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The local structure of mixed-ion perovskites

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Abstract

The temperature-dependent Nb K-edge absorption spectra of several mixed-ion Pb-containing perovskite compounds were analysed to determine the Nb displacement and to trace its changes through the phase transitions. Both extended x-ray absorption fine structure (EXAFS) and the pre-edge region of the spectra were involved in the analysis. The results show that, in the compounds studied, Nb occupies an off-centre position with symmetry lower than that implied by macroscopic symmetry. The magnitude and direction of the Nb off-centre displacement do not display any noticeable temperature change and are not affected by the change in macroscopic symmetry. The Nb–O distribution and its temperature evolution do not show any distinct dependence on the degree of compositional ordering and properties of the samples.

1. Introduction

The mixed-valence Pb-containing perovskites $\text{Pb}(\text{B}', \text{B}'')\text{O}_3$, which have structural formula $\text{PbB}_{2/3}^{5+}\text{B}_{1/3}^{2+}\text{O}_3$ or $\text{PbB}_{1/2}^{5+}\text{B}_{1/2}^{3+}\text{O}_3$ ($\text{B}^{5+} = \text{Nb}, \text{Ta}$; $\text{B}^{3+} = \text{In}, \text{Sc}$; $\text{B}^{2+} = \text{Mg}, \text{Zn}, \text{Ni}, \text{Co}$) are important materials for many practical applications. Many of them are relaxor ferroelectrics displaying a broad frequency-dependent maximum of the dielectric permittivity in the vicinity of the ferroelectric–paraelectric phase transition. The relaxor properties are known to be directly related to the degree of compositional disorder resulting from the mixed-ion B site. In $\text{PbB}_{1/2}^{5+}\text{B}_{1/2}^{3+}\text{O}_3$, the 1:1 ordering of the B^{5+} and B^{3+} cations at the B site totally suppresses the relaxor properties, so ordered modifications behave as ordinary ferroelectric $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ (PSN) or antiferroelectric $\text{PbIn}_{1/2}\text{Nb}_{1/2}\text{O}_3$ (PIN) [1, 2]. The possibility of long-range 1:1 ordering at the B site in $\text{PbB}_{2/3}^{5+}\text{B}_{1/3}^{2+}\text{O}_3$ is also intensively debated [3, 4].

The structural origin of the relaxor behaviour is not yet clear. Its understanding requires detailed information about the structure and its temperature changes on the local, intermediate, and macroscopic scales. Diffraction provides indications that the structure of relaxors is

Table 1. Structure symmetries, phase transition temperatures, and properties of PMN, PZN, ordered PIN, disordered PIN, ordered PSN, and disordered PSN.

| Compound | Phase transition temperature (°C) | Macroscopic symmetry of the low-temperature phase | Type of the phase transition |
|--|-----------------------------------|---|------------------------------|
| PbMg _{1/3} Nb _{2/3} O ₃ (PMN) | −10 | Rhombohedral | Relaxor ferroelectric |
| PZN | 140 | Rhombohedral | Relaxor ferroelectric |
| PIN, ordered | 180 | Orthorhombic | Antiferroelectric |
| PIN, disordered | 80 | Rhombohedral | Relaxor ferroelectric |
| PSN, ordered | 80 | Rhombohedral | Normal ferroelectric |
| PSN, disordered | 100 | Rhombohedral | Relaxor ferroelectric |
| BSN | | Cubic | Paraelectric |

highly distorted, with atoms disordered around averaged positions [5–8]; however, it is much less specific about the types and magnitudes of those distortions, interatomic distances, and relative atomic shifts. The large number of parameters to be refined and the strong correlation between them, together with absorption and extinction correction problems, make it difficult to refine atomic positions, as the difference between the *R*-factors for alternative models appears to be quite small and the accuracy of the structure determination is low. Even for the most intensively studied compound PbMg_{1/3}Nb_{2/3}O₃ (PMN), the structural model is still under discussion [5, 6].

