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Atomic displacements in $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ under high pressures

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Abstract

We have investigated the chemical structure of $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) relaxor ferroelectric at room temperature under hydrostatic pressures up to 8.37 GPa and at ambient pressure as a function of temperature. The refinement of the crystal structure shows that the amplitude of the displacements of the Pb ions from the (0 0 0) position decreases with increasing pressure. On the other hand, the thermal displacement parameters of Mg/Nb ions are almost insensitive to pressure. The decrease in the Pb displacements correlates with an increase in the anisotropy in the thermal displacement parameter of the O ions. These results are in agreement with those obtained in $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ (PMT) and show further evidence that the Pb displacements play an important role in the relaxor behavior. The aim of this study is to clarify the microscopic origin for the anomalous pressure effects observed in relaxors as well as to provide new data for the understanding of this class of materials.

1. Introduction

There are many ferroelectrics that have a classic ABO_3 perovskite-type structure. A subclass of perovskite ferroelectric materials is formed by the relaxors, or relaxor ferroelectrics [1]. Relaxors can be distinguished from classical ferroelectrics by the frequency dependent and very high value of the dielectric susceptibility peak, which extends over hundreds of degrees kelvin and which is usually not linked directly to a structural phase transition. In addition, many physical properties of relaxors exhibit anomalies in the vicinity of the peak in the dielectric permittivity. Due to these properties, the relaxor ferroelectrics have attracted increasing interest from experimental as well as theoretical points of view. Despite being studied for more than 50 years, relaxors are still not well understood [1–5]. First, it was believed that the anomalous behavior of the dielectric properties was due to fluctuations in composition that may or may not be accompanied by local phase transitions [1]. Later, it was found that the relaxor ferroelectrics are homogeneous, but have

polar nanoregions below some characteristic temperature [6], which may play an important role for the lattice dynamics and, thus, for the dielectric properties. It was suggested recently, that the dynamic component of the diffuse scattering (quasi-elastic scattering) and the static component (central peak) observed in relaxors results from scattering by dynamic and static nanoregions [7, 8].

$\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) is a model relaxor. In PMN, the ions are displaced from the ideal Wyckoff positions and these displacements are found to be temperature-dependent [9]. However, the preferred direction of these displacements remains unknown and it is believed that they are random in both amplitude and direction (for a discussion see e.g. [10]). The peak in the real part of the dielectric permittivity ϵ' of PMN appears at around ~ 270 K [1] at a frequency $f = 1$ kHz. PMN has cubic $Pm\bar{3}m$ structure at all temperatures in the absence of an external electric field [9]. However, in an applied electric field, PMN undergoes a structural phase transition at $T \sim 210$ K [11]. $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ (PMT) is closely related to the PMN relaxor ferroelectric [1]. Among all the similarities between PMN and PMT, we note here the departure from a linear law in the temperature variation of the optical refraction index [12], the temperature-dependent diffuse scattering [13]

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and ionic displacements [14], which have been reported for both materials.

Recently, the properties of the relaxors under application of hydrostatic pressure has aroused interest. It was found that the applied pressure suppresses in PMN the peak in the dielectric permittivity [15, 16] and the diffuse scattering [17]. The chemical structure of PMN was studied under hydrostatic pressure by means of powder neutron diffraction [18]. A pressure-induced decrease of the Pb displacements from the (0 0 0) ideal Wyckoff position, which correlates with an increase of the anisotropy of the oxygen temperature factor, was found. It was suggested that these changes in the chemical structure of the relaxors may link to the suppression of the dielectric permittivity and of the diffuse scattering [15, 17] under pressure. We also note that in classical ferroelectric PbTiO_3 , Pb displacements decrease with hydrostatic pressure [19] and are accompanied by a decrease of tetragonal distortion [20].

The aim of this study is to examine the behavior of the chemical structure of PMN as a function of temperature at ambient pressure and as a function of hydrostatic pressure at room temperature in order to find similarities and/or differences in this class of materials and to provide further evidence that Pb displacements are directly related to the macroscopic properties of relaxors.

2. Experimental description

The measurements were carried out with the multidetector high-resolution powder diffractometer (HRPT) [21] located at the neutron spallation source SINQ [22] at the Paul Scherrer Institut, Switzerland. The temperature-dependent measurements at ambient pressure were performed with $\lambda = 1.1545 \text{ \AA}$ and the pressure experiment at $\lambda = 1.4940 \text{ \AA}$. The polycrystalline sample of PMN was placed into cylindrical containers of 10 mm diameter and 50 mm height. Using a closed-cycle refrigerator, the temperature range 30–410 K was covered. Measurements at ambient temperature and applied pressure were carried out using opposed-anvil techniques, employing a Paris-Edinburgh VX 5 press (details of the experimental setup are described elsewhere [18, 23]). A 4:1 mixture of methanol:ethanol granted hydrostatic conditions within the pressure range. The powder sample had a volume of 30 mm^3 . The applied pressures were estimated from the change in the unit cell volume of PMN by using the third-order Birch–Murnaghan equation of state [24] with $B = 104 \text{ GPa}$, $B' = 4.7$ [17]. The crystal structure refinement was carried out using Fullprof [25].

