

## Pressure-Induced Suppression of the Diffuse Scattering in the Model Relaxor Ferroelectric $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$

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We report an investigation of the relaxor ferroelectric  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  by combining the external parameter high pressure with x-ray diffuse scattering. The observed total suppression of the relaxor-characteristic x-ray diffuse scattering is unusual and points to important pressure-induced changes in the local order. The observed behavior might well be a general feature in relaxor ferroelectrics under high pressure.

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Among ferroelectrics, the so-called relaxor ferroelectrics (relaxors) form a special class of materials of which the understanding remains a challenging problem. Recently, it has been reported that relaxor-based materials exhibit outstanding electromechanical properties near structural phase boundaries [1,2].

It is generally admitted that the peculiar physical properties of relaxors, such as diffuse phase transitions and a dielectric relaxation, are related to an intrinsic nano-scaled local structure. However, one of the major challenges in the analysis and understanding of relaxors is the experimental access to such local properties with respect to the average structure, which is often at best a difficult task. Diffuse scattering has shown to be one of the rare techniques for a direct observation of the relaxor-characteristic local structure [3–5]. Here we present an investigation of the model perovskite-type relaxor  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN) by combining the parameter high pressure and x-ray diffuse scattering (XDS) at a synchrotron source.

In the past, pressure-dependent studies on relaxors have been limited to modest pressures ( $< 1.5$  GPa). We should, in particular, note investigations by Samara *et al.* [6], which illustrate for soft mode ferroelectrics a pressure-induced crossover from long- to short-range order (ferroelectric-to-relaxor crossover), which has been interpreted by considering a decrease in the correlation length for dipolar interactions with pressure. Further investigations by Samara [7] of the relaxor PMN at 0.8 GPa suggest that the relaxor-characteristic polar nanoregions decrease in size with increasing pressure, and it is argued that this strengthens its relaxor character. It is only very recently that investigations of relaxors have been extended to *high* pressure ( $< 20$  GPa) revealing important structural and polar changes with pressure [5,8,9]. Concerning PMN, a high-pressure Raman study has illustrated pressure instabilities; for instance, the observation of a new sharp spectral signature suggested

that PMN undergoes a structural rearrangement above  $\approx 4.5$  GPa (Ref. [9]). However, the investigation of PMN by Raman spectroscopy could not provide detailed information about the pressure-dependent changes of the size, order, and structure of the local and average structure. The objective of this study is to address the latter points and to extend, in a general matter, our current limited knowledge on the effect of high pressure on relaxors.

PMN single crystals have been prepared by flux technique. The presented high-pressure synchrotron x-ray scattering experiments were performed at room temperature in the 1 bar to 10 GPa range at the European Synchrotron Radiation Facility on the ID30 high-pressure beam line. High-pressure experiments on a crystal 50  $\mu\text{m}$  in size were performed with the focused beam on a diamond anvil cell with a 4:1 methanol:ethanol mixture as the pressure transmitting medium.

Before discussing in detail the pressure-dependent evolution of PMN, it is useful to inspect the x-ray scattering imaging (XRSI) pattern at low pressure by considering the interpretations suggested in the literature for the case where no pressure is applied [3,10]. Figure 1(a) shows an XRSI pattern of PMN at 0.1 GPa, where Bragg reflections, diffuse scattering, and weak superstructure reflections are observed. In agreement with the literature, the observed Bragg reflections illustrate that PMN adopts on average the ideal cubic perovskite structure ( $Pm\bar{3}m$ ,  $O_h$ ). However, both the XDS and the weak superstructure reflections offer corroborative evidence for local deviations from this average structure, which is in agreement with the idea of a somehow peculiar nanostructure in relaxors.

