Effect of high pressure on relaxor ferroelectrics

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We report results of a high-pressure investigation by Raman spectroscopy of a classic relaxor ferroelectric (relaxor) $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), which is considered to be a model system for the understanding of relaxor and relaxor-related materials. The observed pressure-dependent Raman spectra are very unusual, pointing to a relaxor-specific spectral signature. We further show that an external pressure of several GPa, as can be met in thin films, alters fundamentally the structural and polar properties of PMN, suggesting that intrinsic instabilities towards pressure play an important role in the reduction of dielectric properties in relaxor and relaxor-related thin films.

Relaxor ferroelectrics (relaxors) form a special class among ferroelectric materials of which the understanding remains a challenging problem. Relaxors are characterized by diffuse phase transitions and dielectric dispersion, which distinguishes them from classic ferroelectrics with well-defined phase transitions and a sharp peak in the dielectric response. Although the true origin of the relaxor behavior remains controversial it is generally admitted that their reported outstanding properties are governed by a peculiar microstructure, which consists of nanoscale polar regions, a reason for which relaxor ferroelectrics are often called ''dirty ferroelectrics.'' The potential impact of thin-film relaxors and relaxor-related materials in various applications, especially related to their ultrahigh piezoelectric effects,[1,2] has stimulated a fast growing interest. Although it has been realized that strain effects at the film-substrate interface modify dramatically their physical properties,[3,4] there is incomplete understanding of the responsible mechanisms.

Most technologically important relaxors, among those the classic relaxor ferroelectric $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), crystallize in the so-called perovskite-type structure. The ideal cubic structure in perovskite-type oxides ABO_3 consists of corner-linked anion octahedra BO_6, the B cations at the center of the octahedra and the larger A cations in the space (coordination 12) between the octahedra. A number of materials deviate slightly from this ideal perovskite, for instance by a rotation (tilting) of BO_6 octahedra or/and by cation displacements.[5] It is the ''off-centering'' of the A and/or B cation that gives rise to ferroelectric (polar) properties. Although the average structure of $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) is cubic, the local structure is characterized by shifts of the A and B cations.[6] These cation shifts occur in different parts of the sample, giving rise to the so-called nanoscale polar regions. Let us point out that relaxors are not the only perovskite-type oxides where the microstructure plays an important role in the determination of outstanding physical properties. There is growing evidence that the observed colossal properties in magnetoresistive oxides are related to local (magnetic, electric or/and structural) phase separation.[7–9] Furthermore, it has been recently proposed that magnetoresistive oxides are from a microstructural point of view similar to relaxors.[10] Here we report results of a high-pressure investigation by Raman spectroscopy of the relaxor PMN, which is considered to be a model system for the understanding of relaxor and relaxor-related systems.

In the past, the usual approach towards the understanding of relaxor ferroelectrics (and manganite-type materials) was mainly through their chemical composition or temperature-dependent behavior. Only recently, mainly through the work of Samara and co-workers (e.g., Refs. 11,12) but also through the work by Yasuda and co-workers[13] on $PbIn_{1/2}Nb_{1/2}O_3$, the importance of pressure as a variable in elucidating ferroelectrics has been emphasized. It has been pointed out that the effect of pressure is a ''cleaner'' variable,[11] compared to other parameters, since it acts only on interatomic interactions. Until very recently,[14] pressure-dependent studies on relaxors have been limited to pressures smaller than 1 GPa and to investigations by diffraction or dielectric measurements only. However, as we will show in the following, a deeper understanding of the physics in relaxors (bulk and films) can be expected from high-pressure investigations by a local probe such as Raman spectroscopy, which is well adapted to the nanoscale where the physics of relaxors takes place.

PMN single crystals have been prepared by flux technique. Raman spectra of PMN powders ground from as-grown single crystals were recorded in back-scattering geometry with a Dilor XY multichannel spectrometer using an Ar^+-ion laser (514.53 nm) as excitation line. High-pressure experiments were performed in a diamond anvil cell.[15] Raman spectra after pressure release are identical to the initial spectra attesting the reversibility of pressure-induced changes. Temperature-dependent Raman spectra and the assignment of room-temperature Raman bands can be found in Ref. 16.

