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High-pressure Raman investigation of the Pb-free relaxor $BaTi_{0.65}Zr_{0.35}O_3$

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We report high-pressure Raman measurements (up to 27 GPa) on the perovskite-type relaxor ferroelectric $BaTi_{0.65}Zr_{0.35}O_3(BTZ_{35})$. Distinct changes of the Raman spectra with increasing pressure illustrate that BTZ_{35} presents important pressure instabilities leading to at least two phase transitions around 5.7 GPa and 15.1 GPa, respectively. The observed pressure-induced spectral changes for BTZ_{35} are reminiscent of features that have been observed for pure $BaTiO_3$, thus for a classic ferroelectric. The latter is surprising since earlier reports indicate a relaxor-characteristic Raman signature as a function of temperature, thus illustrating that BTZ_{35} might well occupy a peculiar niche in perovskite-type ferroelectrics.

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ABO_3 perovskite-type oxides, and in particular solid solutions among them, are well known for exhibiting a wide range of dielectric properties. One of the best known and most studied examples is $PbZr_{1-x}Ti_xO_3$ (PZT) which exhibits remarkable piezoelectric properties. Furthermore, so-called relaxor ferroelectrics (relaxors)[1] have attracted considerable attention since the recent discovery of ultrahigh strain and giant piezoelectric properties in relaxor-based single crystals like $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (e.g., Refs. 2 and 3). However, the toxicity of lead-containing oxides has caused an increasing interest in environmental-friendly ferroelectric materials such as the Pb-free $BaTi_{1-x}Zr_xO_3$ (BTZ),[4–7] which has been reported to exhibit interesting relaxorlike properties for $x \geqslant 0.25$.

Common relaxor ferroelectrics, like the classic relaxors $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) or $Na_{1/2}Bi_{1/2}TiO_3$ (NBT), share three characteristics. (i) The presence of Pb^{2+} or Bi^{3+}, both showing a lone pair effect, on the A site of the perovskite structure. (ii) A heterovalent disorder on, at least, one of the A or B sites. (iii) The formation of a chemical *compound*, i.e., a substance of fixed composition in opposition to a solid solution. BTZ, which involves a homovalent Ti^{4+}/Zr^{4+} substitution on the B site, does not respond to any of the latter characteristics, revealing that the observed relaxation is intriguing. The objective of the present study is to investigate the peculiar relaxor BTZ with $x = 0.35$ (denoted hereafter BTZ_{35}) via high-pressure Raman spectroscopy, a technique which has been reported to be well adapted for the investigation of relaxor-characteristic features.[8,9]

BZT_{35} powder samples have been prepared by solid state reaction and x-ray diffraction results indicate a pure phase with an average $Pm\text{-}3m$ cubic structure ($a = 4.0759$ Å). Depolarized Raman spectra of BZT_{35} powders were recorded in back-scattering geometry with a Jobin Yvon T64000 spectrometer equipped with a microscope objective and the 514.5-nm line of an Ar^+ ion laser as excitation line. High-pressure experiments up to 27 GPa (on the 300 K isotherm) were performed on a powder sample, which was placed in a chamber (∅ 200 μm) of a diamond anvil cell using a 4:1 methanol-ethanol-mixture as a pressure-transmitting medium. Raman spectra after pressure release are identical to the initial spectra attesting the reversibility of pressure-induced changes.

Figure 1(a) presents the pressure-dependent evolution Raman spectra for BTZ_{35}, which undergo important pressure-induced changes that can be described by both variations in the band characteristics and the appearance of new spectral features. Figure 1(b) displays a Lorentzian-shape decomposition for some selected pressures. In principle, any phase change in the crystal structure or physical properties leads to a variation in the phonon behavior that can be more or less pronounced in wave number, intensity and/or linewidth. In our study the characteristics wave number and intensity have turned out to be pertinent for the detection of phase changes. Let us namely outline the following most prominent changes.

(i) One of the dominating features in the initial spectrum, the intense and well defined band at roughly 520 cm^{-1}, decreases dramatically in intensity with increasing pressure. (ii) The spectral signature in the 200-to-300 cm^{-1} region, with initially differentiated bands, evolves notably with increasing pressure. (iii) When going to higher pressures we observe the appearance of new bands while others disappear. The latter qualitative observations (i) to (iii) indicate the presence of pressure instabilities and point to notable modifications of the structural and polar properties in BTZ_{35} under high pressure. It is further interesting to note that the pressure-dependent evolution of the Raman signature observed for BTZ_{35} (Fig. 1) is reminiscent of features that have been reported in a high-pressure Raman study of polycrystalline $BaTiO_3$ (Ref. 10). The latter is somehow surprising since the temperature-dependent changes in BTZ_{35}, reported by Farhi *et al.*,[7] do *not* resemble the observed temperature-dependent Raman signature of $BaTiO_3$. We will come back to this key feature later in this article, notably in the framework of the following spectral analysis.