As shown in Figs. 1(b) and 1(c), the XDS, related to local deformations of the crystal lattice [3], is localized along  $\langle 110 \rangle$  directions in the reciprocal lattice, indicating  $\{110\}$ -type defect planes in the direct space. In principle, both structural deviations ( $BO_6$  octahedra tilts or/and cation displacements) and a local substitution-type

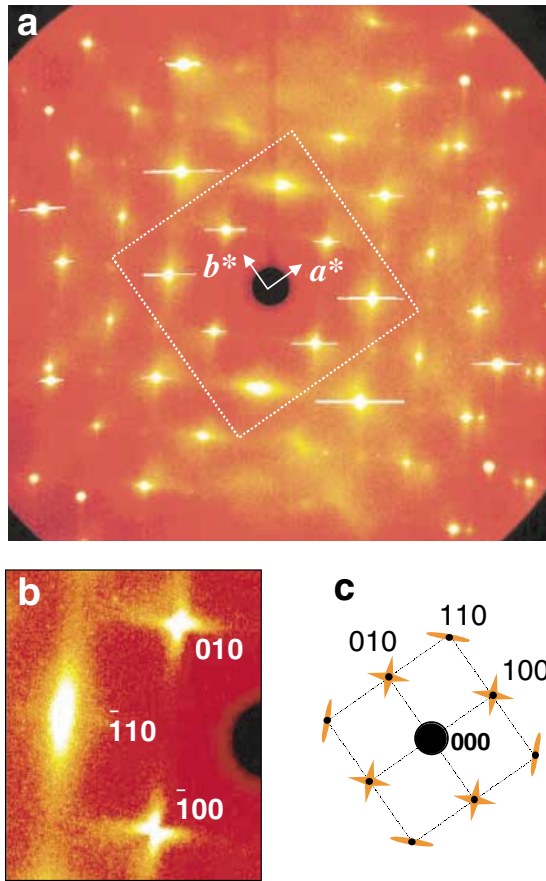


FIG. 1 (color online). (a) X-ray scattering imaging pattern for  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  at a hydrostatic pressure of 0.1 GPa. The pattern is obtained from a  $-15^\circ$  to  $+15^\circ$  oscillation, with respect to the incoming monochromatic synchrotron beam ( $\lambda = 0.3738 \text{ \AA}$ ). The sharp horizontal lines are due to the saturation of the detector. Several intense reflections, not corresponding to the PMN lattice, come from the diamond anvil cell. (b) Pattern obtained from small oscillations to emphasize the diffuse scattering. (c) Schematic representation of the diffuse scattering in the dotted area of (a).

(chemical) disorder have to be considered as the origin of the XDS. We discard a substitution-type disorder in the form of chemical segregation, since such a disorder would produce XDS around both Bragg reflections *and* the direct beam, but this is not observed [Fig. 1(a)], which is in agreement with small-angle scattering experiments. Furthermore, we see in the following that the pressure-dependent changes of the XDS cannot be explained by considering a chemical origin, which would be essentially pressure independent. As a consequence, we should consider a structural origin, namely, in the form of local cation displacements, which then act as defects.

Further information about the local structure can be gained from weak  $1/2(hkl)$ -type superstructure reflections, hereafter denoted  $(hkl)_{1/2}$ , which are usually attributed to a local chemical ordering in PMN since the reflections remain almost constant with increasing tem-

perature. On the basis of the full width at half maximum (FWHM) of the observed  $(hkl)_{1/2}$  reflections, the size of such nanoregions is estimated to 50  $\text{\AA}$ .

Let us now turn to the pressure-dependent evolution of PMN as illustrated in Fig. 2. Figure 2(a) presents a high-pressure XRSI pattern of a selected part of the reciprocal space, Figs. 2(b) and 2(c) present the pressure-dependent evolution of the diffuse scattering around the (300) reflection, while Fig. 3 presents the pressure evolution of the volume fitted between 0.1 and 4.5 GPa with a third-order Birch-Murnaghan equation of state. Figures 2(b) and 2(c) illustrate that PMN undergoes important changes with increasing pressure, and already the qualitative inspection of the pressure-dependent pattern reveals one of the most important results: As pressure increases we observe that the XRSI images clear up; i.e., the XDS disappears and at high pressure the pattern ends up with well-defined Bragg reflections [Fig. 2(a)], indicating only small local structural deviations from the average structure, if any. The simplest qualitative explanation of the latter would consist in admitting a transition to a long-range high-symmetry cubic phase as occurs under high pressure for a

