

High-pressure Raman study of a relaxor ferroelectric: The $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ perovskite

J. Kreisel* and A. M. Glazer

Clarendon Laboratory, University of Oxford, Parks Road, Oxford OX1 3PU, United Kingdom

P. Bouvier and G. Lucazeau

Laboratoire d'Electrochimie et de Physicochimie des Matériaux et des Interface, 1130 rue de la piscine, Boite Postale 75, 38402 Saint Martin d'Hères Cedex, France

(Received 29 August 2000; published 5 April 2001)

We report high-pressure Raman measurements (up to 19 GPa) on the perovskite-type relaxor ferroelectric sodium-bismuth-titanate, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT). Distinct changes in the Raman spectra have been analyzed in the light of a rhombohedral-to-orthorhombic ($R3c$ -to- $Pnma$) phase transition. Results show that this transition, involving a change in the tilt system *and* the cation displacement, does not occur in a single step, but goes through an intermediate phase (2.7 to 5 GPa). The frequency evolution of characteristic bands in the Raman spectra allows us to propose a scenario where in the early stage of the transition a change in the *A*-cation displacement ($[111]_p \rightarrow [010]_p$) takes place, while at least one other change, i.e., *B*-site cation displacement ($[111]_p \rightarrow [000]$) or the tilt change ($a^-a^-a^- \rightarrow a^-b^+a^-$), appears to happen only at higher pressures. A pressure-induced breakdown of the Raman intensity, preceding the phase transition, has been observed for the bands at 135 and 275 cm^{-1} . It is suggested that a change in the polar character of nanosized $\text{Bi}^{3+}\text{TiO}_3$ and $\text{Na}^{1+}\text{TiO}_3$ clusters is at the origin of this observation, being, in fact, the signature of a pressure-induced relaxor-to-antiferroelectric crossover in NBT. Raman spectroscopy is shown to be an effective technique to investigate the pressure-dependent behavior in relaxor ferroelectrics.

DOI: 10.1103/PhysRevB.63.174106

PACS number(s): 77.80.-e, 77.84.-s

I. INTRODUCTION

In the past, ABO_3 perovskite-type oxides have been extensively studied mainly because of their technologically important piezoelectric and dielectric properties. Relaxor ferroelectrics (relaxors) form a special class of ferroelectrics and are characterized by a dielectric response with a broad peak as a function of temperature and a frequency-dependent response, rather than a sharp frequency-independent peak as in classical ferroelectrics. The true origin of the relaxor behavior in perovskites is still controversial, but is most likely due to heterovalent disorder. Well known perovskite relaxors include $\text{Pb}(B_{1/3}\text{Nb}_{2/3})\text{O}_3$ ($B = \text{Mg}, \text{Zn}, \text{Ni}, \text{Sc}$), $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$, $\text{K}(\text{Ta}_{1-x}\text{Nb}_x)\text{O}_3$, or La-modified $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$.

Only a limited number of studies of mixed *A*-site relaxors like $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$ (KLT) or $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) have appeared in the literature. The latter relaxor NBT, discovered in 1961 by Smolenskii,¹ is for several reasons interesting to study. (i) From a structural point of view NBT has the special and rare feature to form a chemical *compound*, i.e., an energetically stable substance of fixed composition, through substitution of the *A*-site cation in the perovskite structure. Among the thousands of variants of substitutional modified perovskites, there is only a handful of cases of *compound* formation resulting from the substitution at the *A*-sites. (ii) Virtually all previous studies of NBT point to the peculiar nature of its temperature-dependent phase transitions (see, e.g., Refs. 1–5). On cooling NBT transforms from a paraelectric (PE) cubic phase to a ferroelectric (FE) tetragonal and then to a rhombohedral relaxor (RR) phase.^{3,5} (iii) Most relaxor ferroelectrics have pairs of isovalent *A* cations

or chemically different *B* cations, but NBT has unlike-valency Na^+ and Bi^{3+} cations at the *A* sites. (iv) For Pb^{2+} it has already been shown that its polarization plays a special role in ferroelectric properties.⁶ The fact that Bi^{3+} ions are isoelectronic with Pb^{2+} , both showing a lone pair effect, encourages further studies into NBT. Such studies might reveal NBT-related perovskites as environmental-friendly alternatives to the currently used lead-based ferroelectric and piezoelectric materials. Recent results on barium-doped NBT, revealing promising piezoelectric properties, are encouraging.⁷

In the past, the usual approach towards the understanding of relaxor ferroelectrics was mainly through their chemical composition- or temperature-dependent behavior and only a few pressure-dependent studies on relaxors have been reported. However, recently, for instance through the work on various perovskites by Samara and co-workers,^{8–11} or on $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$ by Yasuda and co-workers,^{12–14} the importance of pressure as a variable in elucidating phase transitions and the physics of mixed perovskites has been emphasized. Interesting results include pressure-induced ferroelectric-to-relaxor crossover observed by Samara *et al.*^{8–11} and relaxor-to-antiferroelectric crossover reported by Yasuda *et al.*^{12–14} The most commonly used techniques for the investigation of pressure-dependent properties in relaxors are dielectric spectroscopy and x-ray diffraction.

Raman spectroscopy is known to be an appropriate technique for the study of pressure-induced phase transitions as has been shown for various perovskite-type titanates [e.g., BaTiO_3 ,^{15,16} PbTiO_3 ,^{17,18} SrTiO_3 ,¹⁹ CaTiO_3 (Ref. 20)]. Although, this technique has been shown to be also useful for temperature- or substitution-dependent investigations of re-

laxors (see, e.g., Refs. 21–27), Raman spectroscopy has, to the best of our knowledge, never been used for the pressure-dependent study of relaxors.

While the physical properties, phase transitions and lattice dynamics of NBT as a function of temperature and substitution rate are fairly well known, the aim of this study is to extend our current understanding of the peculiar relaxor NBT with special regard to pressure-induced phase transitions. In this paper we present a pressure-dependent investigation of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ from ambient pressure up to 19 GPa along the 300-K isotherm using Raman spectroscopy as a probe of the change in structure.

II. EXPERIMENT

NBT powder samples have been prepared at the University of Warwick, experimental details are given in Ref. 4. Phase characterization and composition were confirmed using x-ray diffraction and microprobe analysis.

Raman spectra of NBT powders were recorded in back scattering geometry with a Dilor XY multichannel spectrometer equipped with a 20slwd microscope objective. The 514.5-nm line of an Ar^+ ion laser was used as excitation line. High-pressure experiments were performed in diamond-anvil cell using a 16:4:1 methanol-ethanol-water mixture as was used as a pressure-transmitting medium. Powder samples were placed in a chamber 250 μm in diameter and 50 μm thick and the pressure was monitored by the shift of the ${}^2F_g \rightarrow {}^4A_{2g}$ fluorescence bands of Cr^{3+} ions in a small ruby crystal placed in the vicinity of the sample.²⁸ NBT was studied from ambient pressure up to 19 GPa. The Raman spectra were systematically decomposed into individual Lorentzian components using the JANDEL Peakfit software.

