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Abstract. We report on the estimation of the compressibility of $Na_{0.5}Bi_{0.5}TiO_3$ and its constituent polyhedra through two different approaches: the so-called polyhedral approach and that based on the pressure dependence of particular Raman-active modes. In order to investigate the reliability of the results obtained for $Na_{0.5}Bi_{0.5}TiO_3$, the two approaches have also been applied to perovskite-type titanates, $ATiO_3$ (A = Ca, Ba, Sr, Pb), and the results are compared with compressibility data reported in the literature. The comparative study shows that (i) $ATiO_3$ compressibilities are overestimated by the polyhedral approach, but can be roughly corrected by an empirical scaling factor, (ii) the A cation has a smaller influence in the compressibility than would be expected in view of the weakly bonded large AO_{12} polyhedra, (iii) TiO_6 compressibilities deduced from Raman spectra are remarkably uniform among different titanates $((4.3 \pm 0.2) \times 10^{-3}\ GPa^{-1})$, (iv) the Raman approach yields compressibilities within 10% of the experimental values.

1. Introduction

The ideal structure of perovskite-type oxides (ABO_3) is essentially simple and can be described as a network of corner-linked octahedra, with the B cations at the centre of the octahedra and the A cations in the space (coordination 12) between the octahedra. Among the large family of perovskites, the so-called titanates, $ATiO_3$, have been extensively studied mainly because of their interesting dielectric and structural properties.

Currently, we are interested in the unusual $A_{0.5}A'_{0.5}TiO_3$ family of titanate crystals, which are typified by sodium bismuth titanate, $Na_{0.5}Bi_{0.5}TiO_3$ (NBT). NBT was discovered by Smolenskii *et al* [1] in 1960. The special and rare feature of this type of perovskite is the formation of a chemical compound, i.e. a 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 are only a handful of cases where the compound formation results from substitution at the A sites. At room temperature, NBT is known to belong to the family of relaxor ferroelectrics [2] and NBT presents several temperature-dependent phase transitions [3–6]. A recent Raman study of $(Na_{1-x}K_x)_{0.5}Bi_{0.5}TiO_3$ has revealed that the microstructure in NBT can be seen as consisting of local $Bi^{3+}TiO_3$ and Na^+TiO_3 clusters [7].

While the physical properties, phase transitions and lattice dynamics of NBT as a function of temperature and substitution rate are fairly well known, our present interest is to extend the

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understanding of the relaxor ferroelectric NBT and related compounds by studying its pressure-dependent behaviour. With this aim, we have recently conducted a pressure dependence investigation of $Na_{0.5}Bi_{0.5}TiO_3$ using Raman spectroscopy; this showed that NBT undergoes a rhombohedral-to-orthorhombic phase transition and that the frequency of several Raman modes increases linearly with pressure from 5 to 19 GPa [8]. Such a linear pressure dependence makes the Raman modes in principle suitable for the determination of the compressibility, assuming that changes in the volume ΔV, and thus in bond distances d, induce changes in force constants and thus in vibrational frequencies. The Grüneisen model assumes that the Grüneisen constant γ correlates the pressure dependence of vibrational frequencies with the unit-cell volume. At constant temperature, the Grüneisen constant is defined by

$$\gamma = -\frac{\partial \ln \nu}{\partial \ln V}\bigg|_T = \frac{1}{\kappa}\frac{\partial \ln \nu}{\partial P}\bigg|_T \tag{1}$$

where ν is the frequency of a vibrational mode, V the unit-cell volume and κ the compressibility given by

$$\kappa = -\frac{1}{V}\frac{\partial V}{\partial P}\bigg|_T. \tag{2}$$

As a consequence, when the pressure dependence of the vibrational modes is known, as well as the Grüneisen parameter, the compressibility can be determined. Unfortunately, to the best of our knowledge, the Grüneisen parameter of NBT has not been reported in the literature. For this reason we have decided to estimate the compressibility in two alternative ways. The first is through the so-called polyhedral approach, based on comparative crystal chemistry and developed by Hazen and Finger [9–12], which allows one in many cases to describe the compressibility of a given polyhedron through an empirical expression. This approach has rarely been applied to perovskites but we can point to the work by Cornelius *et al* [13] in which the latter approach has been used for estimation of anisotropic compressibilities of high-temperature superconductors (HTSC), which contain perovskite-type structural blocks. In the second approach, we use a method that has been proposed by Lucazeau and co-workers [14–16] and which allows an estimation of elastic properties of a crystal through the analysis of particular Raman modes, without explicit knowledge of the Grüneisen parameter.