Figure 1 presents pressure-dependent Raman spectra of PMN where several features can be discerned for increasing pressure. First, we observe new spectral features, the most visible being the apparition of a sharp mode at roughly 370 cm^{-1}. Second, we observe a dramatic decrease in intensity
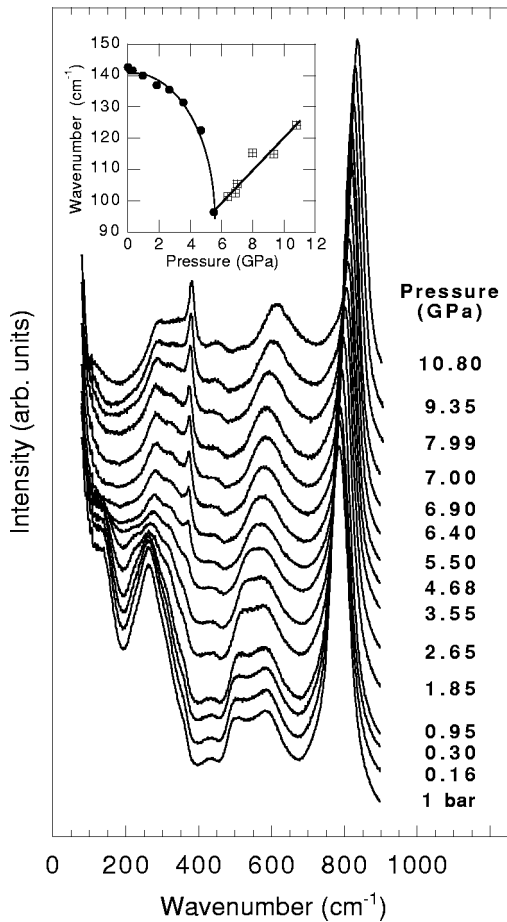
FIG. 1. Representative pressure-dependent Raman spectra of PbMg$_{1/3}$Nb$_{2/3}$O$_3$ (PMN). Modifications of the spectral signature reveal structural and polar instabilities of PMN towards pressure. The inset displays the pressure-dependent evolution of a band (initially at 143 cm^{-1}) related to Pb^{2+}-O^{2-} vibrations. The lines are guides for the eye to emphasize spectral changes.
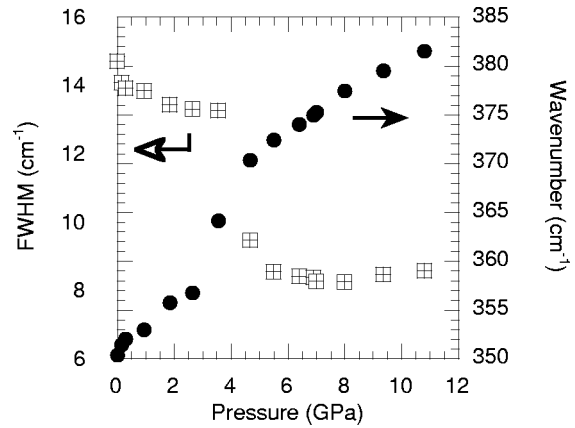

FIG. 2. Evolution of the FWHM (left) and frequency (right) for the initially 350 cm^{-1} band in the pressure-dependent Raman spectra of PbMg$_{1/3}$Nb$_{2/3}$O$_3$ (PMN).

of the features around 200 to 300 cm^{-1}. Third, the spectral deconvolution of the Raman spectra reveals slight but significant changes in the frequency, intensity, and width of all modes. Each of the latter features points to pressure-induced structural changes in PMN.

Let us first discuss the pressure-induced appearance of the sharp band at 370 cm^{-1}. As shown in Fig. 2, the intensity increase of this band at 4.68 GPa is accompanied by anomalies in the evolution of the full width at half maximum (FWHM) and in frequency. The observation of such anomalies adds further evidence for a fundamental pressure-induced change in PMN. Bearing in mind that the FWHM of a Raman band is inversely proportional to the lifetime of the belonging phonon, the sharpening points to a well-established long-range order of the corresponding new phase. Despite the clear evidence for a change, it is not straightforward to relate this new structural fingerprint to the related structural characteristics and, thus, it is worthwhile considering already known spectral signatures. First, let us remind that perovskite-type manganites, which are since recently known to have a peculiar and somehow relaxor-similar microstructure,[7-10] show a similar striking sharp band

in the same frequency region.[17,18] This band has been attributed to a rhombohedral structure.[17,18] Considering now that Raman spectra of even different perovskites often show similar spectral signatures, it is tempting to conclude on the presence of a rhombohedral distortion in the high-pressure phase of PMN. Second, we might consider a Raman investigation of PbSc$_{1/2}$Ta$_{1/2}$O$_3$ (PST) samples with different degrees of chemical order on the B site, which shows that the appearance of a sharp peak at 365 cm^{-1} can be related to ordering on the B site.[19] It is not implausible to imagine for PMN a pressure-induced change of the ordering scheme since it is known that pressure can affect the order-disorder character in materials: for instance, in geological systems pressure tends to increase order.[20,21] If the latter reveals to be true, pressure (and possibly also strain in thin films) would then constitute a new way to introduce order in PMN samples, which is not possible through heat treatments. However, although a rhombohedral and/or an order-disorder character of the high-pressure phase appear to be good candidates to explain the observed behavior, the precise structural characteristics remain to be established by complementary methods.