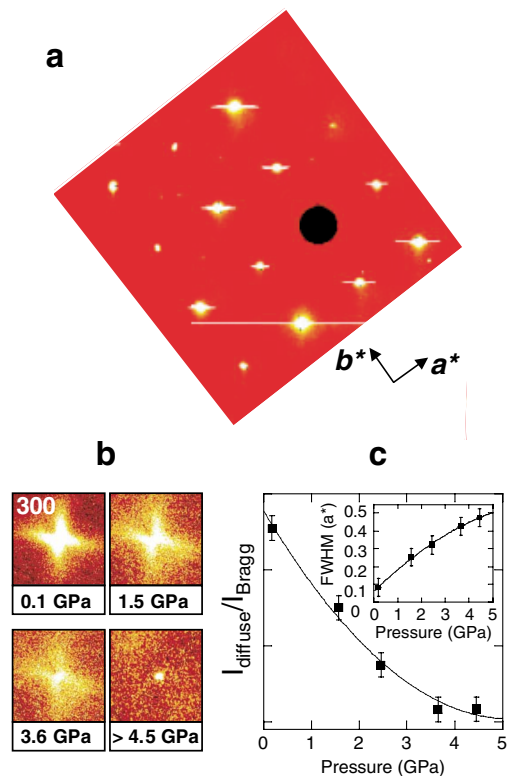


FIG. 2 (color online). (a) X-ray scattering imaging pattern for  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  at a hydrostatic pressure of 6.5 GPa. (b) Illustration of the pressure dependence of the diffuse scattering around the 300 reflection. (c) Evolution of the intensity and FWHM (inset) of the diffuse scattering around the 300 reflection. The lines are guides to the eye to emphasize changes.

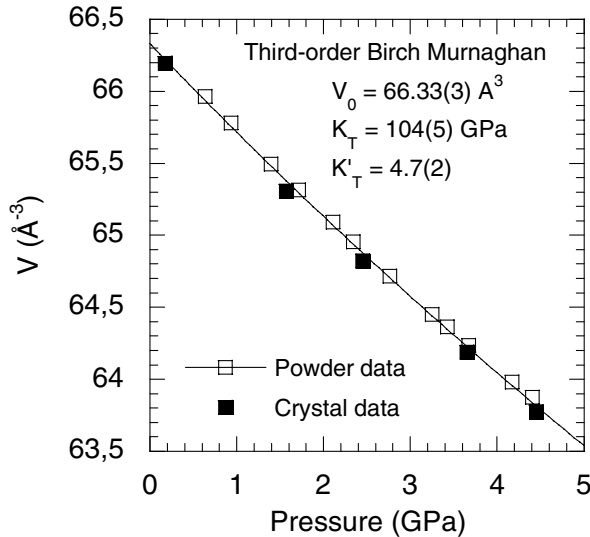


FIG. 3. Pressure-dependent evolution of the unit-cell volume of PMN by considering a pseudocubic  $Pm\bar{3}m$  space group up to 4.5 GPa. The parameters extracted from a fit with a third-order Birch-Murnaghan equation of state (plain line) of crystal and powder diffraction data are displayed on the graph.

number of classical ferroelectrics such as  $\text{BaTiO}_3$  or  $\text{KNbO}_3$ . However, the report [9] of a persistent Raman signal at high pressure can refute this for PMN and we should thus consider a noncubic long-range structure.

The interpretation of the reduced XDS beyond the simple conclusion of a somehow reduced disorder is not trivial. In the discussion of the low-pressure phase we have mentioned that the diffuse scattering is related to local lattice deformations with respect to the average structure, but we have not yet discussed the origin of this deformation. Both an electrostatic origin and/or a mechanical origin have been suggested in the literature [11]. An electrostatic origin (due to the  $\text{Nb}^{5+}$  and  $\text{Mg}^{2+}$  charge difference) is expected to change only little with pressure if we exclude the unlikely cation diffusion at high pressure. As a consequence, the observed pressure-induced disappearance of the XDS (Fig. 2) suggests that the electrostatic origin is at least not the dominating contribution. Concerning the mechanical origin, the above high-pressure argument also allows ruling out an important contribution coming from a pure (pressure-independent) cation-size effect due to different sizes of  $\text{Nb}^{5+}$  and  $\text{Mg}^{2+}$ . As a consequence, we suggest a mechanical origin coming from different cation displacements among different sample regions (i.e., matrix and polar nanoregions). In this scenario the pressure-suppressed XDS is explained by a suppression of the local mechanical strain when the polar nanoregions and the matrix adopt the same noncubic structure. Support for pressure-induced changes in the cation displacements comes from recent high-pressure Raman data [8,9].

