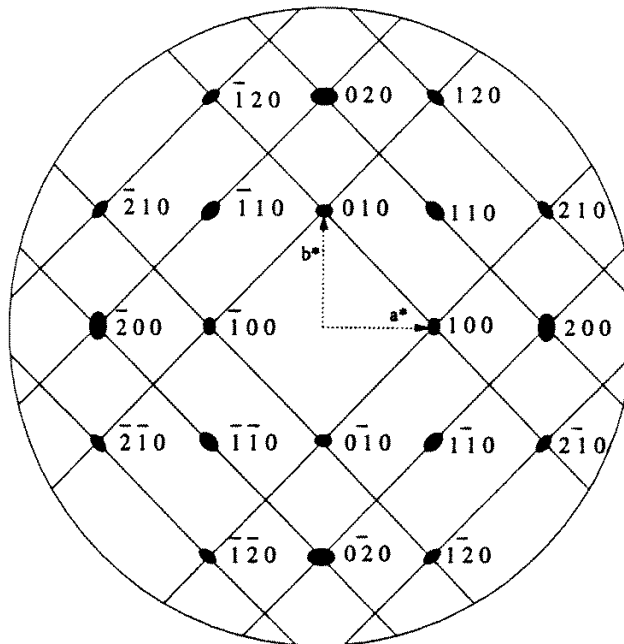
Table 4. The structural evolution of disordered PSN and a comparison with the rhombohedral ferroelectric phase of PMN–PT 75:25 (from [9]), BaTiO₃ (from [26]) and the tetragonal phase of PbTiO₃ (from [5]); in this latter case the δ shifts are along the four fold axis of figure 5.

	dis. PSN				PbTiO ₃		BaTiO ₃		PMN75/PT25	
	<i>R3m</i>			<i>Pm3m</i>	<i>P4mm</i>	<i>Pm3m</i>	<i>R3m</i>	<i>Pm3m</i>	<i>R3m</i>	<i>Pm3m</i>
	10 K	300 K	360 K							
A–O (Å)	2.55(1)	2.64(3)	2.76(3)		2.52(3)		2.77(3)		2.59(3)	
	2.91(1)	2.89(2)	2.88(2)	2.89(1)	2.80(2)	2.84(3)	2.83(2)	2.85(3)	2.86(1)	2.85(3)
	3.23(2)	3.13(3)	3.00(2)		3.22(2)		2.90(3)		3.12(3)	
B–O (Å)	1.99(1)	2.02(3)	2.04(1)		1.77(2)		1.88(3)		2.00(3)	
	2.10(2)	2.06(2)	2.04(1)	2.04(1)	1.99(2)	2.01(2)	2.13(2)	2.01(3)	2.03(3)	2.01(3)
					2.39(1)					
δ_{A-O} (Å)	0.39(5)	0.28(4)	0.10(5)	0	0.49(4)	0	0.10(5)	0	0.29(5)	0
δ_{B-O} (Å)	0.16(6)	0.07(6)	0.10(4)	0	0.31(5)	0	0.18(6)	0	0.07(6)	0

phase of PMN–PT 75:25 (from [9]), BaTiO₃ (from [26]) and the tetragonal phase of PbTiO₃ (from [5]). In this latter case the δ shifts are along the four fold axis of figure 5 and three (instead of two) different Ti–O distances exist. The 10 K ferroelectric phase of PSN appears to be of the same type as PMN–PT but with stronger polar shifts, and different from those of BaTiO₃ and PbTiO₃. In the case of BaTiO₃ the titanium cation δ shift is about the same as that of the scandium/niobium cation of PSN at 10 K, but the barium cation is far less shifted than the lead cation. In the case of PbTiO₃ the lead cation is strongly shifted from its cubic position, as in PSN, but the titanium cation is also equally and strongly shifted, in contrast to PSN and BaTiO₃.



(a)



(b)

Figure 6. (a) A precession photo of the $(hk0)^*$ plane recorded with an image plate; (b) a schematic representation of the $(hk0)^*$ plane precession photos. Note that horizontal lines passing through the intense Bragg spots in (a) are an artifact due to the image plate scanning and therefore are not taken into account, as well as some 'satellite' spots between Bragg peaks which are λ/n harmonic spots of strong Bragg reflections.

Examination of table 2 also shows that high values of thermal parameters are still observed at 10 K for the lead and oxygen atoms, thus indicating the existence of a persisting disorder, which is obviously static at this temperature.

Precession photos of the $(hk0)^*$ plane have been obtained in a disordered PSN single crystal, at room temperature and at 100 K (no temperature dependence has been evidenced). In this plane (figure 6), diffuse scattering in the form of lines parallel to the $[1-10]^*$ and $[110]^*$ directions is observed in addition to the Bragg peaks. These lines connect Bragg peaks (for instance 020, 110, and 200). In order to ascertain the three-dimensional extension of this diffuse intensity (which could have planar shape) we have taken photos of the $(hk0.5)^*$ plane. In this plane, no diffuse scattering is observed. This indicates that the diffuse scattering is three-dimensional line shaped along all $\langle 1-10 \rangle^*$ equivalent directions.