Although this study has been primarily motivated by an investigation of NBT, we came to realize in the course of this study that a meaningful discussion of the two approaches requires a comparison with findings for other perovskites. As a consequence, throughout the article we have applied the two approaches simultaneously to NBT and to other perovskite-type titanates, $ATiO_3$ (A = Ca, Ba, Sr, Pb).

2. Compressibility estimation by the polyhedral approach

The so-called polyhedral approach, developed by Hazen and Finger [9–12], has been shown to be useful in predicting elastic properties of a large number of solids (see [10] and references cited therein). The approach is based on the observation that the identification of cation–oxygen polyhedra, M_xO_y, not only simplifies the description of complex crystal structures but also allows a better understanding of physical properties for materials containing similar polyhedra. The study of the compressibility of MgO_6 octahedra in various materials is one of the striking examples which reveals a remarkable uniform compressibility in spite of great differences in polyhedral linkage [10].

2.1. The empirical formula and general considerations

On the basis of a systematic study of a large number of compounds concerning the influence of the bond length and the anion/cation charge of a given polyhedron on the compressibility, Hazen and Finger derived the following empirical expression for the compressibility of a given polyhedron [10]:

$$\kappa_{\text{poly}} = \frac{4}{3} \frac{d^3}{S^2 Z_c Z_a} \text{ GPa}^{-1} \tag{3}$$

where Z_a is the anion charge, Z_c the cation charge, d the bond length in Å and S^2 an ionicity scaling factor equal to 1/2 for oxygen-based polyhedra.

The extension of the polyhedral approach is to assume that the bulk compressibility of complex crystals with linked polyhedra can be derived when κ_{poly} for each polyhedron is known. Such a derivation is not necessarily straightforward because elastic properties do not only depend on changes in cation–anion distances, but might, for instance, also depend on angles between polyhedra (polyhedra tilting) [10]. However, on the basis of a study of the compressibility for different ATiO$_3$ titanates, Fischer *et al* [17] have proposed that polyhedron tilting surprisingly does not have an important effect on elasticity in perovskites and thus, in a first approximation, its role will be neglected in the following.

The easiest model to use to deduce the bulk compressibility, κ_{bulk}, from the compressibility of each constituent polyhedron is that based on building the volume-weighted sum of the individual polyhedra according to

$$\kappa_{\text{bulk}} = \sum_i x_i \frac{V_i}{V_0} \kappa_i^{\text{poly}}$$

$$\kappa_{\text{NBT}} = 0.5 \frac{V_{\text{NaO}_{12}}}{V_{\text{NBT}}} \kappa_{\text{NaO}_{12}} + 0.5 \frac{V_{\text{BiO}_{12}}}{V_{\text{NBT}}} \kappa_{\text{BiO}_{12}} + \frac{V_{\text{TiO}_6}}{V_{\text{NBT}}} \kappa_{\text{TiO}_6} \tag{4}$$

where the index i refers to a given type of cation–anion polyhedron and x_i is the concentration on a crystallographic site. V_i and V_0 are the volumes of a given polyhedron and the unit cell, respectively, with $\sum_i (x_i V_i / V_0) = 1$. Equation (4) has been proposed and applied in references [14–16] for estimation for different perovskite-type materials. Although this approach is intuitively valuable for averaging compressibilities of separated parts (like clusters in a crystal), the model is questionable in the case of interwoven polyhedral linkage in perovskites. To overcome this problem and to estimate the compressibility of the perovskite layer in HTSCs, Cornelius *et al* [13] proposed another model, where the compressibility of a pseudo-cubic perovskite layer is estimated according to a 'parallel circuit' of the constituent polyhedra, leading to

$$\frac{1}{\kappa_{\text{bulk}}} = \sum_i x_i \frac{V_i}{V_0} \frac{1}{\kappa_i^{\text{poly}}} \tag{5}$$

using the same notation as in equation (4). In order to determine which of the two models represents reality best, we have applied equations (4) and (5) to different perovskite-type titanates ATiO$_3$ (A = Ca, Ba, Sr, Pb). The comparison of the results obtained with observed compressibility data shows that equation (5) systematically leads to a better agreement (e.g. for CaTiO$_3$: $\kappa^{\text{equation (4)}} = 8.75$, $\kappa^{\text{equation (5)}} = 6.7$, $\kappa^{(\text{obs})} = 5.6$; all values in units of 10^{-3} GPa). As a consequence, throughout this article equation (5) has been retained for calculations of the polyhedron $\rightarrow$ bulk transition.