A remaining question concerns the mechanism that leads to the suppression of the mechanical strain. For

this it is instructive to inspect the pressure evolution of the FWHM and intensity of the XDS near the (300) reflection, which allows a detailed investigation [3]. Figure 2(c) shows that an increase in pressure leads to both a decrease in intensity and an increase in the FWHM of the XDS, which gives evidence for a size reduction of the local defects with increasing pressure. The latter is in agreement with interpretations by Samara [7], which were based on dielectric measurements of PMN at 0.8 GPa. Furthermore, we should note that high-pressure Raman spectroscopy measurements suggested a collective pressure-induced reduction of the cation displacement [9]. As a consequence, we propose that the effect of pressure leads for the polar nanoregions to the decrease of both the polar correlation length  $r_c$  and the displacement amplitude.

Further insight into pressure-induced change can be gained from the pressure-dependent evolution of the  $(hkl)_{1/2}$  superstructure reflections, which is illustrated in Fig. 4. It is interesting to observe that from 4.0 GPa onwards the superstructure reflections appear to be composed of two components: one diffuse reflection (already present at ambient conditions) superimposed with a new sharp Bragg reflection. As shown in the inset in Fig. 4, the FWHM of the diffuse reflection is rather pressure independent, which adds further support to its above-suggested chemical origin. On the other hand, the pressure-induced sharp reflection is related to a structural cell doubling, which might originate in antiphase tilts of octahedra and/or antiphase cation displacements. Such a superimposition of two components related to a unit cell

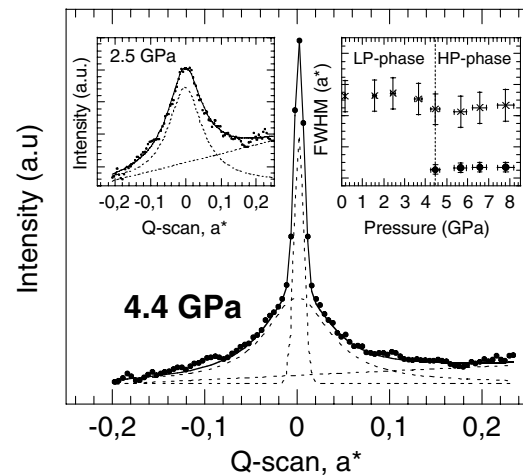


FIG. 4. Illustration of the pressure dependence of a representative  $1/2(135)$  superstructure reflection. The main graph illustrates the superimposition of diffuse scattering with a “cell-doubling” Bragg reflection at 4.4 GPa. The left inset illustrates the diffuse (chemical) scattering as typically observed in the low-pressure (LP) phase ( $p < 4.5$  GPa). The right inset presents the evolution of the FWHM of the diffuse and sharp features as a function of pressure.

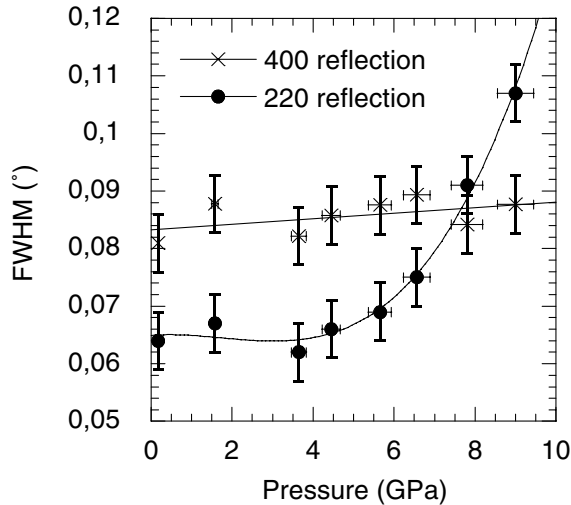


FIG. 5. Pressure-dependent evolution of the FWHM of the 400 and 220 reflections. The lines are guides to the eye to emphasize changes.

