Anomalous pressure dependence of the atomic displacements in the relaxor ferroelectric $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$

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The crystal structure of the $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ relaxor ferroelectric was studied under hydrostatic pressure up to ~ 7 GPa by means of powder neutron diffraction. We find a drastic pressure-induced decrease of the lead displacement from the inversion center, which correlates with an increase by $\sim 50\%$ of the anisotropy of the oxygen temperature factor. The vibrations of the Mg/Ta are, in contrast, rather pressure insensitive. We attribute these changes being responsible for the previously reported pressure-induced suppression of the anomalous dielectric permittivity and diffuse scattering in relaxor ferroelectrics.

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$\text{AB}_x\text{B}_{1-x}'\text{O}_3$ complex perovskites are model compounds for the study of ferroelectricity in disordered crystals. In many of these compounds, ferroelectricity occurs without a structural phase transition, and they are referred as relaxor ferroelectrics, or simply relaxors.¹ Relaxors have a frequency-dependent peak in the dielectric permittivity, which typically extends over hundreds of degrees Kelvin. In addition, many physical properties of relaxors exhibit anomalies in this temperature range attributed to a so-called diffuse phase transition. Despite numerous studies, the physics of systems exhibiting diffuse phase transitions is not yet well understood.

A well-known example of relaxors is $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN).¹ This crystal has $\text{Pm}\bar{3}\text{m}$ symmetry; however, displacements of ions from the ideal Wyckoff positions are present and these displacements are temperature dependent.² The first evidence for the appearance of correlations on a short-range scale was found by Burns and Scott³ who observed that the optical refraction index departs from linear law at $T_d \sim 620$ K, i.e., far above the mean Curie temperature $T_{cm} \sim 270$ K. They interpreted this anomaly in terms of growing polarization in small regions of nanometer scale [polar nanoregions (PNR)]. The existence of short-range order was later confirmed by neutron and x-ray diffraction that observed diffuse scattering in the vicinity of Bragg peaks of PMN (Refs. 2, 4 and 9) at temperatures lower than T_d . A very similar behavior is reported in another well-known relaxor $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ (PMT).¹ The departure from linear law in the temperature variation of the optical refraction index of PMT was observed⁵ at $T \sim 570$ K. As for PMN, temperature-dependent diffuse scattering⁶ and ionic displacements⁷ were also found in PMT.

In the course of studies of PMN and PMT, a close relationship between the diffuse scattering and the amplitude of the displacements of the ions from the special Wyckoff positions in the perovskite structure has been found.^{7,8} In addition, it was observed recently that the susceptibility of the dynamic (quasi-elastic) component of the diffuse scattering in PMN follows well the peak of the dielectric permittivity.⁹

Most of the studies on relaxor ferroelectrics have concentrated on temperature and electric-field effects. Recently, in-

terest in the properties of the relaxors under hydrostatic pressure has aroused.¹⁰⁻¹⁷ Hydrostatic pressure applied to relaxors usually causes: (i) the suppression of the peak in the dielectric permittivity, as found, e.g., in PMN (Ref. 15) or in $\text{PbIn}_{1/3}\text{Nb}_{1/2}\text{O}_3$ (PIN)¹¹ and (ii) the decrease in the intensity of the diffuse scattering as observed also, e.g., in PMN (Ref. 16) and PIN.¹² However, up to now there exists no attempt to link these two effects to the underlying structural changes in these systems.

Here, we present a detailed structural investigation under pressure, aimed to clarify the microscopic origin for the anomalous pressure effects reported in relaxors. We applied neutron diffraction taking advantage of a better sensitivity on the oxygen position as compared to x-ray studies. The experiments were carried out on PMT, which at ambient pressure, shows a broad frequency-dependent anomaly of the dielectric response with a maximum at a frequency of 10 kHz in the vicinity of 170 K.¹ In the entire range of temperatures and applied electric fields, the symmetry of PMT is known to remain cubic (space group $\text{Pm}\bar{3}\text{m}$).^{1,7,18}

The powder diffraction experiment was carried out at ambient temperature on the multidetector high-resolution powder diffractometer (HRPT)¹⁹ at the spallation neutron source SINQ (Switzerland).²⁰ Measurements were performed with a neutron wavelength of $\lambda = 1.494$ Å. Typical exposure times were ~ 15 h. The polycrystalline sample of PMT had a volume of ≤ 100 mm³ and was loaded into an encapsulated zero-matrix TiZr gasket²¹ with a deuterated methanol-ethanol (4:1) mix as a pressure-transmitting medium thus enabling hydrostatic pressure conditions up to the highest investigated pressure of ~ 7 GPa. To apply pressure, the VX3 version of the Paris-Edinburgh press²² was used. A detailed description of this opposed-anvil setup is given in Ref. 23. The values of the applied pressure were estimated to better than ± 0.2 GPa from the change in the unit cell volume of PMT. To this end, the third-order Birch-Murnaghan equation of state²⁴ was used with parameters taken from Ref. 16.