Table 1. Compressibilities deduced from the polyhedral approach and the parameters used. (A) $Na_{0.5}Bi_{0.5}TiO_3$. (B) Perovskite-type titanates $ATiO_3$ (A = Ca, Ba, Sr, Pb).

	Material	Space group (at 300 K)	Entity	$\langle d \rangle$ (Å)[a]	Z_c	κ (10^{-3} GPa^{-1}) Polyhedral approach (3), (5)[b]	(3), (6)[c]	Literature
(A)	NBT	$R3c$	NaO_{12}	2.757	1	27.8		
			BiO_{12}	2.757	3	9.3		
			TiO_6	1.959	4	2.5		
			Na^+TiO_3 cluster			10.3	7.7	
			$Bi^{3+}TiO_3$ cluster			6.4	4.8	
			$Na_{0.5}Bi_{0.5}TiO_3$			8.4	6.3	
(B)	$CaTiO_3$	$Pbmn$	CaO_{12}	2.470	2	10.0		
			TiO_6	1.954	4	2.5		
			$CaTiO_3$			6.7	5.0	4.7[d], 5.6[e]
	$BaTiO_3$	$P4mm$	BaO_{12}	2.816	2	14.8		
			TiO_6	1.977	4	2.6		
			$BaTiO_3$			8.3	6.2	5.1[f], 6.4[g], 7.2[h]
	$SrTiO_3$	$Pm\bar{3}m$	SrO_{12}	2.756	2	13.9		
			TiO_6	1.949	4	2.5		
			$SrTiO_3$			7.9	5.9	5.6[i], 5.8[j]
	$PbTiO_3$	$P4mm$	PbO_{12}	2.519	2	10.6		
			TiO_6	1.976	4	2.6		
			$PbTiO_3$			7.0	5.3	4.9[j]

[a] Interatomic distances from reference [36].
[b] According to equations (3) and (5).
[c] According to equations (3) and (6), taking into account an empirical scaling factor; see the text.
[d] Crystal data [37].
[e] Powder data [17, 38].
[f] Powder data (cubic phase) [17].
[g] Crystal data (cubic phase) [39].
[h] Powder data (tetragonal phase) [17].
[i] Powder data [17].
[j] Crystal data [40].

2.2. Results and discussion (polyhedral approach)

Table 1(A) presents estimated compressibilities for NBT, its constituent polyhedra (AO_{12} and TiO_6) and the nano-clusters ($Bi^{3+}TiO_3$ and Na^+TiO_3). The bond lengths under ambient conditions, used to estimate the compressibilities of NBT, are derived from neutron diffraction experiments [4–6]. In principle, the cation–anion distances in a disordered polyhedron will vary from unit cell to unit cell, depending on the cation present on the specific crystallographic site. Such a dependence might be especially expected for NBT due to Na^+ and Bi^{3+} being chemically very different. Unfortunately diffraction techniques only allow the determination of the mean bond distance, d, averaged over the entire crystal for each distinct polyhedron. However, on the basis of equation (3), we might assume that the introduced error, i.e. taking the same d for Na^+–O and Bi^{3+}–O bonds, is small compared with the impact of the valence state.

As shown in table 1(A), the compressibility for NBT is estimated to take the value

$\kappa_{\text{NBT}} = 8.4 \times 10^{-3} \text{ GPa}^{-1}$ which is of the order of magnitude generally observed for oxides [10]. As expected from the intuitive idea of a larger dodecahedron volume and a closer-packed (stiff) octahedron, the dodecahedra are estimated to be more compressible than the octahedra: $27.8 \times 10^{-3} \text{ GPa}^{-1}$ for NaO_{12} or $9.3 \times 10^{-3} \text{ GPa}^{-1}$ for BiO_{12}, compared with $2.5 \times 10^{-3} \text{ GPa}^{-1}$ for TiO_6. Finally, Na^+TiO_3 and $Bi^{3+}TiO_3$ clusters are estimated to have rather different compressibilities, with estimated values of $10.3 \times 10^{-3} \text{ GPa}^{-1}$ and $6.4 \times 10^{-3} \text{ GPa}^{-1}$, respectively.