III. GENERAL CONSIDERATIONS

A. Crystal structure and phase transitions

The ideal structure of perovskite-type oxides (ABO_3) is essentially simple, with corner-linked anion octahedra, the B cations at the center of the octahedra, and the A cations in the space (co-ordination 12) between the octahedra. Since the discovery of NBT (Ref. 1) its 300-K crystal structure has been controversial for a long time, rhombohedral,²⁹ triclinic,³⁰ and monoclinic (ICSD database and Ref. 31) structures being considered. Recent structure refinements of temperature-dependent neutron data of NBT (Refs. 3,4 and 32) confirm that NBT undergoes a first phase transition from the high-temperature cubic prototype phase I to phase II of tetragonal symmetry ($P4bm$) and then a second one with strong diffuse character to phase III of rhombohedral symmetry ($R3c$). The phases in the nomenclature of Toledano *et al.*³³ are given by

$$\text{I} | >530 \text{ }^\circ\text{C} | Pm\bar{3}m \text{ (221)} |$$

$$Z=1 \text{ | nonferroic | paraelectric, paraelastic}$$

$$\text{II} | 140\text{-}560 \text{ }^\circ\text{C} | P4bm \text{ (100)} |$$

$$Z=2 \text{ | ferroic | three ferroelectric, three ferroelastic variants}$$

$$\text{III} | <300 \text{ }^\circ\text{C} | R3c(161) |$$

$$Z=6 \text{ | ferroic | four ferroelectric, four ferroelastic variants.}$$

With respect to the cubic $Pm\bar{3}m$ structure the rhombohedral and tetragonal structures can be obtained by rotation of the adjacent TiO_6 octahedra and cation displacement. Phase II is then characterized by having $[001]_p$ cation displacements (where the subscript p refers to pseudocubic perovskite axes) and the $a^0a^0c^+$ octahedral tilt system (Glazer notation^{34,35}). Phase III has $[111]_p$ cation displacements with the $a^-a^-a^-$ tilt system. Note that the transition from phase II to phase III involves a drastic change, not only to the directions of the cation displacements, but also to the sense of octahedral tilts, and therefore cannot proceed by a continuous or second-order phase transition.

B. Raman-active phonons

Concerning the phonon picture of NBT, the ten atoms in the unit cell of the rhombohedral or tetragonal structures give rise to 27 ($\mathbf{k}=0$) optical modes that can be characterized according to the space group using group-theoretical methods. Such a treatment has recently been presented²⁴ and leads for rhombohedral NBT ($R3c$, C_{3v}^6 , $Z=2$) to 13 Raman-active modes,

$$\Gamma_{\text{Raman},R3c} = 7A_1 + 6E,$$

and for tetragonal NBT ($P4bm$, C_{4v}^2 , $Z=2$) to 15 Raman-active modes,

$$\Gamma_{\text{Raman},P4bm} = 3A_1 + 3B_1 + 2B_2 + 7E,$$

On the other hand, in the ideal cubic perovskite structure ($Pm\bar{3}m$) none of the vibrational modes is Raman active. Experimental NBT-Raman data at ambient pressure as a function of temperature or chemical composition are given in Refs. 22,24,36 and 37).

C. Ordering scheme

For B -site substituted perovskites ordering often occurs when there is a substantial charge difference between two cation species on the same crystallographic site. In this view, the chemical nature of NBT raises the question of a possible ordering scheme of the cations on the A site. However, to the best of our knowledge, there has so far been no convincing published evidence for any long-range cation ordering in this compound. On the other hand, a recent Raman study of $(\text{Na}_{1-x}\text{K}_x)_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ gives some insight into the NBT microstructure. Based on the observed two-mode behavior of a

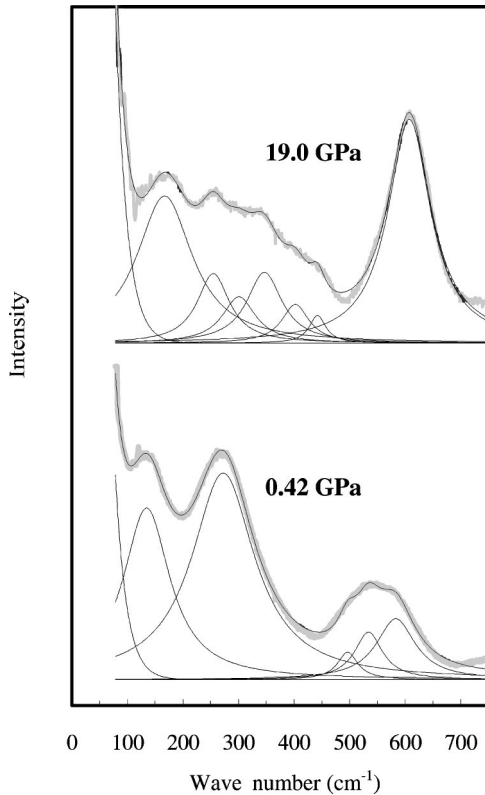


FIG. 1. Raman spectra of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) at low pressure (0.42 GPa) and 19 GPa, respectively. The gray continuous lines represent the experimental data, while the solid thin lines display the spectral deconvolution.

particular Raman mode at 135 cm^{-1} , it has been reported²⁴ that NBT shows locally nanometer-size domains, which should be seen as local $\text{Bi}^{3+}\text{TiO}_3$ and $\text{Na}^{1+}\text{TiO}_3$ clusters (but no superstructure). Preliminary electron microscopy and diffuse x-ray scattering investigations support this type of local arrangement over several unit cells.

IV. RESULTS

A. Raman spectra at ambient pressure and 19 GPa

Before discussing in detail the phonon characteristics of NBT at different hydrostatic pressures it is useful to inspect the Raman data for the end members of our study. Raman spectra at low pressure and 19 GPa are shown in Fig. 1 together with their spectral deconvolution into Lorentzian-shape peaks. In agreement with literature results (see Refs. 22,24,36 and 37) the Raman bands of NBT are relatively broad. The NBT Raman spectrum at ambient conditions can be deconvoluted in the $100\text{--}700\text{-cm}^{-1}$ range into five peaks located at roughly 135 , 275 , 490 , 530 , and 580 cm^{-1} . The spectral signature at 19 GPa is dominated by a band at 600 cm^{-1} together with a density-of-state-like feature at lower frequencies, which can most likely be deconvoluted into 6 bands at roughly 165 , 255 , 300 , 345 , 400 , and 445 cm^{-1} . The obvious difference in the Raman-spectra at low- and high-pressure, as displayed in Fig. 1, points to a structural rearrangement with applied pressure.