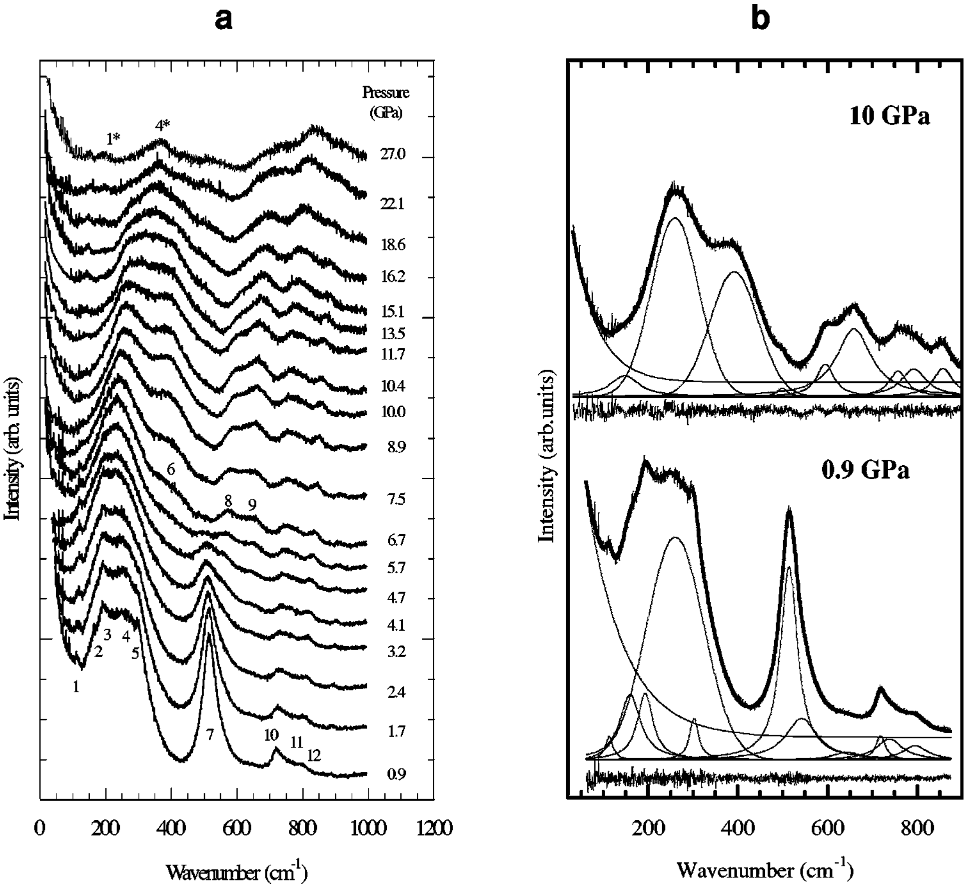

FIG. 1. (a) Representative pressure-dependent Raman spectra of $BaTi_{0.65}Zr_{0.35}O_3$ (BTZ_{35}). Modifications of the spectral signature (appearance/disappearance of bands, shift in wave number, etc.) reveal pressure-instabilities of BTZ_{35} towards pressure. The band numbers are related to the notation introduced in the text. (b) Representative Lorentzian-shape deconvolution of Raman spectra at selected pressures.

The weak low-wave-number band around 115 cm^{-1} (band 1) shows no notable change with pressure apart from a slight high-wave-number shift that can be attributed to pressure-induced bond shortening. Note that this band is not observed for $BaTiO_3$ but reported for IR measurements[11] in $BaZrO_3$ and, based on the latter, Farhi *et al.*[7] have proposed that band 1 can be assigned to a normal mode involving Zr ions which further indicates a local rhombohedral structure.[7] We should add that the latter assignment of band 1 implies the important consequence that nanometer-size Zr (or Zr-rich) domains exist, because otherwise the phonon lifetime would have been too short to result in a defined separated Raman peak. The latter spectral signature is known as the so-called two-mode scenario (in opposite to a virtual ion behavior) in which the material may be viewed as an alternation of zones richer in one constituent than the other, these zones being of nanometer size, in such a way that diffraction cannot reveal a phase separation. On the basis of our high-pressure study we rather exclude local pure $BaZrO_3$ zones, but rather propose Zr-rich domains, because $BaZrO_3$ presents for $p > 12$ GPa a well-defined Raman signature[12] with sharp and intense bands around 400 and 620 cm^{-1} which are not observed in our high-pressure spectra.