We will show in the following that the observed spectral changes reveal furthermore fundamental changes in the polar properties of PMN. Let us first draw the attention to a peculiar spectral signature. The intensity breakdown in the middle-frequency region around 250 to 350 cm^{-1}, occurring together with an almost unchanged intensity of the high-frequency bands (Fig. 3). Such a spectral signature is very unusual and, to the best of our knowledge, the only similar spectral signature has been reported in a very recent investigation for another relaxor ferroelectric Na$_{1/2}$Bi$_{1/2}$TiO$_3$ (NBT).[14] In order to emphasize this spectral signature and the striking similarity between PMN and NBT, Fig. 4 presents their pressure-dependent Raman spectra directly superimposed and normalized to the bands around 600 cm^{-1}. At first sight, it is rather surprising that PMN and NBT show a similar behavior since (i) they are very different from a chemical point of view, (ii) they are B- site (PMN) compared to A-site (NBT) substituted, and (iii) they show a cubic (PMN) compared to rhombohedral (NBT) average structure at ambient conditions. On the other hand, PMN and NBT
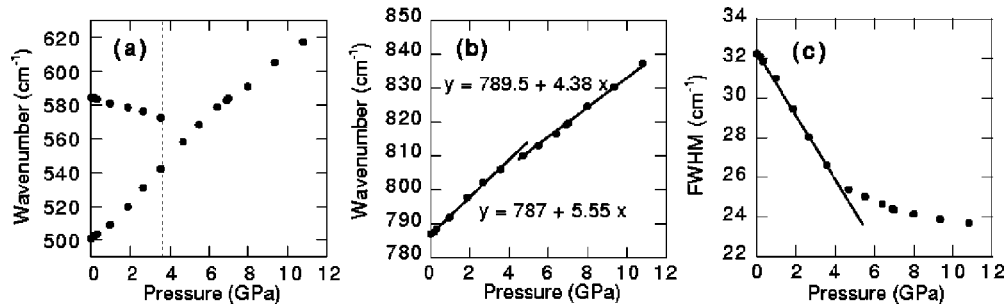
FIG. 3. Pressure-dependent evolution of the high-frequency Raman bands in $PbMg_{1/3}Nb_{2/3}O_3$ (PMN). (a) Band position change for two initially separated bands at 500 and 580 cm^{-1} (LO-TO splitting, see text), which merge into a single band. (b) Band position change for the most intense band at initially 785 cm^{-1}. The lines and equation are relative to a linear fit and can be used as a reference to estimate compressive stress in PMN thin films. (c) Bandwidth change for the band at 780 cm^{-1}. The pronounced sharpening is interpreted as the coalescence of two underlying components into a single band.

have also common characteristics that are related to their common relaxor ferroelectric behavior: they both have a peculiar microstructure with polar regions and they both are characterized by a cation displacement on the A and B site in different parts of the samples. We believe that the latter common relaxor-like characteristics are at the origin of the similar behavior, and we propose that the above Raman signature might well be a unique pressure-dependent spectral signature for polar changes in relaxor ferroelectrics.

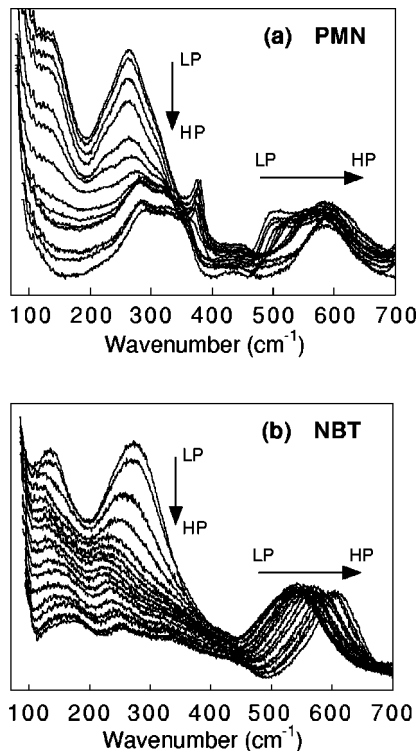How should we imagine the mechanisms of the pressure-