3. Results and discussion

We model the structure of PMN in a similar way to PMT [14] in order to facilitate comparison of the results obtained for the two compounds. A starting set of the parameters for the chemical structure of PMN within the $Pm\bar{3}m$ space group was obtained from the data collected at ambient conditions with high statistics. For the refinements, the chemical composition of PMN was fixed at the stoichiometric values. Pb ions were

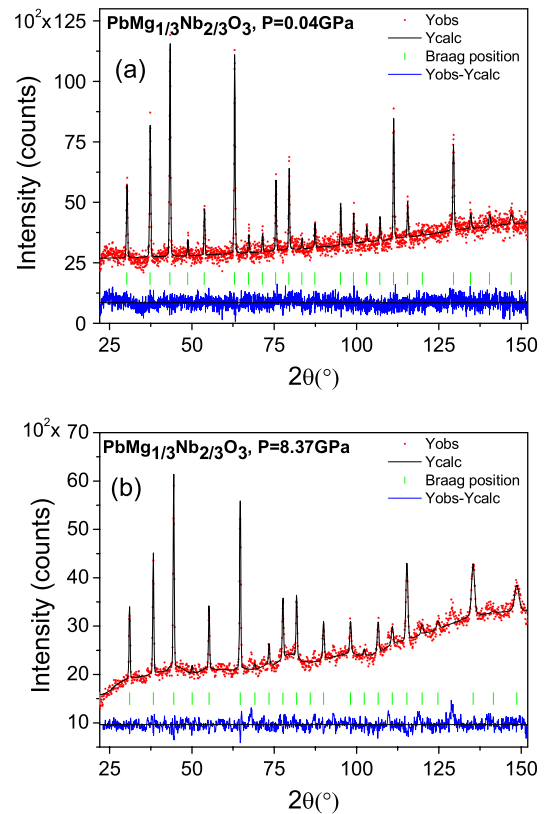


Figure 1. Neutron powder diffraction patterns of PMN collected at nominal pressures of (a) $P = 0.04 \text{ GPa}$ and (b) $P = 8.37 \text{ GPa}$. Observed data points, calculated profiles and difference curves are shown. The row of ticks corresponds to the calculated positions of diffraction peaks. Peaks at $2\theta = 86.5^\circ$ and 128.5° are from the cubic boron nitride anvils.

(This figure is in colour only in the electronic version)

considered as being displaced from the (0 0 0) special position along the $\langle 110 \rangle$ direction, as this direction corresponds to the minimum of χ^2 and smallest value of the B -factors. Mg and Nb ions are randomly distributed in the center of the cube according to their stoichiometric ratio. The O atoms were placed at $(\frac{1}{2} \frac{1}{2} 0)$ -type positions on the cubic faces, forming an octahedron. The temperature factors of the Pb and Mg/Nb ions were assumed to be isotropic while for the oxygen ions anisotropic components of the temperature factors were considered too. To avoid unwanted correlations between displacement amplitudes and the B -factor of Pb, the latter were fixed to a value of 0.931 \AA^2 obtained at ambient conditions. The possible displacements of the Mg/Nb or oxygen ions are taken into account by their temperature factors. We note that the parameters of the chemical structure of PMN obtained in the present study are in good agreement with previously reported results [9].

Figure 1 shows representative diffraction patterns obtained close to ambient pressure and at highest pressure $P = 8.37 \text{ GPa}$ in order to emphasize the changes. Sharp superlattice reflections indexed as $(\frac{h}{2}, \frac{k}{2}, \frac{l}{2})$ (h, k, l - odd) have been reported previously [17] above $\sim 4 \text{ GPa}$ in PMN by x-ray diffraction. Within the statistical accuracy of the present measurements, reflections of this type are not observed and