One of the questions which is not resolved yet is that of the role of the B'' atom in the relaxor behaviour. The B'' atom has much smaller size than B', and this mismatch may be an additional source of structural distortions, along with random electric fields, resulting from compositional disorder. Chen argues that the size mismatch is the key element that is essential for relaxor properties, and that the relaxation behaviour must be due to a relatively easy off-centre site switching of smaller and thus ferroelectrically active B'' cations below the Curie temperature [9, 10]. A precise study of shifts of B atoms from the ideal positions by diffraction techniques is very difficult due to the insensitivity of the *R*-factors to these shifts and due to the correlation between the positional and temperature parameters of B' and B'' atoms occupying the same crystallographic position.

XAFS, which is the powerful modern tool for use in local structure investigations, provides a good likelihood of obtaining additional structural information on the materials. Recent intensive XAFS studies of the phase transitions in perovskites [11–14] made a significant contribution to the understanding of the nature and mechanisms of the ferroelectric phase transitions. However, only few XAFS studies have been reported so far for relaxor perovskites [5, 9, 15, 16].

In order to get more information on the local structure and its temperature changes in relaxor materials, we examined Nb K XAFS spectra of a number of Nb-containing mixed perovskite compounds of both 1/3 and 1/2 type, such as: PMN, PbZn_{1/3}Nb_{2/3}O₃ (PZN), PSN, and PIN, and traced their temperature changes through the phase transitions. A comparison of their local structure to that of other Nb-containing perovskites, such as NaNbO₃, KNbO₃ and BaSc_{1/2}Nb_{1/2}O₃ (BSN), has been also performed. The information on the structure symmetry, properties, and phase transition temperatures of the samples is presented in table 1.

As can be seen from table 1, the macroscopic symmetries of the low-temperature phases of all the materials studied except ordered PIN are rhombohedral, as determined by diffraction measurements [11–14, 17]. However, in PMN the rhombohedral distortion is negligible and can be hard to detect. The temperatures and types of the phase transitions in ordered and disordered samples of PIN and PSN are different: disordered samples display diffuse ferroelectric phase transitions, while ordered modifications undergo ordinary antiferroelectric and ferroelectric phase transitions. The study of disordered relaxor and ordered forms of PIN and PSN, whose characteristics and properties are substantially different, provides a good opportunity to compare the Nb–O distribution and its temperature changes through the phase transitions in relaxor and non-relaxor materials of the same composition.

2. Experimental procedure

Powder samples of PIN and PSN were obtained by solid-state reaction using the standard synthesis procedure described in detail elsewhere [18]. Variation of the degrees of ordering in PIN and PSN was achieved by annealing the powder samples. The disordered samples were obtained by annealing for 1 h at 1050 °C; i.e. the temperature of annealing exceeded the temperature of the compositional order–disorder phase transition, equal to 1010 °C. The highly ordered powders were obtained by annealing at 500 °C for 8 h. To prevent PbO losses, both synthesis and annealing were carried out in a sealed alumina crucible filled with PbZrO₃ powder. PZN and PMN powder samples were prepared by grinding the flux-grown crystals. All the samples were prepared in the Institute of Physics, Rostov State University.

The powders were carefully ground, mixed with BN powder, and pressed to form pellets about 1 mm thick. The Nb K-edge spectra were measured in transmission at BL-10B, at the Photon Factory. The x-ray beam was monochromatized using a Si(111) crystal in the energy range 18 600–19 800 eV (the Nb K-edge energy is 18 986 eV). The ring energy and current were 2.5 GeV and 300 mA, respectively. Spectra were obtained at about ten temperature points in the range from 20 to 300 °C, which contains the temperatures of the phase transition for all the materials investigated except PMN. Data analysis was performed using the UWXAFS code [14]. The EXAFS signal was extracted via standard procedures. Fourier transformation of the k^3 -weighted spectra was performed over the range $2.7 \text{ \AA}^{-1} < k < 13 \text{ \AA}^{-1}$. The fitting to the experimental spectra was performed using theoretical spectra simulated by means of FEFF-7 [19]. Analysis of the data was performed taking into account the results of our previous studies for other ferroelectric materials and using similar approaches [12, 13, 20]. Several possible models of the Nb–O distribution were assumed. At first we considered the ideal cubic model for all the compounds studied. The deviations of the real structure from the ideal cubic model were characterized by high-order cumulants in the same way as in [20] using a cumulant expression for the EXAFS:

$$\chi(k) = \sum_j \text{Im} \left[\frac{S_0^2}{kR_j^2} f_j^{eff}(k, R_j) \exp \left(i\phi_j + 2ikR_j - 2\sigma_j^2 k^2 - \frac{4i}{3} k^3 \sigma_j^{(3)} + \frac{2}{3} k^4 \sigma_j^{(4)} \right) \right]$$

where S_0^2 is an overall amplitude factor, R_j is the averaged distance of the j th scattering path, $f_j^{eff}(k, R_j)$ is the effective scattering amplitude, ϕ_j is the phase shift, and σ_j^2 is the Debye–Waller factor. The non-Gaussian contribution originating from distortion of the ideal cubic structure was taken into account by means of the third- and the fourth-order cumulants, $\sigma_j^{(3)}$ and $\sigma_j^{(4)}$, which are equal to zero in the harmonic case of undistorted structure. This expression does not describe the radial distribution function of the distorted structure adequately, just giving a better approximation than the expression for the pure harmonic case. However, it

involves additional parameters, which do not directly correspond to any specific structural characteristic, but can serve as quantitative indicators of local structure distortions, varying from 0 (in the case of the ideal structure) to quite substantial values.

The high-order cumulants were included in the list of variable parameters of the fit along with values of the Debye–Waller factor σ^2 and the average Nb–O distance R .

The pre-edge region of the spectra was also analysed for all the samples. The pre-edge peak, which was not clearly resolved, was extracted from the spectra by taking the difference of the experimental spectra and the curve obtained as a result of their Fourier-filter smoothing. Then the integral intensity of the pre-edge peak, which is known to be directly related to the absolute magnitude of the Nb displacement [21], was calculated.

3. Results and discussion

3.1. Pre-edge structure

The pre-edge structure of the K-edge XAFS spectra of the 4d elements is known to be very sensitive to the symmetry of the nearest neighbourhood of these atoms. It has been shown that the intensity of the pre-edge peak in polarized Ti K-edge absorption spectra of BaTiO₃ and PbTiO₃ is directly related to the magnitude of the Ti displacement from the centre of the oxygen octahedron in the direction of the vector of x-ray polarization. It has also been noted that the main-edge peak for ordered materials is greater than that for disordered materials with similar near-neighbour environments of the central atoms. This effect is due to random phase decoherence among close multiple-scattering passes. This effect has been studied in detail for Ti spectra [11, 21].

The same effects have been observed in the polarized Nb K XAFS spectra of KNbO₃ and NaNbO₃ [13, 22]. It has been shown that although the pre-edge peak is not clearly resolved, it can still be extracted and analysed. It has been shown also that Nb off-centre displacement has a drastic effect on the integral intensity of the pre-edge peak, so its magnitude can be used for evaluation of the displacement.

In figure 1 the near-edge regions of the Nb K XAFS spectra of PMN, PIN, PZN, and PSN, taken at room temperature and at high temperature, are shown, together with the polarized Nb K-edge XAFS spectra of KNbO₃ and NaNbO₃. The Nb displacements from the centres of the oxygen octahedra, Δx , in KNbO₃ and NaNbO₃ given in that figure were determined from EXAFS data. It can be seen that the near-edge structures display clear correlations with the Δx values: spectra corresponding to the smallest Δx values display the smallest pre-edge peaks A and the sharpest near-edge structures.

All the spectra of the materials studied—both relaxors and non-relaxors—display a quite pronounced pre-edge peak A, although it is not clearly resolved. The main peak and near-edge structure are very broad and diffuse compared to those in KNbO₃ spectra. All these features are unaffected by temperature variation. We managed to extract the pre-edge peak and to estimate its intensity for all the compounds studied. The resulting integral intensities of the pre-edge peak measured at several temperatures are presented in table 2. It can be seen that for all the compounds studied the values are very close and almost temperature independent.