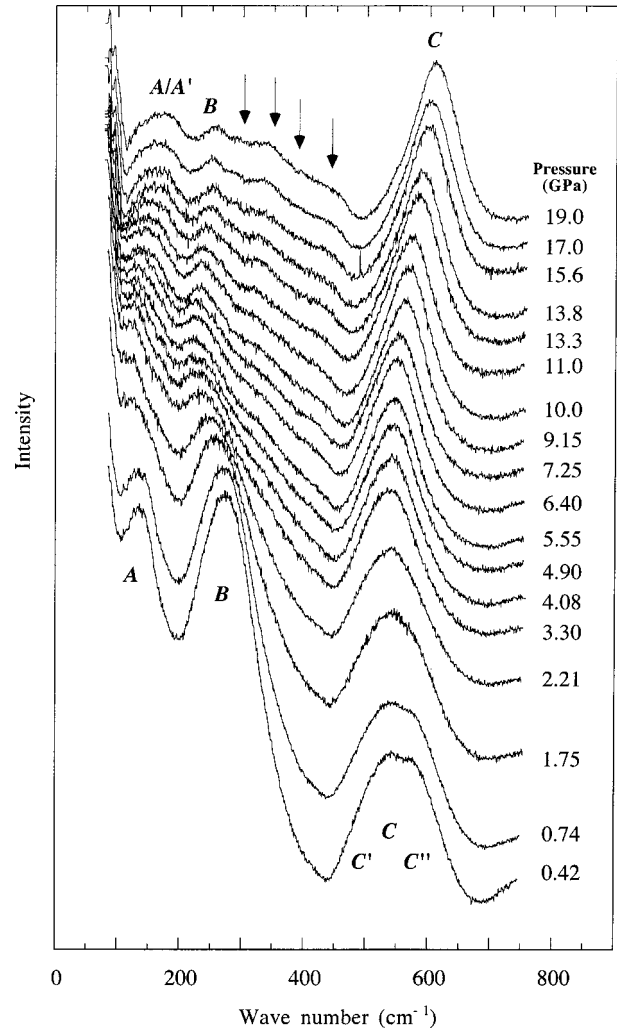


FIG. 2. Pressure-dependent Raman spectra for $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. The shifts and splitting of the phonon bands are due to structural phase transitions with increasing pressure (see text).

B. Pressure-dependent Raman spectra

Figure 2 presents the overall evolution of the NBT Raman spectra with applied hydrostatic pressure up to 19 GPa, while Fig. 3 shows the pressure-dependent evolution of the band frequencies deduced from the spectral deconvolution. The notations used throughout this paper for the different bands in the NBT Raman spectra (A to C) are given in Fig. 2. Several qualitative features in the NBT Raman spectra can be discerned for increasing hydrostatic pressure:

- (i) In the low-frequency range, band A , around 135 cm^{-1} , shows an important low-frequency shift from ambient pressure up to 2.7 GPa . When the pressure is then further increased, one observes a slope change and the band starts to shift at a rate $\approx +3.2\text{ cm}^{-1}/\text{GPa}$ to higher frequencies. This anomaly seems to be accompanied by a splitting into two overlapping components $A(A')$, mainly observed through the increasing peak width. However, for the frequency-shift displayed in Fig. 3 a single band has

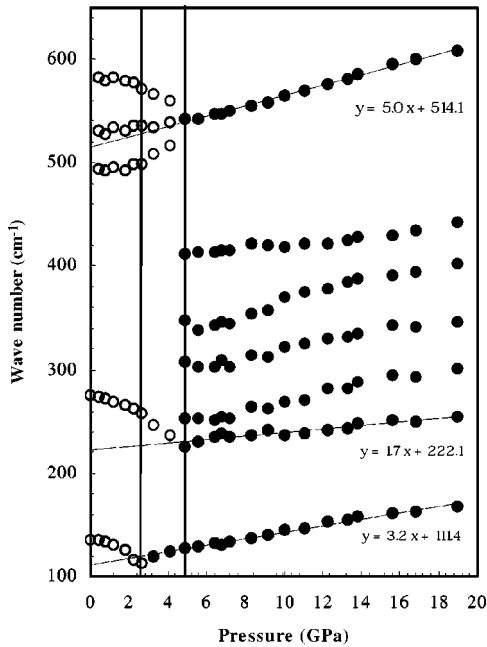


FIG. 3. Band position change as a function of pressure in the Raman spectra of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. The lines are guides for the eye to emphasize spectral changes and equations are relative to a linear fit in the 5–19-GPa range.

been used in order to facilitate the fit of this band, which is close to the central peak.

- (ii) The broad band B centered on 275 cm^{-1} shows a negative frequency shift from ambient pressure up to 5 GPa, where a discontinuity is observed, after which band B shifts by $\approx 1.7\text{ cm}^{-1}/\text{GPa}$ to higher frequencies.
- (iii) A number of new bands appear in the middle-frequency region at a pressure higher than 5 GPa.
- (iv) The overlapping C , C' , and C'' high-frequency bands, observed around $500\text{--}600\text{ cm}^{-1}$ at ambient pressure, merge into a single band at 5.0 GPa. This band displays now an important $\approx 5\text{ cm}^{-1}/\text{GPa}$ linear high-frequency shift up to 19 GPa.
- (v) The high-frequency feature around 600 cm^{-1} (bands C , C' , C'') behaves differently in comparison with the low- and middle-frequency region ($100\text{--}400\text{ cm}^{-1}$). Once bands C , C' , and C'' are merged together, the single band remains almost unchanged in its shape and intensity with increasing pressure, while the features at lower frequencies decrease dramatically in intensity.

V. SPECTRAL ANALYSIS

Each of the points mentioned above, describing discontinuous or distinct changes in the Raman spectral features, can be seen as an indication of a pressure-induced structural change for NBT in the 2.7–5-GPa region. The determination of the symmetry in the high-pressure structure is not straightforward. Intuitively one might consider first the “parent” cubic perovskite structure. However, for the following rea-

sons one has to be careful to argue on the basis of Raman spectra only.

Although any first-order Raman scattering is forbidden in the ideal cubic perovskite structure, Raman spectra have been observed for several cubic perovskites. One well-known example is the Raman spectrum of BaTiO_3 , which is observed even well beyond the pressure-induced tetragonal to cubic phase transition.¹⁶ This observation has been attributed to disorder in the Ti positions, leading to a breakdown of the Raman-scattering selection rules. Furthermore, Uwe *et al.*³⁸ have shown that the presence of ferroelectric microregions, acting as symmetry-breaking defects, can lead as well to first-order Raman scattering in the cubic phase.