FIG. 4. Directly superimposed pressure-dependent Raman spectra (HP: high pressure, LP: low pressure). (a) $PbMg_{1/3}Nb_{2/3}O_3$ and, for comparison (b) very recently (Ref. 14) reported results for $Na_{1/2}Bi_{1/2}TiO_3$. It is the common (and very unusual) feature of these two materials that for increasing pressure the intensity drops dramatically in the 200–300 cm^{-1} region while the features in the 500–600 cm^{-1} region remain almost unchanged in its intensity.

induced polar changes on a microstructural level? Let us first consider the pressure-induced spectral changes in the middle-frequency region (250–350 cm^{-1}), which is dominated by vibrations involving the B-cation displacement and tilts of the BO_6 octahedra. As a matter of fact, a loss of intensity in this region, as observed here for PMN (and NBT),[14] is a commonly used direct signature to evidence polar changes on the B site related to the restoring of the cation towards the center of the octahedron (e.g., Refs. 14,22,23). A further support for polar changes on the B site comes from the evolution of the high-frequency modes, which are dominated by vibrations of O^{2-} anions involving the most rigid cation-oxygen bonds inside the BO_6 octahedra (breathing and bending of BO_6). Although the polar B cation is not directly involved, such modes can give us indirect insight into polar properties due to the fact that polar B-O bonds condition a splitting into longitudinal (LO) and transversal (TO) components. On this basis, we interpret the pressure-dependent change of the high-frequency bands in PMN (Fig. 3) as the gradual suspension of an initial LO-TO band splitting (conditioned by the restoring of the B cation). A similar LO-TO split was observed for NBT,[14] where the initial split is smaller due to a less important displacement of the B cation compared to PMN. Finally, the persisting intensity of the high-frequency bands with increasing pressure is interpreted as a local noncubic structure (i.e., through nonpolar octahedron tilts), at least in some parts of the sample.

A further argument for pressure-induced changes of the polar properties in PMN comes from the evolution of the band around 140 cm^{-1}, which belongs to vibrations of the A cation (Pb-O stretching mode of A_{1g} symmetry).[16] The softening of this Pb-O band followed by a slope change (around 5.5 GPa, see inset Fig. 4) gives direct evidence for fundamental changes in the Pb^{2+} displacement. It is tempting to attribute this slope change to a modification of the type of displacement, for instance from parallel to antiparallel and/or in the direction of displacement.

It becomes clear that PMN presents structural and polar instabilities towards external pressure. We should emphasize that the here observed pressure-induced fundamental modifications of the polar properties take place at both cation sites of the perovskite structure, although presumably at different

pressures (3.55 GPa on the *B* site, 5.50 GPa on the *A* site) suggesting a different pressure-dependent behavior for different nanoregions. One of the structural mechanisms that we should take into consideration to understand the latter point is based on the consideration of chemically different nanoregions, which have different compressibilities[24] thus leading to a different behavior with applied pressure.

The observed pressure instabilities further suggest that an intrinsic mechanism contributing to the reduction of the electrical and electromechanical properties in relaxor films is a fundamental change in the cation displacement. This is well in line with the observation[4] that compressive stress in relaxor films reduces dramatically the relative dielectric constant ϵ_ρ (in virtue of the reduction of the cation displacement), which is linearly related to the important piezoresponse d_{33}; the latter suggesting rather the synthesis of tensile-strained relaxor films, in agreement with recent observations.[4] On the basis of dielectric measurements of bulk PMN up to 0.8 GPa Samara has recently suggested[12] that a decrease in the correlation length for dipolar interactions with pressure allows interpreting the pressure-induced reduction of the dielectric constant and the glasslike transition temperature (T_m). Our measurements do not allow confirming or contesting Samaras model and a coexistence of his and the here presented model is, in principle, conceivable. However, we believe that at least the reduction of the dielectric constant is dominated by a collective change in the cation displacement for which we have direct experimental evidence.

Finally, let us point out that the identification of a unique pressure-dependent spectral feature in relaxors is not only interesting from a fundamental point of view but also because the denomination relaxor (and thus interpretation) of a given material often leads to long-standing and controversial discussions, this is particularly true in the case of thin films.[25] We have shown that high-pressure Raman spectroscopy is an alternative and effective technique to handle this problem. We expect that further pressure-dependent investigation by local probes such as Raman but also extended x-ray absorption fine structure or NMR, will reveal insight into materials with outstanding properties that are driven by a peculiar microstructure (relaxors, manganite-type oxides[7,8] etc.).

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