Let us now consider the pressure-induced spectral changes in the spectrum-dominating mid-wave-number region, which is at low-pressure characterized by four bands at roughly 160 (band 2), 190 (band 3), 250 (band 4), and 300 cm^{-1} (band 5). In the literature, notable changes in the 200-to-450 cm^{-1} spectral region of ferroelectric perovskites have been attributed to vibrations associated to polar BO_6 octahedra, thus this region is considered to be a good probe for ferroelectric changes. Concerning BTZ_{35} the pressure-dependent evolution of the Raman spectra, illustrated in Fig. 1, shows qualitatively that the 200-to-450 cm^{-1} region undergoes important pressure changes. Figure 2 displays more quantitatively the evolution of the band position with pressure as obtained from the spectral decomposition. One of the prominent changes is the initial low-wave-number shift of band 4 followed by a slope change around 5.7 GPa, a similar signature was interpreted for $BaTiO_3$ as a restoring of the

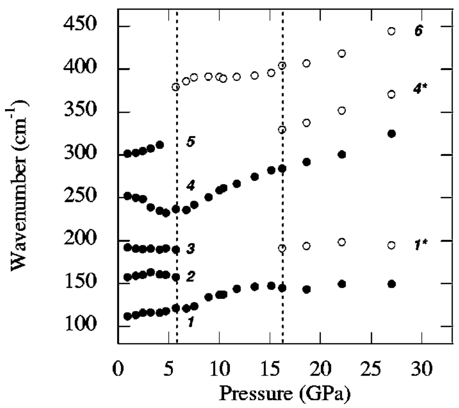

FIG. 2. Pressure-dependent evolution of the band position in the low- and mid-wave-number region (band 1 to 6) in the Raman spectra of $BaTi_{0.65}Zr_{0.35}O_3$(BTZ_{35}).

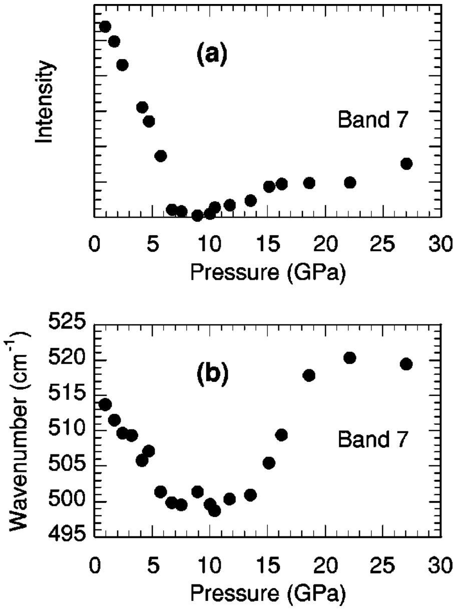

FIG. 3. Pressure-dependent evolution of (a) the intensity and (b) the band position of the 510 cm^{-1} feature (band 7) in the Raman spectra of $\mathrm{BaTi_{0.65}Zr_{0.35}O_3}$($\mathrm{BTZ_{35}}$).

polar $\mathrm{Ti^{4+}}$ (Ref. 10). Although a qualitative inspection of Fig. 1 seems to indicate that this slope change occurs together with a merging of bands 2, 3, and 4, our fits suggest that this is only apparent and rather related to an approach of the different features, due to the softening of band 4, accompanied by a progressive disappearing of bands 2 and 3. The latter spectral changes lead to a single band for $p > 5.7$ GPa which displays an almost linear high-wave-number shift with ≈ 4 cm^{-1}/GPa. However, the most significant change in the mid-wave-number region remains the appearance at around 5.7 GPa of a new broad band at ≈ 380 cm^{-1} (band 6). This new spectral signature together with the low wave number shift of band 4 and the intensity decrease of bands 2 and 3 point to a new (at least local) symmetry from ≈ 5.7 GPa onwards.

$\mathrm{BTZ_{35}}$ undergoes a further change in the mid-wave-number range around $p_{c2} = 15.1$ GPa. As a matter of fact, we observe from p_{c2} onwards at least two new bands: a weak band around 190 cm^{-1} (band 1*) and a new more intense feature at around 330 cm^{-1} (band 4*) that grows in between bands 4 and 6. The latter new signature clearly indicates again some kind of local structural rearrangement. Let us point out that the Raman intensity of the high-pressure phase decreases notably with increasing pressure, which is especially seen in the two spectra at 22.1 and 27.0 GPa, respectively, which allow a first preliminary exploration of the $p > 20$ GPa domain. The latter observation might well indicate the arrival of a cubic average structure with only very small persisting local distortions.