The above results indicate that in all the compounds studied, Nb has a strongly asymmetric nearest environment, which may be resulting from an off-centre displacement of Nb. The magnitude of the displacement does not show a noticeable dependence on the composition, chemical ordering, or macroscopic symmetry of the structure. In all the materials studied, the distortions persist well into the paraelectric phase.

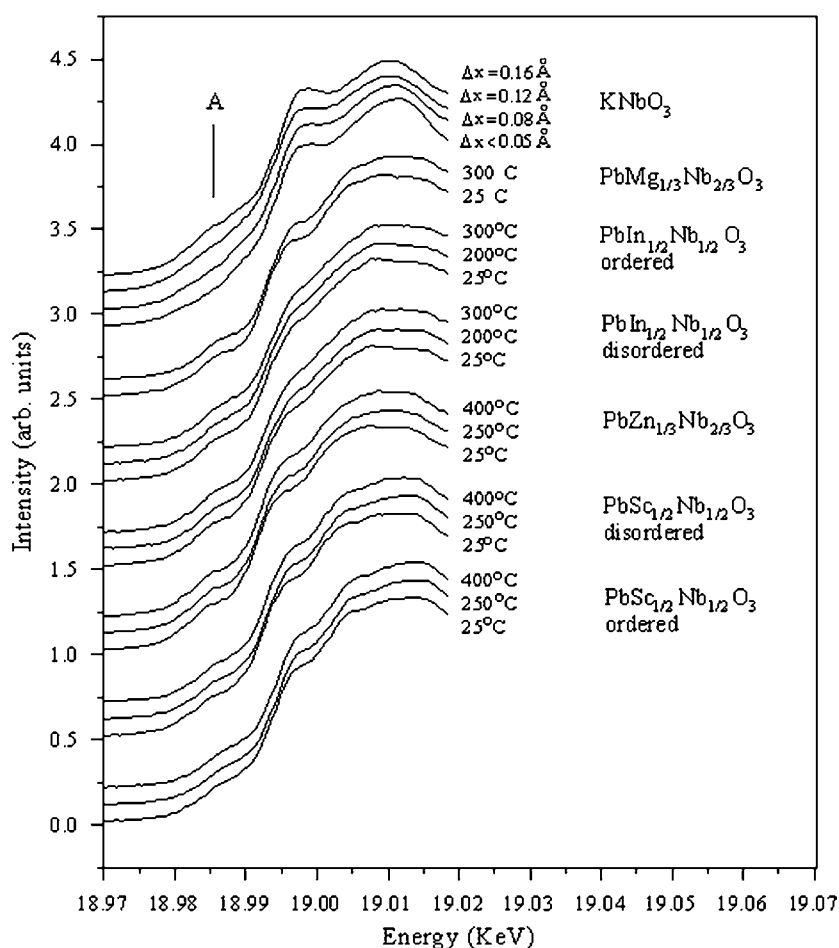


Figure 1. The near-edge region of the Nb K XAFS spectra for PMN, PIN, PZN, and PSN, taken at room temperature and at high temperature, as well as the polarized Nb K-edge XAFS spectrum of KNbO₃. The value Δx displays the Nb off-centre displacement in the direction of the vector of x-ray polarization.

3.2. EXAFS

Nb K-edge XAFS is very sensitive to the Nb displacements in perovskites. In figure 2(a) we show the FT for three spectra taken from single-crystal and powder samples of NaNbO₃ which are used as model spectra and represent three different cases of Nb location relative to the octahedron centre:

- (1) Nb is very close to the octahedron centre.
- (2) Nb is shifted along the [111] direction and forms two sets of equal Nb–O distances each involving three bonds. Such a distribution is typical for the case of rhombohedral distortion of a perovskite.
- (3) Nb is shifted along the (110) perovskite direction by about 0.1 Å and there are two (equal) small, two intermediate, and two large Nb–O bonds.

It can be seen from the figure that in the range from 1 to 2 Å, which corresponds to Nb–O distances, the XAFS FT are rather different for these three cases and can be easily distinguished.