Even though we cannot exclude underlying second-order scattering, as in SrTiO_3 ,¹⁹ we believe that the detected Raman signal, being persistent over 14 GPa (from 5 to 19 GPa), should most likely be attributed to first-order scattering and thus to a rhombohedral→noncubic phase transition. Such a structural change is supported by very recent results from a pressure-dependent study of NBT using synchrotron radiation.³⁹ In the latter study Jones *et al.*³⁹ observed a phase transition at 2.6 GPa to a new high-pressure phase of NBT which is isomorphic to the orthorhombic structure of CaTiO_3 perovskite [space group $Pnma$, $\Gamma_{\text{Raman}, Pnma} = 7A_g + 7B_{1g} + 5B_{2g} + 5B_{3g}$ (Ref. 20)]. In the following, the different characteristic spectral changes will be separately discussed, particularly in the light of the rhombohedral ($R3c$) to orthorhombic ($Pnma$) phase transition.

A. $80\text{--}200\text{-cm}^{-1}$ region (band A)

At ambient pressure this region is dominated by an intense band at 135 cm^{-1} (earlier assigned to A_1 symmetry³⁶), which has been associated with Na-O vibrations.²⁴ In the rhombohedral $R3c$ structure the Na cation occupies $2a$ (x, x, x) positions, being therefore displaced along $[111]_p$ from the center of a dodecahedral coordination of oxygens in the ideal perovskite structure. A vibrational mode directly associated with this cation is expected to be sensitive towards phase transitions when the site symmetry is changed. As a consequence, the slope change in the pressure-dependent frequency evolution of band A in NBT (Fig. 3) gives evidence for a structural change, which is associated with a symmetry change of the Na site, i.e., to another type of cation displacement.

In the orthorhombic $Pnma$ structure the Na cation occupies $4c$ ($x, 1/4, z$) positions, i.e., showing antiparallel displacements along the $[100]_p$ direction. As a consequence, the anomaly of the 135-cm^{-1} band can be interpreted as a pressure-induced change in the cation displacement from parallel $[111]_p$ to antiparallel $[100]_p$ displacements, i.e., for a pressure-induced relaxor ferroelectric→antiferroelectric phase transition.

B. 275-cm^{-1} band (band B)

The broad and intense band B centered on 275 cm^{-1} (of A_1 symmetry³⁶ and assigned to TiO_6 octahedra²⁴) is the dominating feature in the NBT Raman spectrum at ambient conditions.

For the discussion of this band it is useful to consider already published Raman studies on materials having a similar crystal structure, like $ATiO_3$ ($A = Ba, Pb$) titanates, where the tetragonal structure is obtained from the cubic structure by a cation-anion displacement without octahedra tilts, thus leading to ferroelectric properties. In the Raman spectra of these titanates a pressure-induced negative frequency shift has been observed for the A_1 bands in the $300 \pm 50\text{-cm}^{-1}$ frequency region, namely in $BaTiO_3$ for the 260-cm^{-1} band,¹⁶ in $PbTiO_3$ for the 350-cm^{-1} band,¹⁷ and in $Ba_{0.78}Pb_{0.22}TiO_3$ for the 300-cm^{-1} band.⁴⁰ This negative frequency shift has been interpreted in terms of a soft-mode behavior describing a pressure-induced tetragonal \rightarrow cubic phase transition, i.e., the reduction of the anion-cation displacement towards totally symmetric anion-cation octahedra in the ideal-perovskites structure.

On the other hand, studies of other isostructural materials seem to indicate a correlation between the vibrational frequency and structural distortion. For instance the A_g band in $RTiO_3$ ($R = La, Ce, Pr, Nd, Sm, Gd$), having an orthorhombically distorted perovskite structure, decrease in frequency from 385 to 275 cm^{-1} with decreasing orthorhombic distortion (although other explanations have been proposed).

In the light of the above discussion, the negative frequency shift and the anomaly observed for the 287-cm^{-1} phonon in NBT suggests that this particular phonon is directly involved in the structural phase transition. We should note that the proposed high-pressure orthorhombic structure for NBT (Ref. 39) has no Ti-cation displacements, but is characterized by an $a^-b^+a^-$ octahedral tilt system. In this context the downshift of the 275-cm^{-1} band in NBT is probably related to a structural rearrangement that is conditioned by both, the restoring of the Ti cation to the center of symmetry ($[111]_p \rightarrow [000]$) and a change in the tilt system ($a^-a^-a^- \rightarrow a^-b^+a^-$).

A remaining question is whether these two structural changes appear together or at different pressures. By having a closer look to the low-frequency shift of band B it is tempting to point to a slope change at 2.7 GPa , which might indicate that the displacement and tilt changes happen at different pressures. However, according to the concept of hard-mode spectroscopy⁴¹ any structural change might affect the whole phonon spectrum, and, as a consequence, this slope change might also be caused by the structural rearrangement described above in Sec. V A.

C. Middle-frequency region ($300\text{--}500\text{ cm}^{-1}$)

This region, which is first dominated by the large wing of the band B , develops a new spectral signature at higher pressures. This new signature, displaying a density-of-state-like appearance with a number of new bands, suggests a transition to a crystal symmetry, whose irreducible representations are characterized by a higher number of Raman active bands. This observation is in agreement with a phase transition from $R3c$ (13 Raman-active modes) to $Pnma$ (24 Raman-active modes).

D. High-frequency bands

High-frequency Raman bands in oxides are dominated by vibrations involving mainly oxygen displacements and can often be interpreted in terms of polyhedra vibrations.^{42–44} For NBT the high-frequency bands C , C' , and C'' have been assigned to vibrations of the TiO_6 octahedra.²⁴ Even though drastic spectral changes (like soft modes) are not expected at high frequency, high-frequency modes have shown to be useful for the determination of phase transitions. For instance, in titanates spectral changes like band splitting²⁴ or band-coalescence,¹⁷ appearance of new bands,¹⁶ as well as intensity changes have shown to be useful criteria.

For NBT the three C , C' , and C'' high-frequency bands merge into a single band at 5 GPa (Figs. 2 and 3). A similar pressure-induced spectral evolution has been interpreted in $PbTiO_3$ as the coalescence of a pair of A_1 and E modes to a single T_{1u} mode at the tetragonal \rightarrow cubic phase transition.¹⁷ Such a transition to a cubic phase should be ruled out in the case of NBT, as discussed above. We believe that the spectral change in NBT is more likely to be due to the overlapping of A_1 and E bands and the loss of their longitudinal (LO) and transversal (TO) character. The arguments are the following. In the rhombohedral phase each of the A_1 and E modes is Raman *and* infrared active and thus a LO-TO splitting can be expected as a result of long-range electrostatic forces. Such a LO-TO splitting has already been reported for $BaTiO_3$ (Ref. 16) and $PbTiO_3$.¹⁷ As a consequence, bands C , C' , C'' , and possibly a fourth masked band, can be tentatively assigned in the rhombohedral phase to $A_1(\text{LO})$, $A_1(\text{TO})$, $E(\text{LO})$, and $E(\text{TO})$ modes. In contrast, in the orthorhombic-phase modes of A_g , B_{1g} , B_{2g} , and B_{3g} symmetry are only Raman active and therefore no LO-TO splitting is expected. Based on this consideration the band merging can be interpreted as a reduction of the LO-TO splitting on approaching the rhombohedral \rightarrow orthorhombic phase transition, together with A_1 and E modes having almost undistinguishable frequencies as reported for pressure-dependent Raman spectra in tetragonal $BaTiO_3$.¹⁶ However, in order to support this scenario, further Raman and IR spectroscopy work on NBT single crystals is needed to determine the actual mode symmetry.