A dominating feature in the Raman spectrum of $\mathrm{BTZ_{35}}$ is the initially intense and well-defined, but asymmetric, band at 520 cm^{-1} (band 7). As can be seen in Fig. 1, band 7 undergoes the most important pressure-induced change among the Raman spectrum of $\mathrm{BTZ_{35}}$. Figure 3 illustrates the progressive pressure-dependent intensity loss of band 7 accompanied by a gradual softening indicating a phase transition related anharmonic contribution. Although we have already discussed in the previous section the occurrence of spectral modifications at $p_{c1} = 5.7$ GPa, it is the complementary evolution of band 7 (disappearance), bands 4 (softening) and band 6 (appearance) that gives the convincing argument for a pressure-induced phase transition at p_{c1}.

It is interesting to note that the pressure-induced changes of the spectral signature observed for polycrystalline $\mathrm{BaTiO_3}$ (Ref. 10) are qualitatively similar to the above, but present also important differences. As a matter of fact, for $\mathrm{BaTiO_3}$ the evolution of bands 4, 6 and 7 have been proposed to indicate not *one* phase transition (as in $\mathrm{BTZ_{35}}$) but *two*:[10] A first I→II phase transition at 2 GPa (softening of band 4) and a second II→III at 5 GPa (disappearance of band 7); band 6 is appearing in between the two phase transitions. Note that the 3.5 GPa spectrum of $\mathrm{BaTiO_3}$ displays already a clear signature of band 6 but maintains some intensity for band 7, while the 3.2 GPa spectrum of $\mathrm{BTZ_{35}}$ displays no significant band 6 (if any) but still an intense band 7. Although it is in principle not surprising that the different materials $\mathrm{BaTiO_3}$ and $\mathrm{BTZ_{35}}$ present different pressure instabilities, the above discussion seems to indicate that $\mathrm{BTZ_{35}}$, compared to $\mathrm{BaTiO_3}$, proceeds directly from phase I to III thus somehow suppressing the intermediate region II which was proposed to be cubic.[10] It is not obvious why this happens but we note that relaxors like PMN (Refs. 9, 13) or NBT (Refs. 8, 14) but also the BTZ-similar PZT (Ref. 15) display up to high-pressure a long-range distortion and do not proceed to a long-range cubic structure. As a matter of fact, considering that the Raman signature of $\mathrm{BTZ_{35}}$ from 5.7 GPa onwards is still well defined and intense, we suggest that the new symmetry is not the prototype $Pm\text{-}3m$ (being not Raman active).

The high-wave-number region of $\mathrm{BTZ_{35}}$, dominated by oxygen vibrations of the $B\mathrm{O_6}$ octahedra, is initially characterized by the occurrence of a low-intensity massif extending from 700-to-800 cm^{-1}. Although some of the high-wave-number bands show slight slope changes with pressure (not shown), their evolution is only little affected by phase transitions and displays a, very common, nearly linear pressure-induced wave number shift towards higher wave number at a rate of 4 to 5 cm^{-1}/GPa, due to progressive band shortening.

Regarding the effect of high-pressure we have reported in earlier work that the model relaxors PMN[9] and NBT[8] show important pressure-induced spectral changes, illustrating that temperature and high-pressure have a very different impact on relaxors. Although this conclusion might appear trivial, it is, however, not expected if we recall that classic ferroelectrics, like $\mathrm{BaTiO_3}$ or $\mathrm{KNbO_3}$, show the same phase transition sequence under high-pressure and temperature (see Ref. 16 for a discussion of experimental and theoretical evidences for $\mathrm{BaTiO_3}$). $\mathrm{BTZ_{35}}$ is rather similar to relaxors like PMN and NBT in the sense that it presents an important evolution under high-pressure and no evolution in temperature. However, we believe that the interpretation of the latter relaxor-similar behavior as further evidence to state $\mathrm{BTZ_{35}}$ as a relaxor would be precipitous, because the actual pressure-induced spectral evolution is very different from what has been proposed to be a relaxor-characteristic signature[8,9] indicating that BTZ_{35} is peculiar compared to model relaxors. This peculiarity is further underpinned by the fact that the high-pressure evolution is very similar to that observed for the standard ferroelectric $BaTiO_3$. This leads to the interesting and unexpected conclusion that BTZ_{35} behaves, at least from a Raman scattering point of view, with temperature as a relaxor but with pressure similar to a classic ferroelectric. To the best of our knowledge, such a spectral signature is unusual and has no precedent among reported Raman studies on ferroelectrics thus indicating a peculiar and possibly rich p-T phase diagram. As a consequence, our study illustrates that although BTZ_{35} shows a dielectric relaxation (and is thus somehow a relaxor), it is not a relaxor in the sense of model relaxors like NBT and PMN as was earlier proposed.[7] The same might well be true for similar $BaTiO_3$-based relaxors like $BaTi_{1\text{-}x}Ce_xO_3$ (BTC).[17]

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