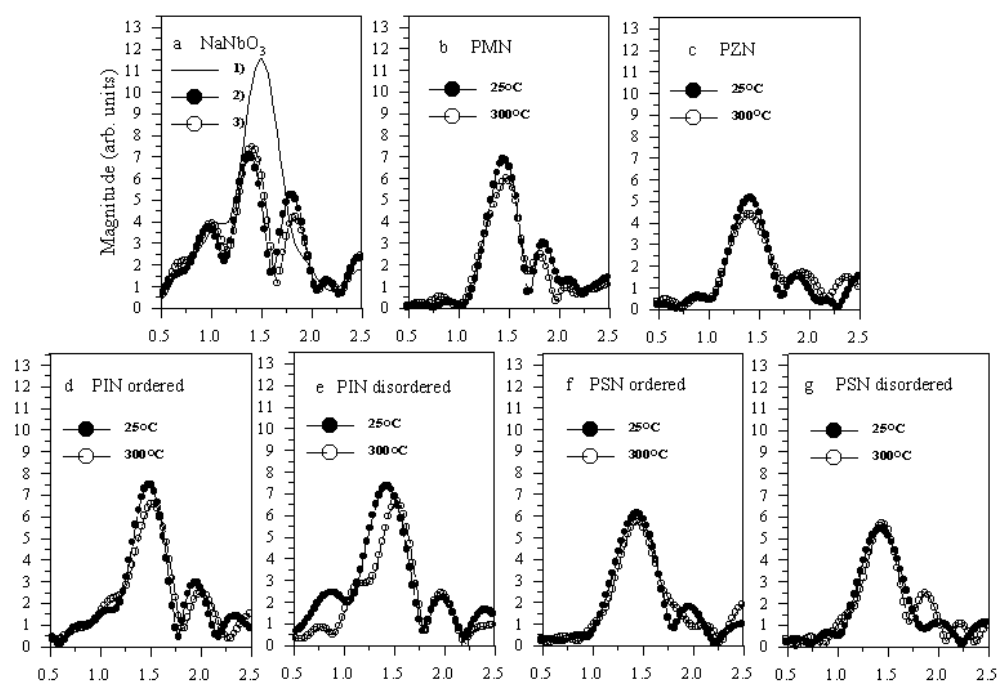


Figure 2. (a) Fourier transforms of the polarized Nb K-edge k^3 -weighted spectra of NaNbO_3 : (1) Nb is very close to the octahedron centre; (2) Nb forms two sets of equal Nb–O distances, typical for rhombohedral distortion of perovskite; (3) Nb is shifted along the (110) perovskite direction by about 0.1 Å. (b)–(f) Fourier transforms of the Nb K-edge k^3 -weighted spectra of PMN, PZN, ordered PIN, disordered PIN, ordered PSN, and disordered PSN at 25 and 300 °C.

Table 2. The integral intensity of the pre-edge peak.

| Compound | Temperature (°C) | Integral intensity (arbitrary units) |
|-----------------|------------------|--------------------------------------|
| PMN | 25 | 3.42 |
| | 300 | 3.25 |
| PZN | 25 | 3.50 |
| | 300 | 3.29 |
| PIN, ordered | 25 | 3.04 |
| | 300 | 3.15 |
| PIN, disordered | 25 | 3.55 |
| | 300 | 3.21 |
| PSN, ordered | 25 | 3.12 |
| | 300 | 2.89 |
| PSN, disordered | 25 | 3.06 |
| | 300 | 2.98 |

In the case of the central position of Nb, only one strong peak can be seen, while rhombohedral distortion gives two separate peaks of much smaller amplitude. (110) shift of the Nb also results in the formation of two peaks; however, the relative intensities of the first and second peaks are different from those in case (2).

The qualitative comparison of the FT of the spectra of the mixed-ion compounds presented in figure 2 shows that in the range from 1 to 2 Å they are surprisingly similar to each other.