In order to discuss the reliability of the estimated compressibility values for NBT, we shall expect some insight from a comparison of values obtained for $ATiO_3$ (A = Ca, Ba, Sr, Pb) with experimental compressibilities. The comparison (table 1(B)) shows that calculated values lie for $ATiO_3$ (A = Ca, Ba, Sr, Pb) within 25% of experimental values and we note that the calculated values are systematically overestimated (even though by less than the 60% overestimate reported for perovskite layers in HTSC [13]). The question is whether this overestimation arises from the polyhedral approach, i.e. equation (3), or the transition from polyhedral to bulk properties, i.e. equation (5). Equation (3) has proven to be a valuable approach for a large number of materials [10, 12]; nevertheless, it has been pointed out that a failure of the polyhedral approach for MO_6 octahedra can be caused by a covalent contribution to the chemical bonding [10]. For titanates, the introduction of such a contribution to the TiO_6 polyhedron compressibility (e.g. lowering the 'ionicity factor' S^2 in equation (3)) would lead to even larger estimated values. As a consequence, the overestimation appears to be linked to the AO_{12} polyhedron or to equation (5). Both of these possibilities imply that the 'soft' AO_{12} polyhedron does not contribute as much to the compressibility as expected, a more important role being taken by the 'stiff' BO_6. If this were true, the compressibility should be relatively similar for $ATiO_3$ perovskites regardless of the A cation. The latter point seems to be experimentally supported by the observation of similar compressibilities for $ATiO_3$ (A = Ca, Ba, Sr) [17].

Finally, although the empirical polyhedral approach has its drawbacks, we believe that it allows at least a rough estimation of the compressibilities for perovskite-type titanates. This is particularly true when the systematic overestimation is taken into account by a phenomenological scaling factor of $s = 3/4$ in equation (5), leading for the compressibility of titanates to

$$\frac{1}{\kappa_{\text{ATiO}_3}} = \frac{1}{s} \sum_i x_i \frac{V_i}{V_0} \frac{1}{\kappa_i^{\text{poly}}}. \tag{6}$$

Applying equation (6) to NBT leads then to estimated compressibilities of $6.3 \times 10^{-3} \text{ GPa}^{-1}$ for the compound and of $7.7 \times 10^{-3} \text{ GPa}^{-1}$ and $4.8 \times 10^{-3} \text{ GPa}^{-1}$ for the Na^+TiO_3 and $Bi^{3+}TiO_3$ clusters, respectively. Results for $ATiO_3$ (A = Ca, Ba, Sr, Pb) are presented in table 1(B).

3. Compressibility estimation from pressure-dependent Raman data

The aim of this section is, on the basis of a recently published high-pressure Raman study on NBT [8], to use the pressure dependence of particular Raman-active modes to estimate its compressibility.

The method presented below is based on the following assumptions:

(i) changes in the lattice parameter a induce changes in force constants k and consequently in the vibrational frequencies (Grüneisen model) and

(ii) polyhedron stretching modes involve mainly one type of force constant and the compressibility of the polyhedron is determined by these microscopic force constants [16].

3.1. Definition and model

Recently, Lucazeau and co-workers [14–16] proposed a method, based on the above approximations, which allows one to estimate elastic properties of a crystal by means of the analysis of particular Raman modes. In the following we will briefly recall some basic definitions and apply them to NBT; for a more detailed presentation of the method we refer the reader to references [14–16].

For NBT it is reasonable to assume a nearly cubic structure ($\alpha \approx 89.92°$ for the $R3c$ room temperature structure) with an average lattice parameter a. When considering furthermore that the unit-cell volume V varies linearly with the applied hydrostatic pressure P, equation (2) becomes

$$\kappa = -3 \frac{\Delta a}{a} \frac{1}{\Delta P}. \tag{7}$$

Assuming further to (i) that the microscopic force constants k depend on interatomic distances d according to $k = Ad^{-(m+n+3)}$, where m and n are exponents relative to attractive and repulsive potentials (for ionic crystals, $m = 9$ and $n = 1$; thus $\beta = m + n + 3 = 13$) [18] and introducing the harmonic oscillator relationship $\omega = (k/m)^{1/2}$, equation (7) leads to

$$\kappa = \frac{6}{\beta} \frac{\Delta \omega}{\omega} \frac{1}{\Delta P}. \tag{8}$$

Thus the compressibility κ can be deduced from the slope of the linear sections of the $\omega = f(P)$ curves for a given mode. It should be remembered that anharmonicity is not considered in this approach and that this equation applies only to particular vibrational modes involving force constants whose dependence on the interatomic distances can be reduced to a simple law.