These observations are an indication of (static or dynamic) correlated displacements of atoms inside the (six fold) $\{1-10\}$ planes with no (or weak) correlation from plane to plane along the perpendicular $\langle 1-10 \rangle$ directions.

We have tried to evidence such a disorder in a $(1-10)$ plane by the Rietveld analysis of the neutron data at 10 K. We have thus performed a disordered split lead atom treatment by introducing shifts along simple directions belonging to this plane: $[111]$, $[001]$, $[110]$ and $[-1-12]$. A significant improvement was obtained (figure 7) for the shifts along a direction perpendicular to the $[111]$ polar axis, i.e. along the $[-1-12]$ direction (which belongs to both $(1-10)$ and (111) planes). Intermediate directions between the polar axis and the $[-1-12]$ direction results in the vanishing of the R minimum for a φ angle of $\approx 12^\circ$ between the considered direction and the (111) plane. In the R minimum a normal B value is recovered (0.66 \AA^2 instead of 1.76 \AA^2 for dis. PSN).

We have also tested whether such disorder could exist in the ferroelectric tetragonal phase of PbTiO_3 using Rietveld analysis, but no significant improvement could be evidenced, coherent with the normal B values which are obtained for all atoms.

4. Summary, discussion and conclusion

The structural situation in the relaxor (and non-relaxor) perovskite PSN appears to be rather complex and the idea that relaxation properties are associated solely with the scandium/niobium disorder has to be completed. First, total scandium/niobium ordering or disordering seems to be only an asymptotic situation. Indeed locally ordered regions are always observed in macroscopically disordered materials (even in single crystals) as well as locally disordered regions inside the ordered compounds. This shows that the ordering of the cations has to be considered not only at a local or long-range scale but also on an intermediate (mesoscopic) scale as well. The observation in ordered PSN of a departure from the Curie law and of a weak relaxation in dielectric constant seems to be a consequence of this inhomogeneous state, which has recently also been evidenced in PST ceramics by electron microscopy [20].

Second, even if scandium and niobium cations play an important part in the dielectric properties of PSN, the study of the influence of the lead atoms is also of great importance. Indeed, changing the lead stoichiometry results in a drastic increase of diffuseness, either when lead vacancies are created (vac. PSN) or when a small substitution of barium for lead is performed. In the extreme case, when total substitution is performed, one obtains BSN, which remains paraelectric whatever the temperature, with no dielectric property.

Moreover, inside the structure, the lead atoms never occupy their ideal positions, in the paraelectric cubic as well as in the rhombohedral ferroelectric phase. Indeed, at high temperature in the cubic phase, statistically disordered shifts along all cubic directions have

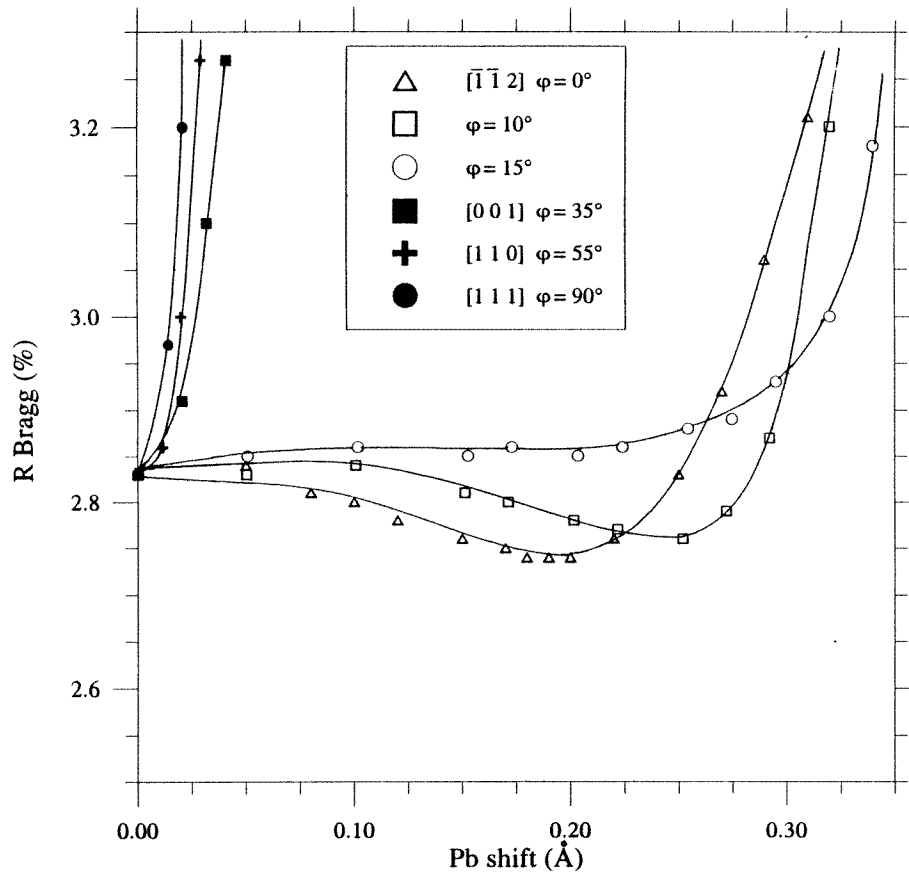


Figure 7. Agreement factor R_B of neutron Rietveld analysis versus disordered shift amplitude for the lead atom in PSN at 10 K. All the tested directions belong to the $(1 - 1 0)$ plane, φ is the angle of the direction with the $(1 1 1)$ plane (see text).