doubling is reminiscent of the temperature-dependent investigation of  $(hkl)_{1/2}$  reflections by Gosula [10], where a new sharp component has been observed at low temperature. However, we should note that the reported “fingerprint” Raman spectra at high pressure [9] and low temperature [12] are different, suggesting that the two phases are not identical.

The comparable FWHM of the new pressure-induced sharp features at  $(hkl)_{1/2}$  and the Bragg reflections indicates that the cell doubling is related to the long-range structure. In this sense, the  $(hkl)_{1/2}$  reflections reflect the long-range deviations from the ideal cubic structure, in agreement with the interpretation above that the disappearing XDS is not due to a cubic overall structure. In order to discuss whether the new pressure-induced superstructure reflections in PMN are related to  $BO_6$  antiphase tilts or antiferroelectric cation displacements, we have performed a preliminary (unpublished) high-pressure neutron powder diffraction investigation which is a better adapted technique for the investigation of the oxygen lattice. In agreement with the synchrotron data, the high-pressure neutron diffraction pattern of PMN shows  $(hkl)_{1/2}$  reflections. However, the low intensity of the  $(hkl)_{1/2}$  reflections (just as with synchrotron radiation) suggests that octahedron tilting is at least not the dominating mechanism behind the  $(hkl)_{1/2}$  reflections and we thus assume that the intensity of  $(hkl)_{1/2}$  reflections measured by x-ray scattering is related to antiparallel cation displacements.

It remains to discuss the possible symmetry of the pressure-induced phase. Figure 5 displays the pressure evolution of the FWHM of a  $\langle h00 \rangle$  reflection together with a  $\langle hk0 \rangle$  reflection. It can be seen that the FWHM of the  $\langle 400 \rangle$  reflection is nearly pressure independent, while the FWHM of the  $\langle hk0 \rangle$  reflections starts to increase at

the phase transition pressure, suggesting an underlying split. In the case of an orthorhombic, monoclinic, or tetragonal structure we would have expected, under the assumption of a high-enough resolution, a split or at least a broadening of the  $\langle h00 \rangle$  reflections; this is not observed. On the other hand, the observed split of  $\langle hkl \rangle$  reflections together with a single  $\langle h00 \rangle$  reflection is a well-known signature for a rhombohedral distortion. Further details of this new structure have been revealed by Raman spectroscopy [9], illustrating that the high-pressure phase of PMN is characterized by nonpolar  $B$  sites, i.e., the Nb and Mg cations are not displaced. Combining the complementary information, we thus propose that the high-pressure phase of PMN is of rhombohedral symmetry with antiparallel displacements of the Pb cations.

In conclusion, we have reported that  $PbMg_{1/3}Nb_{2/3}O_3$  undergoes important pressure-induced changes on a local and average scale. In particular, we have shown that the initial diffuse scattering of  $PbMg_{1/3}Nb_{2/3}O_3$  dramatically decreases with applied pressure and finally vanishes at 4.0 GPa where we observe new superstructure reflections (Fig. 4). The latter observations illustrate important pressure-induced changes in the short-range order and a new long-range structure at  $p > 4.0$  GPa. Note that pressure usually tends to increase disorder in oxides. However, our present study, together with very recent results on the relaxor  $Na_{1/2}Bi_{1/2}TiO_3$  (Ref. [5]), suggests that the observed pressure-induced suppression of the diffuse scattering might well be a general feature in relaxor ferroelectrics under high pressure. As a matter of fact, high pressure appears to suppress the displacement disorder related to the  $B$  site of the perovskite structure with the important consequence that the local competition between  $A$ -site and  $B$ -site displacements (inhibiting a long-range order) is also suppressed, which then allows the establishment of a new long-range structure.

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