The crystal structure was refined with Fullprof²⁵ following a structural model of PMT developed in Ref. 7. This study established that the structure is best described by Pb ions displaced along the $\langle 110 \rangle$ direction from the (0 0 0)

FIG. 1. Neutron powder diffraction patterns of PMT collected at nominal pressures of (a) $P=0.04$ GPa and (b) $P=7.05$ GPa. Observed data points with background originating from the pressure cell is subtracted, calculated profiles and difference curves are shown. The row of ticks corresponds to the calculated positions of diffraction peaks. The peak in the vicinity of $2\theta=45^\circ$, which is not fitted well within our model, is due to scattering from an impurity of pyrochlore (Ref. 7).

special position. The temperature factors of all ions are assumed to be isotropic with the exception of the oxygen ions where anisotropic components are also considered. For the Mg/Ta ions, we assume a random occupation of the Mg/Ta ions over the B sites (0.5 0.5 0.5) of the PMT perovskite structure according to the stoichiometric ratio. To avoid unwanted correlation between the refined values of the displacement amplitudes and the B factor of Pb, latter was fixed to a value of $1.14 \text{ \AA}^2$ obtained at $T=300 \text{ K}$.⁷ We note that we cannot rule out a displacement of the Mg/Ta or oxygen ions but assert these displacements to be small in comparison to the temperature factors.⁷ The reliability factors for $P=0.04$ GPa are $\chi^2=1.4$, $R_{\text{exp}}=2.73$, $R_{\text{wp}}=3.23$, $R_{\text{Bragg}}=8.22$, and for $P=7.05$ GPa, they are $\chi^2=1.47$, $R_{\text{exp}}=1.82$, $R_{\text{wp}}=2.21$, $R_{\text{Bragg}}=11.1$.

Figure 1 shows representative observed and calculated diffraction patterns obtained for PMT close to ambient and at the highest pressure of nominally $P=7.05$ GPa. Apart from the trivial shift of all peaks to higher scattering angles related to the contraction of the PMT lattice, the effect of pressure is to modify significantly the relative peak intensities, as seen, for example, on the (220) and (420) reflection. The latter results from the combined effects of the isostructural displacement of the ions within the unit cell and microstrains that broadens Bragg peaks and which may be quantified by a Rietveld analysis of the data. Here we note that sharp superlattice reflections are observed above ~ 4 GPa in PMN and

FIG. 2. (a) Dependence of the amplitude of lead displacements $\text{Pb}_{\langle XX0 \rangle}$ in PMT against lattice parameter. Error bars are within the size of the symbols. (b) Root-mean-square displacements of the oxygen ions against lattice parameter: note that the $\langle 110 \rangle$ ($\langle 001 \rangle$) direction points toward Pb (Mg/Ta). (c) Root-mean-square displacements of the Mg and Ta ions against lattice parameter. All graphs have the same scale to emphasize the significant difference in the pressure dependences of these parameters. Values of corresponding pressures can be found in Table I.

~ 6 GPa in PZN at room temperature^{16,26} by x ray. These reflections are indexed as $(h,k,l)/2$ (h,k,l - odd) and, hence, correspond to cell doubling. Within the statistical accuracy of the present measurements, these reflections are not observed and the chemical structure of PMT is well described in the $Pm\bar{3}m$ space group at all pressures.

Figure 2 shows the evolution of the lead displacements ($\text{Pb}_{\langle XX0 \rangle}$) and the root-mean-square (rms) displacements of Mg/Ta and oxygen in PMT as a function of the lattice parameter.²⁷ These quantities vary approximately linearly with the lattice parameter, however, with opposite slopes and with different rates: e.g., whereas the displacement of $\text{Pb}_{\langle XX0 \rangle}$ decreases by about $0.07 \text{ \AA}$ as the lattice contracts, the rms of the Mg/Ta ions increases by about $0.02 \text{ \AA}$. It is worth noting that all observed changes in the $\text{Pb}_{\langle XX0 \rangle}$ displacements and

TABLE I. Pressure, lattice parameter and amplitude of lead displacement of PMT (equation of state with $B=104$ GPa, $B'=4.7$ taken from Ref. 16).