Finally, as mentioned earlier, band C shifts linearly to higher frequencies. This sensitivity of band C towards applied pressure together with its easy observation makes it usable for pressure determination in NBT samples. Furthermore, it is tempting to use this mode for an estimate of the NBT compressibility. A detailed discussion of the compressibility in NBT, estimated from pressure-dependent Raman spectra, will be presented elsewhere.⁴⁵

As a conclusion of this section, we wish to point out that lattice dynamics calculations as a function of pressure are desirable for NBT in order to understand in more detail the coupling of phonons to the phase transition as brought out by our present study.

VI. PHASE-TRANSITION MECHANISM

How can we imagine the mechanism of the structural phase transition? Let us recall that the pressure-induced

rhombohedral→orthorhombic phase transition represents a drastic structural change that can be described by the following characteristics:

Na/Bi cations (*A* site):

$$[111]_p \text{ (parallel)} \rightarrow [100]_p \text{ (antiparallel)},$$

Ti cation(*B* site):

$$[111]_p \text{ (parallel)} \rightarrow [000],$$

TiO₆-tilt system:

$$a^- a^- a^- \rightarrow a^- b^+ a^-.$$

[000] means the displacement has gone to zero. As has already been pointed out,^{5,24,26,27} it appears plausible that for such a large structural change, i.e., in the cation displacement and octahedra tilts, the phase transition does not occur in a single step. We should rather expect an intermediate “buffering” phase which makes such a change energetically more plausible. Similar mechanisms for other perovskites have been recently discussed in the literature. Experimental evidence for such an intermediate phase has been, for instance, found for the substitution-induced $R3c \rightarrow P4bm$ phase transition in a NBT-related solid solution, $(\text{Na}_{1-x}\text{K}_x)_{0.5}\text{Bi}_{0.5}\text{TiO}_3$.²⁴ Very recently Noheda *et al.*⁴⁶ reported a synchrotron x-ray-diffraction experiment on $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ giving evidence for a monoclinic phase, which provides a “bridge” between tetragonal and rhombohedral phases. Finally, the $R3c$ phase in barium cerate is seen as a bridge between its orthorhombic and cubic phase.⁴⁷

As can be seen from Fig. 3, the pressure-induced rhombohedral→orthorhombic change in NBT appears to proceed indeed through an intermediate phase. A first transition is found around 2.7 GPa, being manifest in the frequency slope change of band *A*, and a second around 5 GPa, being manifest by the evolution of bands *B* and *C*. Although the intermediate phase, existing over 2.3 GPa, does not appear to have its own characteristic signature, it is clearly distinguished through distinct changes in the Raman spectra. As discussed in the previous Sec. V, characteristic vibrations dominate bands *A*, *B*, and *C* and so we propose three hypothetical scenarios for the phase transition, at (1) 2.7 GPa and (2) 5 GPa:

$$(i) (1) \text{ A-cation } [111]_p \rightarrow [100]_p,$$

$$(2) \text{ B-cation } [111]_p \rightarrow [000]$$

$$\text{and } a^- a^- a^- \rightarrow a^- b^+ a^-,$$

$$(ii) (1) \text{ A-cation } [111]_p \rightarrow [100]_p$$

$$\text{and B-cation } [111]_p \rightarrow [000],$$

$$(2) a^- a^- a^- \rightarrow a^- b^+ a^-,$$

$$(iii) (1) \text{ A-cation } [111]_p \rightarrow [100]_p$$

$$\text{and } a^- a^- a^- \rightarrow a^- b^+ a^-,$$

$$(2) \text{ B-cation } [111]_p \rightarrow [000].$$

The common point of these scenarios is that the first structural rearrangement is accompanied by a change in the displacement of the *A*-site cation. Concerning the *B*-site displacement and the octahedron tilt, which belong to the same chemical entity, one would rather expect first a restoring of the cation to the center of the octahedron and only secondly a tilt change. The latter argument, together with the indication of a slope change in the frequency of band *B* at 5 GPa, favors scenario (ii) over the other two. Given that antiparallel cation-anion displacements lead to antiferroelectric properties, while polyhedra tilts are not polar, scenario (ii) points to a

relaxor→antiferroelectric *I* →antiferroelectric *II*

phase sequence. We expect pressure-dependent dielectric spectroscopy measurements, similar to those reported in Refs. 8–13, to give more insight into the dielectric character of the occurring phase transitions.

We finally point out that the space groups $R3c$ and $Pnma$ are not in a pure or simple super- or subgroup relation. This would have simplified the symmetry identification of the intermediate phase as Salje and Bismayer^{26,27} have reported for the relaxor $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$. In fact, the space groups $R3c$ and $Pnma$ in NBT are only related over a cascade of numerous symmetry changes through a common super- or subgroup. For instance, the cubic space group $Pm\bar{3}m$ is the common supergroup of $R3c$ and $Pnma$ according to the following cascades:

$$Pm\bar{3}m \rightarrow R\bar{3}c \rightarrow R3c,$$

$$Pm\bar{3}m \rightarrow P4/mmm \rightarrow Cmmm \rightarrow Cmcm \rightarrow Pnma.$$

On the basis of our Raman spectra we should rule out a cubic intermediate phase, since no associated spectral signature has been observed. Given the large number of phases in the cascade, and knowing that in principle all intermediate steps in such a cascade of phase transitions might be considered,^{26,27} we think that for NBT no further judgment about the intermediate phase is reasonable on the basis of our data. To clarify the actual symmetry of the intermediate

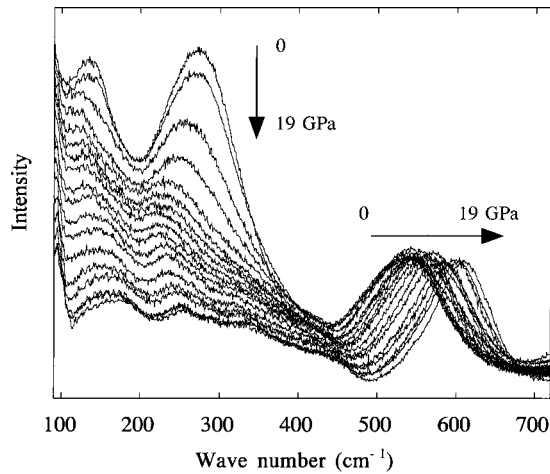


FIG. 4. Representative pressure-dependent Raman spectra for $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, directly superimposed and normalized to band C.

phase further pressure-dependent experimental work on this phase is needed.