been evidenced. These shifts allow the paraelectric phase bonding lengths (between 2.60 and 3.20 Å instead of 2.88 Å), which are cooperatively observed at lower temperatures in the polar phase. At lower temperature, in the polar rhombohedral phase, a disorder of lead atoms is still persistent in the form of a correlated shift in the $\{1 - 1 0\}$ planes, perpendicular to the $\langle 1 1 1 \rangle$ polar directions.

The part played by this disorder on the A site of perovskites is not completely understood. In barium based perovskites BaTiO_3 and BSN no disorder was evidenced but disordered shifts are observed in all PSN compounds and in PbTiO_3 . In the case of PbTiO_3 this disorder is obviously critical as it is confined to temperatures close to and above T_c : it is thus dynamic. In the case of PSN the situation is less clear. On one hand an isotropic disorder is observed in the cubic phase not only close to T_c but whatever the temperature, thus indicating a non-critical phenomenon; on the other hand, in the ferroelectric phase this disorder is 'reduced' and is observed only perpendicular to the $[1 1 1]$ polar direction. Whether dynamic or static, this disorder is evidenced in all samples of PSN and thus plays no direct part in the dielectric properties.

All different types of PSN compound transform into the same average polar rhombohedral structure by cooperative shifts of lead and scandium/niobium atoms relative to the oxygen network, showing as in PMN–PT the possibility of observing relaxation in a ferroelectric phase. The ferroelectric shifts are similar to those of the PMN–PT rhombohedral phase but are different from those of rhombohedral BaTiO_3 and tetragonal PbTiO_3 .

From these structural data we would like to address the physical picture of the phase transformation. Indeed for the relaxor PMN compound, two main types of physical model have been proposed to explain its relaxation properties and the short-range polar order at low temperature. The concept of dipole glasses, which are structural analogues to the magnetic spin glasses, have been used. In particular the observation of a departure from Curie law above T_{max} in the thermal dependence of the dielectric constant has been explained by the existence of polar regions, which manifest themselves also by strong electrostriction [27]. At high temperature these regions should be dynamic and non-interactive (superparaelectric model) but could interact at lower ones, leading to a freezing. A Vogel–Fulcher law for T_{max} versus frequency of dielectric constant [28] is observed similarly as in the magnetic susceptibility of spin glasses. Kinetic effects in the temperature and electric field dependence of dielectric constant [29] and in diffraction experiments [30] could be interpreted in the framework of this picture.

The second class of model is based on the physical picture of nanodomains. In particular, the existence of an electric field induced phase transition have been explained by the collapse and growing up of these nanodomains into macrodomains; for instance birefringence experiments under an electric field have been interpreted by pinning and depinning of a nanopolar region [31].

These two classes of models have very different underlying physical origins. The dipole glass state of PMN should arise from the existence of local competition (i.e. ferroelectric versus antiferroelectric ordering), leading to structural frustration. The nanodomain state should result from random electric fields which prevent the long-range ferroelectric order happening [32], as predicted by Imry and Ma in the case of isotropic (Heisenberg) order parameter [33]. Nanometric non-stoichiometric charged and ordered regions with local composition $\text{PbMg}_{1/2}\text{Nb}_{1/2}\text{O}_3$, as shown from electron microscopy observations [2], could act as the source of random fields.

The controversy still continues, as shown for instance by the recent demonstration that the Vogel–Fulcher law is not obviously to be associated with the freezing of short-range polar order [10], or a high-resolution diffraction study of the q dependence of the Bragg peak, which shows the absence of sharp boundaries for the polar regions of PMN [34].

In the case of PSN a macroscopic polarization appears at low temperature, in contrast with PMN, but the lead atoms remain disordered in this ferroelectric phase. In the framework of the dipole glass model the analogy could be still maintained by enlarging the concept to that of ‘re-entrant dipole glass’. On the other hand the idea that dipolar interactions are strong enough to overcome the random fields and give rise to ferroelectricity could be also coherent with the nanodomain picture of PMN: the existence of lead vacancies or its substitution with barium should screen these interactions, thus increasing the diffuse/relaxor effect. However in the former case the physical origin of competition/frustration should have to be identified, as well as in the later case, the sources of the random electric (or eventually elastic) fields.

In any case the understanding of the relaxor effect will require a deeper investigation of the order and disorder, one difficulty being that local scale, mesoscopic scale and macroscopic scale should be considered.

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