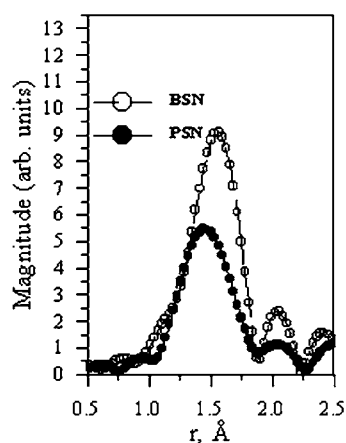


Figure 3. Comparison of the Fourier transforms of BSN and PSN, disordered, at 25 °C.

They each contain one dominant peak, whose amplitude is much smaller than the amplitude of the single peak in the XAFS FT for NaNbO_3 in case (1), and whose position is shifted to lower r .

From figure 3, which shows the FT of the Nb K XAFS for PSN and BSN, we can see that there is also a clear difference between Pb-containing mixed compounds and Ba-containing ones, which are known to be cubic down to very low temperatures and have undistorted perovskite structure. The Nb–O peak in the XAFS FT of PSN has a much smaller amplitude and a more asymmetric shape than that of BSN, which is an indication of a much broader distribution of Nb–O distances.

The fit to the data assuming the ideal cubic model gives a high discrepancy factor and too short a Nb–O distance. A noticeable improvement of the fit was achieved, however, by adding additional parameters—high-order cumulants ($\sigma^{(3)}$, $\sigma^{(4)}$), which describe non-Gaussian components of the radial atomic distribution and thus characterize the structural distortion of the ideal cubic structure. The results of two fits to the experimental data for ordered PSN are shown in figure 4. Curve 1 represents experimental spectra, curve 2 is the result of the fit assuming a cubic model with σ^3 and σ^4 set equal to zero, curve 3 was obtained with $\sigma^{(3)}$ and $\sigma^{(4)}$ allowed to vary. It can be seen that the deviations of curve 2 from curve 1 are quite significant, while curve 3 is in reasonable agreement with the experiment. The values of all the refined parameters at several temperatures are presented in table 3. It can be seen that they are fairly close for all the compounds and rather constant over the whole temperature range. The high-order cumulants are almost independent of temperature and their values are about 6–10 times higher than those typical of structurally ordered compounds (usually of about 0.0002 and 0.0001 for the third- and the fourth-order cumulant respectively). This indicates that the Nb–O radial atomic distribution contains a large static non-Gaussian contribution due to there being several different Nb–O distances. This supports the conclusion derived from analysis of the near-edge structure that Nb is well away from the octahedron centre in all the compounds, both below and above the phase transition point.

For all the compounds, the Debye–Waller factor is almost independent of temperature. This behaviour can be explained if one takes it into account that in fitting spectra of highly distorted perovskites with the ideal cubic model, the total Debye–Waller factor contains both the input originating from temperature mean square displacements and the static ‘disorder’ contribution. So if the static component is temperature independent, the temperature changes

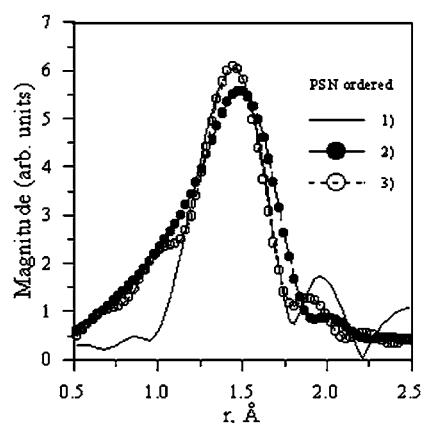


Figure 4. Comparison of Fourier transforms of fitted spectra with the experimental one for the Nb K edge of ordered PSN at 25 °C. Curve 1 represents experimental spectra, curve 2 is the result of the fit assuming the cubic model with σ^3 and σ^4 set equal to zero, curve 3 was obtained with $\sigma^{(3)}$ and $\sigma^{(4)}$ allowed to vary.