VII. RELAXOR-TO-ANTIFERROELECTRIC CROSSOVER

One of the striking features in the pressure-dependent Raman spectra is that band C remains almost unchanged in its shape and intensity (once C, C', C'' are merged), while the bands at lower frequencies decrease dramatically in intensity. In order to emphasize this spectral signature Fig. 4 presents the pressure-dependent Raman spectra directly superimposed and normalized to band C, emphasizing that the intensity of the low-frequency region drops by a factor of roughly 3 on going from ambient pressure to 19 GPa. To the best of our knowledge, such a spectral signature with increasing pressure is very unusual and has no precedent among reported Raman studies on perovskites.

The reason for this unusual change is not immediately obvious and several possible causes should be taken into consideration.

(i) Looking at the spectral evolution in Fig. 2 one might be tempted to attribute the evolution to a change in the central peak, especially because central-peak features have been observed to be phase transition sensitive in several other perovskites like $\text{PbMg}_{1/3}\text{Nb}_{1/3}\text{O}_3$,⁴⁸ BaTiO_3 ,⁴⁹ or KNbO_3 .⁴⁹ However, such changes, which have been attributed to underlying quasielastic Rayleigh-scattering,⁴⁸ are expected at lower frequencies and are unlikely to be the origin.

(ii) Since Raman spectroscopy is a local probe, the order-disorder character of a given material can affect its Raman spectrum. It is therefore important to realize that pressure can affect the order-disorder character in materials: for instance in geological systems pressure tends to increase order.^{50,51} Although the possibility of an disorder-order transition occurring in NBT cannot be ruled out, it is unlikely that this is the origin of the observed important intensity changes, because an order-disorder transition is expected to affect the widths of peaks rather than decreasing the intensity.

(iii) Figure 5 presents in more detail the pressure-dependent intensity evolution of bands A, B, and C. While

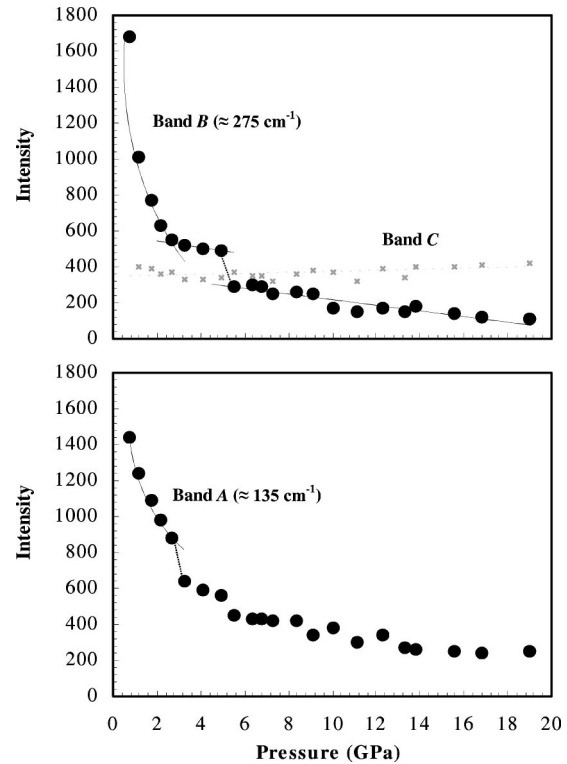


FIG. 5. Evolution of the integrated intensity of bands A (\bullet), B (\circ), and C (gray \times) in the Raman spectra of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ as a function of pressure. The lines are guides for the eye to emphasize spectral changes.

the intensity of band C remains almost constant up to 19 GPa, bands A and B have at 6 GPa already lost roughly 70 and 85% of their intensity, respectively. Note that Raman spectra in ferroelectric perovskites are often analyzed on the basis of so-called transverse modes (TO modes) such as bands A and B in NBT. The intensity-evolution of such TO modes is believed to reflect the ferroelectric state in complex perovskites through the coupling of the light to the polarization in polar microregions, and has therefore been used to identify ferroelectric phase transitions (see, e.g., Ref. 52). Two arguments let us believe that in NBT polar clusters are present at ambient conditions. First, such clusters are commonly observed in relaxors like NBT.² Second, a recent Raman scattering study,²⁴ where a band associated with Na-O vibrations has been observed, indicates polar $\text{Na}^{1+}\text{TiO}_3$ clusters (and for stoichiometry reasons also polar $\text{Bi}^{3+}\text{TiO}_3$ clusters) which are large enough (nanometer-sized) to allow the associated phonon to be observed. The coupling of light to such polar clusters leads to TO bands, where the intensity reflects their ferroelectric state and where broadening can be due to disorder or to the dynamics of polar clusters.⁵²⁻⁵⁴ As a consequence, we believe that the drastic intensity change of bands A and B indicates a change in the polar character of the clusters in NBT. For a discussion of such a change, it is instructive to consider already published investigations discussing pressure-induced phase transition in mixed perovskites.

Yasuda *et al.*^{12–14} reported dielectric and diffraction studies of $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PIN), ordered PIN being antiferroelectric with 80–100-nm clusters and disordered PIN being a relaxor with 20–30-nm clusters. For disordered PIN a pressure-induced relaxor-to-antiferroelectric crossover ($R3m \rightarrow Pbam$), similar to that in NBT, has been observed and the authors propose a model where the crossover is conditioned by precursor antiferroelectric-nanoclusters that become larger with increasing pressure (for clusters > 80 nm macroscopic antiferroelectricity appears). Through the work on various perovskites, Samara and co-workers^{8–11} have proposed pressure-induced ferroelectric-to-relaxor crossover to be a general feature of soft-mode ferroelectrics. According to these authors the ferroelectric-to-relaxor crossover can be interpreted in terms of pressure-induced changes in the correlation length, r_c , between polar nanodomains. In their view r_c decreases markedly even by applying modest pressure, and, as consequence, when r_c becomes sufficiently small the correlation among polar domains becomes too small to establish a macroscopic ferroelectric state, i.e., one observes a transition to a relaxor state.