Pressure (GPa)	Lattice parameter (Å)	Pb displacement (Å)
0.04	4.04019(7)	0.211(3)
2.28	4.01260(7)	0.180(3)
4.47	3.98822(9)	0.169(5)
5.86	3.9738(1)	0.144(5)
7.05	3.9620(2)	0.140(6)

rms displacements of the other ions (e.g., Mg/Ta, 20%) are considerably larger than that of the cell volume of PMT ($\sim 6\%$).

Further inspection of Fig. 2 shows that the decrease in the $Pb_{(XX0)}$ is accompanied by an increase in the anisotropy of the oxygen temperature factor. However, a reliable analysis of the components of the anisotropic temperature factors requires high statistical quality of the data. This is hardly achieved in the present experiment under high pressures and correspondingly small sample volumes. Thus, in order to unambiguously analyze the change in the anisotropy of the oxygen vibrations, we have combined earlier temperature-dependent studies of the PMT structure⁷ with the present results. It turns out that the amplitude of the $Pb_{(XX0)}$ is a suitable variable common to both the pressure- and temperature-dependent studies. Figure 3 thus shows the components of the oxygen thermal ellipsoid in relation to the amplitude of Pb displacements. It is clearly seen that the $\langle 110 \rangle$ and $\langle 001 \rangle$ components of the oxygen temperature factor evolve in the opposite direction; whereas, the component directed along the Pb-O bond increases significantly as the amplitude of the Pb displacements decreases, and the component directed along the Mg/Ta-O bond exhibits a slight decrease. In fact, the latter component of the oxygen temperature factor is the only structural parameter, which has a similar relative change as the PMT cell volume.

The above-evidenced pressure-induced changes of the temperature factors in PMT are, by far, anomalous and may be contrasted to what is expected for a simple solid. In the latter case, the temperature factors are related to the phonons and thus should decrease with increasing pressure at a rate of approximately the average Grüneisen-parameter, that is close to 1. This implies the relative change of the temperature factors to scale with the change in the unit cell volume. Obviously, the corresponding changes in PMT are in excess to such scaling and even show opposite trends for Mg/Ta and for one of the components of the oxygen temperature factors.

Because the perovskite-type materials constitute a significant part of the Earth's mantle, their properties under high pressure are widely studied. However, we are not aware that substantial changes of the atomic temperature factors in these compounds have been reported before, e.g., the temperature factors of the ions in $GdAlO_3$ and $GdFeO_3$ crystals do not change significantly up to pressures of about 8 GPa.²⁸ The relative changes of the atomic positions in these materials all

FIG. 3. Components of the oxygen thermal ellipsoid vs the amplitude of lead displacements. Data points shown by open symbols are taken from earlier temperature-dependent studies of the structure of PMT (Ref. 7) at ambient pressure. These points were measured at $T=588, 450, 300, 200, 85$, and 1.5 K, correspondingly. We note that smaller Pb displacements correspond to higher temperatures.

scale well with the changes in the unit cell volume.

On the other hand, it is known that hydrostatic pressure suppresses the ferroelectric properties in perovskites.²⁹ For example, at sufficiently high pressures $BaTiO_3$ (Ref. 30) and $KNbO_3$ (Ref. 31) restore the paraelectric cubic structure.³² However, even such significant changes are not accompanied by profound changes in the temperature factors. In the case of the tetragonal-to-cubic pressure-induced phase transition of $BaTiO_3$, there is a shift of the Ti ion by ~ 0.02 Å and the temperature factor of Ti increases by a factor of 2, whereas the structure parameters of the other ions remain essentially unchanged.³⁰

From the discussion above, we suggest that the pressure-induced changes in the structural parameters of PMT might also be observed in similar relaxors. The most significant of these changes is the decrease of the amplitudes of Pb displacements and increase of the component of the anisotropic temperature factor of oxygen ions directed toward Pb. On the other hand, the change in the temperature factor of Mg/Ta is much less pronounced. From the analysis of the Bragg peak intensities, we cannot infer direct information about the short-range correlations between the displaced ions. However, it is reasonable to expect that as the value of the ionic displacements decreases, the associated short-range order (static and/or dynamic) diminishes, which, in turn, causes (i) the reduction of the diffuse scattering and (ii) the suppression of the dielectric permittivity peak. Thus, our observations give a microscopic explanation for the aforementioned suppressions in lead-containing relaxors, namely, by the anomalous correlated displacements of the lead and oxygen ions. A quantitative model to describe such relationship is a matter of future theoretical and experimental studies. High pressure measurements of the diffuse scattering using single crystals would be highly desirable.

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