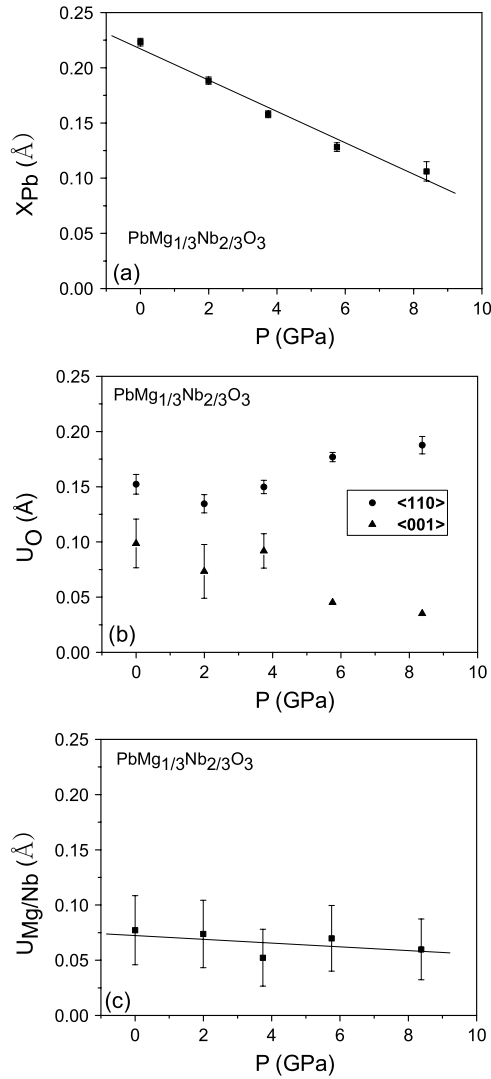


Figure 2. (a) Pressure dependence of the amplitude of lead displacements X_{Pb} in PMN. (b) Root mean square displacements of the oxygen ions versus applied pressure. The values $U_{O(110)}$ of oxygen corresponding to 5.75 and 8.37 GPa were fixed at the minimum positive values in such a way that the reliability factors take minimum values. (c) Root mean squares of the Mg/Nb ions versus applied pressure.

the chemical structure of PMN is well described in the $Pm\bar{3}m$ space group at all pressures.

Figure 2 shows the evolution of the Pb displacements along the $\langle 110 \rangle$ direction (X_{Pb}) and the root mean square (RMS) displacements of Mg/Ta and oxygen in PMN as a function of pressure. All these quantities vary approximately linearly with pressure. The main effects observed in the present study are a significant decrease of the amplitude of the Pb displacements and an increase of the anisotropy of the oxygen temperature factors at higher pressures. These results are very similar to the case of PMT, apart from the fact that the RMS of Mg/Ta in PMN was found to increase with increasing pressure [18] while the RMS of Mg/Nb in PMN does not vary significantly up to ~ 8 GPa. As for PMT, we analyse the changes in anisotropy of the oxygen temperature factors as a function of the amplitude of the

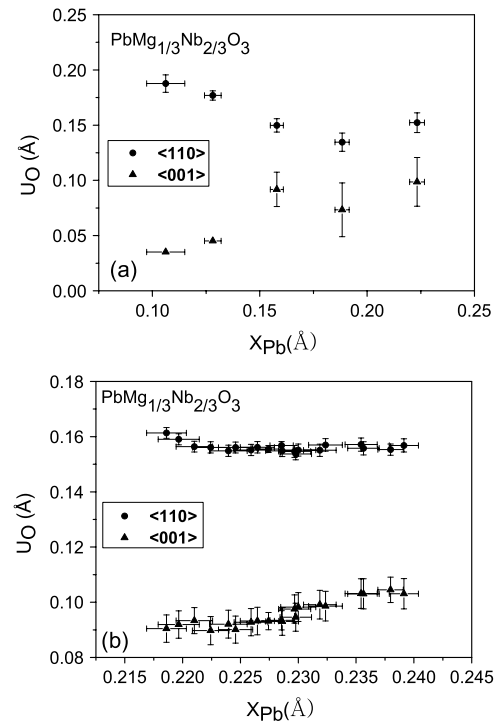


Figure 3. (a) Components of the oxygen thermal ellipsoid versus the amplitude of lead displacements measured as a function of pressure. The values of pressure and corresponding amplitudes of the Pb displacements are given in table 1. (b) Components of the oxygen thermal ellipsoid measured at ambient pressure in the temperature range $T = 30\text{--}410$ K.

Table 1. Pressure, lattice parameter and amplitude of the lead displacement of PMN. The pressure was calculated from the Birch–Murnaghan equation of state with $B = 104$ GPa, $B' = 4.7$ taken from [17].

Pressure (GPa)	Lattice parameter (\AA)	Pb displacement (\AA)
0.04	4.048 42(6)	0.223(3)
1.99	4.023 68(6)	0.188(3)
3.74	4.003 76(5)	0.157(3)
5.75	3.982 45(5)	0.128(4)
8.37	3.956 9(1)	0.106(9)

Pb displacements, combining the pressure and temperature-dependent results. The lattice parameters, nominal pressures and the amplitudes of the Pb displacements are given in table 1. Figure 3 shows the evolution of the $\langle 110 \rangle$ and the $\langle 001 \rangle$ components of the oxygen temperature factor as a function of the amplitude of the lead displacements X_{Pb} . As is clearly seen, these components are evolving in opposite directions: the component directed from Pb to O increases significantly with decreasing Pb displacement and the Mg/Nb–O bond exhibits a slight decrease.

4. Conclusion

In this study we report a structural investigation of PMN using neutron powder diffraction between ambient pressure and 8.37 GPa along with a temperature-dependent study of

the PMN structure at ambient pressure. The data treatment revealed that the Pb displacements decrease linearly with pressure, similarly to PMT. These changes in the amplitude of the Pb displacements affect the local structure and, thus, the short-range order. It was pointed out earlier [18] that such changes in the structural parameters were not observed in materials other than relaxors. Thus the present study further supports qualitatively the idea that the correlated displacements of the lead and oxygen ions are anomalous and may be linked to the decrease of the diffuse scattering and of the peak in the dielectric permittivity in lead-containing relaxors under pressure.

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