Even though pressure-dependent dielectric measurements on NBT are not yet available to discuss in all detail the mechanism in the relaxor-to-antiferroelectric transition, we might draw, on the basis of the above literature results and our Raman spectra, the following microstructural picture. At ambient conditions NBT would present polar $\text{Na}^{1+}\text{TiO}_3$ and $\text{Bi}^{3+}\text{TiO}_3$ clusters in a matrix (probably antiferroelectric as discussed below; disordered or ordered, yet to be discovered), the latter matrix preventing the onset of a macroscopic ferroelectric ordering and leading to the observed relaxor behavior. When hydrostatic pressure is applied the polar volume of the clusters decreases and with further pressure-increase long-range antiferroelectricity permeates throughout the sample. As has been discussed for PIN,^{12–14} the presence of a small fraction of ordered antiferroelectric domains, already present in the relaxor phase, facilitates the development of antiferroelectricity. As a consequence, it is conceivable for NBT that the matrix already presents local antiferroelectric ordering, acting as a precursor for the phase transition. Such complex antiferroelectric regions have already been observed through a transmission electron microscopy study of another perovskite-type compound, $\text{PbCo}_{1/2}\text{W}_{1/2}\text{O}_3$ (PCW).⁵⁵ Furthermore, it is interesting to notice that birefringence images of rhombohedral NBT show very complex pattern together with an unexpected orientation of the optical indicatrix. Both have been attributed to twinning coupled with strain, i.e., strain-induced birefringence dominating natural birefringence,⁵ the origin of the strain being unknown. On the basis of the above model an antiferroelectric matrix could be one of the origins of the observed strain, caused by inequivalent parallel or antiparallel dipole ordering between clusters and the matrix. Finally, we remark that an antiferroelectric precursor phase, although at higher temperatures, has already been considered for the interpretation of dielectric² and acoustic⁵⁶ behavior in NBT.

Raman spectroscopy supports the above phase transition picture and allows insight into some microstructural details as discussed below. (i) As stated earlier, we believe that the

intense and broad TO bands *A* and *B* are related to the presence of polar nanoclusters, and, in respect thereof, their intensity breakdown observed in the 1-bar \rightarrow 2.8-GPa region (Figs. 4 and 5) mirrors the progressive vanishing of polar microregions. (ii) The intensity loss of bands *A* and *B* is mainly important up to 2.7 GPa, and thus we believe that the first transition at 2.7 GPa is a relaxor-antiferroelectric transition. The second transition at 5 GPa, having a less pronounced intensity change, might be the signature of an antiferroelectric-to-antiferroelectric transition, i.e., through octahedron tilts leading to the intensity jump observed for band *B*. However, we cannot rule out that the 2.7–5 GPa pressure range reflects a situation where relaxor and antiferroelectric states still compete. (iii) The persistence of band *A* (attributed to Na-O vibrations) over the whole pressure range indicates that $\text{Na}^{1+}\text{TiO}_3$ and $\text{Bi}^{3+}\text{TiO}_3$ clusters still exist, i.e., they change only their dielectric character but not their ordering scheme via diffusion. (iv) The reversibility of pressure-induced changes in the Raman spectra indicates that the relaxor state with its polar nanoclusters are not the result of an incomplete reaction during sample preparation but corresponds to a stable state of the sample at 1 atm.

VIII. CONCLUSION

We have studied the pressure-dependent Raman spectra of polycrystalline $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, which belongs at ambient conditions to the family of relaxor ferroelectrics. The pressure-induced evolution of the Raman spectra has been discussed in the light of changes in the structural and ferroelectric properties of NBT.

Through discontinuous or distinct changes in the Raman spectra we have observed two phase transitions which have been analyzed in terms of a rhombohedral-to-orthorhombic ($R3c$ -to- $Pnma$) phase transition, which involves a large symmetry change in the tilt system and the cation displacements. Our results, in agreement with symmetry considerations, show that this transition does not occur in a single step, but goes through an intermediate phase (2.7–5 GPa), which makes such a change energetically more plausible. The frequency evolution of characteristic bands in the Raman spectra allows us to propose a model where a change in the A-cation displacement ($[111]_p \rightarrow [100]_p$) takes part in the early stage of transition, while at least one out of the other changes, i.e., B-site displacement ($[111]_p \rightarrow [000]$) or the tilt change ($a^-a^-a^- \rightarrow a^-b^+a^-$), appear to happen only in a second stage.

We have observed an unusual pressure-induced breakdown of the Raman intensity in the 100–400- cm^{-1} frequency region, namely for the bands at 135 and 275 cm^{-1} . This intensity breakdown, preceding the phase transition at 2.7 GPa, has been attributed to a change in the polar character of nanosized $\text{Bi}^{3+}\text{TiO}_3$ and $\text{Na}^{1+}\text{TiO}_3$ clusters, seen as a signature of a pressure-induced relaxor-to-antiferroelectric crossover in NBT. We have proposed a model in which the size of polar clusters is reduced with pressure, while an antiferroelectric matrix acts as a precursor for long-range antiferroelectricity, which percolates the sample with increasing pressure.

However, further detailed studies on the influence of pressure in NBT and other relaxor perovskites are needed to improve our understanding of pressure-induced changes in the dielectric properties of relaxor ferroelectrics. Further to dielectric spectroscopy and transmission electron microscopy, which are known to be useful for such studies, it has been demonstrated in this study that Raman spectroscopy is an effective technique for the study of pressure-dependent characteristics in relaxor materials and it is hoped that this study will stimulate other studies.

ACKNOWLEDGMENTS

The authors are grateful to the Engineering & Physical Science Research Council (United Kingdom) for a grant that enabled this work to be pursued. We are also grateful to G. O. Jones and P. A. Thomas (University of Warwick) for providing NBT samples and for information about their pressure-dependent synchrotron study on NBT. V. Jennings (University of Warwick) is acknowledged for information about his calculations of the phonon dynamics of NBT.