Table 3. Radii ($R_{\text{Nb-O}}$), Debye–Waller factors (σ^2), third and fourth cumulants ($\sigma^{(3)}$, $\sigma^{(4)}$) obtained by fitting of the EXAFS data.

| Compound | Temperature (°C) | $R_{\text{Nb-O}}$ (Å) | σ^2 (units of 10^{-2}) | $\sigma^{(3)}$ (units of 10^{-3}) | $\sigma^{(4)}$ (units of 10^{-4}) |
|-----------------|------------------|-----------------------|----------------------------------|--------------------------------------|--------------------------------------|
| PMN | 25 | 2.01(1) | 0.015(3) | 0.000 86(25) | 0.000 21(5) |
| | 300 | 2.02(1) | 0.018(2) | 0.000 99(20) | 0.000 24(6) |
| PZN | 25 | 2.00(1) | 0.017(1) | 0.001 0(1) | 0.000 22(2) |
| | 300 | 2.01(1) | 0.02(01) | 0.001 1(2) | 0.000 26(4) |
| PIN, ordered | 25 | 2.00(1) | 0.0132(10) | 0.000 46(13) | 0.000 15(3) |
| | 300 | 2.00(1) | 0.0142(10) | 0.000 57(14) | 0.000 21(3) |
| PIN, disordered | 25 | 1.99(1) | 0.0136(8) | 0.000 2(1) | 0.000 14(2) |
| | 300 | 2.00(1) | 0.0148(10) | 0.000 3(1) | 0.000 16(4) |
| PSN, ordered | 25 | 2.01(1) | 0.0128(20) | 0.000 7(3) | 0.000 12(7) |
| | 300 | 2.02(1) | 0.0143(30) | 0.000 8(3) | 0.000 18(6) |
| PSN, disordered | 25 | 2.02(1) | 0.0144(10) | 0.000 8(1) | 0.000 19(2) |
| | 300 | 2.03(1) | 0.0162(12) | 0.000 9(2) | 0.000 24(3) |
| BSN | 25 | 2.05(1) | 0.006(04) | 0.000 31(6) | 0.000 04(1) |

of the total Debye–Waller factor are expected to be small compared to its value. The fact that we do not observe any temperature changes of the Debye–Waller factor is further evidence of significant Nb off-centre displacement over the whole temperature region, including that of the cubic phase.

Further comparison with the NaNbO_3 EXAFS FT shows that the Nb–O distribution in mixed-ion compounds is also rather different from that in case (2), and displays the largest similarity with case (3), as it gives the relationships between the amplitudes of the first and the second Nb–O peaks in the EXAFS FT which are closest to those observed for the experimental spectra of the compounds studied. So it can be concluded that the direction of Nb off-centre displacement is closest to the 110 direction in the compounds, independently of the macroscopic symmetry. It should be noted that for PMN, the above conclusion is in agreement with the structural model proposed on the basis of the diffraction data [5], which also assumes a [110] Nb shift in the cubic phase of PMN. Further support is provided by our

recent x-ray diffraction study of ordered PIN, which will be published in detail elsewhere [23]. According to the results, Nb is shifted towards the octahedron edge by about 0.1 Å, giving three sets of Nb–O bonds with lengths equal to 1.91, 2.00, and 2.09 Å. It should be especially noted that the Nb environments appear to be very similar in all the compounds, independently of the macroscopic symmetry. Three of the compounds considered—PZN, disordered PIN, and disordered PSN—are macroscopically rhombohedral. However, the Nb–O distribution is similar to that in orthorhombic ordered PIN.

4. Summary

Our temperature-dependent XAFS study of a number of mixed-ion perovskites showed that in the cubic phase the local structure around the Nb atom deviates from the ideal cubic form in all the compounds studied. It has been revealed that the changes in macroscopic symmetry do not have any noticeable impact on the local structure, which is highly distorted both in the low-temperature and in the cubic phases of all the materials. In the low-temperature disordered PSN, rhombohedral phases of PZN, disordered PIN, and disordered PSN, the Nb displacement direction is close to [110] rather than [111]. The magnitude of the Nb displacement does not change through the phase transition point. This shows that order–disorder-type processes play an important role in structural transformations of the compounds.

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