- *Author to whom correspondence should be addressed. Present address: Laboratoire des Matériaux et du Génie Physique, ENS de Physique de Grenoble, BP 46, 38402 St. Martin d'Hères Cedex, France. Email address: kreisel@inpg.fr
- ¹G.A. Smolenskii, V.A. Isupov, A.I. Agranovskaya, and N.N. Krainik, *Fiz. Tverd. Tela (Leningrad)* **2**, 2982 (1960) [*Sov. Phys. Solid State* **2**, 2651 (1960)].
 - ²C.S. Tu, I.G. Siny, and V.H. Schmidt, *Phys. Rev. B* **49**, 11 550 (1994).
 - ³G.O. Jones, P.A. Thomas, and A. Hewat (unpublished).
 - ⁴G.O. Jones and P.A. Thomas, *Acta Crystallogr., Sect. B: Struct. Sci.* **B56**, 426 (2000).
 - ⁵M. Geday, J. Kreisel, K. Roleder, and A.M. Glazer, *J. Appl. Crystallogr.* **33**, 909 (2000).
 - ⁶R.E. Cohen, *Nature (London)* **358**, 136 (1992).
 - ⁷Y.-M. Chiang, G.W. Farrey, and A.N. Soukhovjak, *Appl. Phys. Lett.* **73**, 3683 (1998).
 - ⁸G.A. Samara, *Phys. Rev. Lett.* **77**, 314 (1996).
 - ⁹G.A. Samara, *J. Appl. Phys.* **84**, 2538 (1998).
 - ¹⁰G.A. Samara, E.L. Venturini, and V.H. Schmidt, *Appl. Phys. Lett.* **76**, 1327 (2000).
 - ¹¹G.A. Samara and L.A. Boatner, *Phys. Rev. B* **61**, 3889 (2000).
 - ¹²N. Yasuda, H. Ohwa, J. Oohashi, K. Nomura, H. Terauchi, M. Iwata, and Y. Ishibashi, *J. Phys. Soc. Jpn.* **66**, 1920 (1997).
 - ¹³N. Yasuda, H. Ohwa, J. Oohashi, K. Nomura, H. Terauchi, M. Iwata, and Y. Ishibashi, *J. Phys. Soc. Jpn.* **67**, 3952 (1998).
 - ¹⁴K. Nomura, T. Shingai, N. Yasuda, H. Ohwa, and H. Terauchi, *J. Phys. Soc. Jpn.* **68**, 866 (1999).
 - ¹⁵A. K. Sood, N. Chandrabhas, D.V.S. Muthu, and A. Jayaraman, *Phys. Rev. B* **51**, 8892 (1995).
 - ¹⁶U.D. Venkateswaran, V.M. Naik, and R. Naik, *Phys. Rev. B* **58**, 14 256 (1998).
 - ¹⁷J.A. Sanjurjo, E. Lopez-Cruz, and G. Burns, *Phys. Rev. B* **28**, 7260 (1983).
 - ¹⁸F. Cerdeira, W.B. Holzapfel, and D. Bauerle, *Phys. Rev. B* **11**, 1188 (1975).
 - ¹⁹A. Grzechnik, G.H. Wolf, and P.F. McMillan, *J. Raman Spectrosc.* **28**, 885 (1997).
 - ²⁰P. Gillet, F. Guyot, G.D. Price, B. Tournier, and A.L. Cleach, *Phys. Chem. Miner.* **20**, 159 (1993).
 - ²¹I.G. Siny and R.S. Katiyar, *Ferroelectrics* **206**, 307 (1998).
 - ²²I.G. Siny, T.A. Smirnova, and T.V. Kruzina, *Ferroelectrics* **124**, 207 (1991).
 - ²³H. Ohwa, M. Iwata, and N. Yasuda, *Ferroelectrics* **229**, 147 (1999).
 - ²⁴J. Kreisel, A.M. Glazer, G. Jones, P.A. Thomas, L. Abello, and G. Lucazeau, *J. Phys.: Condens. Matter* **12**, 3267 (2000).
 - ²⁵M. ElMarssi, R. Farhi, and D. Viehland, *J. Appl. Phys.* **81**, 355 (1997).
 - ²⁶U. Bismayer, V. Devarajan, and P. Groves, *J. Phys.: Condens. Matter* **1**, 6977 (1989).
 - ²⁷E. Salje and U. Bismayer, *J. Phys.: Condens. Matter* **1**, 6967 (1989).
 - ²⁸G.J. Pieramini, S. Block, J.D. Barnett, and R.A. Forman, *J. Appl. Phys.* **46**, 2774 (1975).
 - ²⁹J. Suchanicz and J. Kwapulinski, *Ferroelectrics* **165**, 249 (1995).
 - ³⁰V.A. Isupov, I.P. Pronin, and T.V. Kruzina, *Ferroelectr. Lett. Sect. 2*, 205 (1984).
 - ³¹V.V. Ivanova, A.G. Kapyshev, Y. Venevtsev, and G.S. Zhdanov, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **26**, 354 (1962).
 - ³²G.O. Jones and P.A. Thomas, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **A55**, 493 (1999).
 - ³³J.C. Toledano, A.M. Glazer, T. Hahn, E. Parthe, R.S. Roth, R.S. Berry, R. Metselaar, and S.C. Abrahams, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **A54**, 1028 (1998).
 - ³⁴A.M. Glazer, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **B28**, 3384 (1972).
 - ³⁵A.M. Glazer, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **A31**, 756 (1975).
 - ³⁶M.S. Zhang and J.F. Scott, *Ferroelectr. Lett. Sect. 6*, 147 (1986).
 - ³⁷I.G. Siny, T.A. Smirnova, and T.V. Kruzina, *Fiz. Tverd. Tela (Leningrad)* **33**, 110 (1991) [*Sov. Phys. Solid State* **33**, 61 (1991)].
 - ³⁸H. Uwe, K.B. Lyons, H.L. Carter, and P.A. Fleury, *Phys. Rev. B* **33**, 6436 (1986).
 - ³⁹G.O. Jones, P.A. Thomas, and M. I. McMahon (unpublished).
 - ⁴⁰G. Burns, J.A. Sanjurjo, and E. Lopez-Cruz, *Phys. Rev. B* **30**, 7170 (1984).
 - ⁴¹U. Bismayer, *Phase Transitions* **27**, 211 (1990).
 - ⁴²J. Kreisel, G. Lucazeau, and H. Vincent, *J. Solid State Chem.* **137**, 127 (1998).
 - ⁴³P. Tarte, *Spectrochim. Acta, Part A* **23A**, 2127 (1967).
 - ⁴⁴P. Tarte, A. Rulmont, M. Ligeois-Duyckaerts, R. Cahay, and J.M. Winand, *Solid State Ionics* **42**, 177 (1990).
 - ⁴⁵J. Kreisel and A.M. Glazer, *J. Phys.: Cond. Matter* **12**, 9689 (2000).
 - ⁴⁶B. Noheda, J.A. Gonzalo, L.E. Cross, R. Guo, S.E. Park, D.E. Cox, and G. Shirane, *Phys. Rev. B* **61**, 8687 (2000).
 - ⁴⁷F. Genet, S. Lorient, C. Ritter, and G. Lucazeau, *J. Phys. Chem. Solids* **60**, 2009 (1999).
 - ⁴⁸I.G. Siny, S.G. Lushnikov, R.S. Katiyar, and E.A. Rogacheva, *Phys. Rev. B* **56**, 7962 (1997).
 - ⁴⁹J.P. Sokoloff, L.L. Chase, and D. Rytz, *Phys. Rev. B* **38**, 597 (1988).

- ⁵⁰R.M. Hazen and H.X. Yang, *Science* **277**, 1965 (1997).
- ⁵¹R.M. Hazen and A. Navrotsky, *Am. Mineral.* **81**, 1021 (1996).
- ⁵²J. Toulouse, P. DiAntonio, B.E. Vugmeister, X.M. Wang, and L. A. Knauss, *Phys. Rev. Lett.* **68**, 232 (1992).
- ⁵³B.E. Vugmeister, P. DiAntonio, and J. Toulouse, *Phys. Rev. Lett.* **75**, 1646 (1995).
- ⁵⁴P. DiAntonio, B.E. Vugmeister, J. Toulouse, and L.A. Boatner, *Phys. Rev. B* **47**, 5629 (1993).
- ⁵⁵C.A. Randall, S.A. Markgraf, A.S. Bhalla, and K. Baba-Kishi, *Physica B* **40**, 413 (1989).
- ⁵⁶I.G. Siny, C.S. Tu, and V.H. Schmidt, *Phys. Rev. B* **51**, 5659 (1995).