3.2. Identification of appropriate Raman modes

Before applying equation (8) to the pressure-dependent Raman spectra of NBT [8] and in order to allow approximation (ii), we need to identify localized modes that are representative for polyhedra compressibility. For ionic materials such as the oxides of Ti^{4+}, vibrational modes are lattice vibrations involving the participation of all atoms. This makes it difficult to propose an empirical assignment of the experimental bands to a particular vibrational mode of the basic structural units of the crystal. However, it is reasonable to assume that the shortest bonds, belonging to the TiO_6 octahedra, will lead to high-frequency modes, while vibrations associated with the Na/Bi–O bonds are expected at lower frequencies.

It has been shown that the comparison of vibrational spectra of crystals having the same polyhedra in their crystal structure is a convenient way of identifying the spectral signature for a given polyhedron [19–21]. Therefore, with respect to the TiO_6 octahedra, it is useful to compare Raman spectra of different titanates. Such a comparison shows that Raman spectra of $ATiO_3$ (A = Ba, Pb, Sr or Ca) [22–28] are characterized by a common feature, namely intense bands in the 500–650 cm^{-1} region which can most probably be assigned to vibrations of TiO_6 octahedra. This assignment is in agreement with work by Gillet *et al* who assigned the high-frequency A_g band for orthorhombic $CaTiO_3$ to symmetric stretching of the TiO_6 octahedron [27]. For NBT [8] we identify an intense Raman band at roughly 530 cm^{-1} (band A) which shifts with applied pressure ($\sim$5.0 cm^{-1} GPa^{-1}) similarly to the 500 cm^{-1} band in $CaTiO_3$ ($\sim$4.7 cm^{-1} GPa^{-1}) [27]. As a consequence, we believe that symmetric vibrations of the TiO_6 octahedra dominate the band at 530 cm^{-1} in the NBT Raman spectrum and, therefore, meeting condition (ii), its pressure-dependent evolution can be considered as representative

for the compression of TiO$_6$ octahedra. This assignment for NBT is supported by very recent calculations of its lattice dynamics [29].

The apparent difficulty in the estimation of the A-site compressibility for NBT is that two different species (Na$^+$ and Bi^{3+}) are present on the A site. However, as we have recently discussed [7], the vibrations associated with the stretching of the A–O bond are expected to display a so-called two-mode behaviour for the following reasons: (a) the mass of the Bi cation is nearly ten times that of the Na cation and (b) the Na$^+$–O^{2-} and Bi^{3+}–O^{2-} chemical bonding (and therefore the force constants) are expected to be different. This scenario is supported by a study of an NBT-related solid solution, (Na$_{1-x}$K$_x$)$_{0.5}$Bi$_{0.5}$TiO$_3$ (NKBT) [7], for which it has been shown that the band at 135 cm^{-1} in the NBT Raman spectrum is dominated by a harmonic oscillator associated with the Na–O bond. The important consequence of the latter point is that the compressibility of NaO$_{12}$ and BiO$_{12}$ dodecahedra (and accordingly Na$^+$TiO$_3$ and Bi^{3+}TiO$_3$ clusters) can be studied independently, provided that Raman bands dominated by Na–O or Bi–O vibrations can be identified. In view of the observations on NKBT [7], the pressure dependence of the band at 135 cm^{-1} in the pressure-dependent NBT Raman spectra [8] can be considered as representative for the compression of NaO$_{12}$ dodecahedra. Unfortunately, because of experimental restrictions, the reported Raman spectra [8] do not allow the observation of the Bi–O band, which is located at low frequency because of the important Bi mass.

3.3. Results and discussion (Raman spectroscopic approach)

In view of the above discussion, we have applied equations (5) and (8) to the NBT Raman bands at 135 and 530 cm^{-1} which display a linear dω/dP shift in the 5–19 GPa region [8]. As shown in table 2(A), this leads to 9.4×10^{-3} GPa^{-1} for the Na$^+$TiO$_3$ cluster and to 4.3×10^{-3} GPa^{-1} and 12.3×10^{-3} GPa^{-1} for the TiO$_6$ and NaO$_{12}$ polyhedra, respectively. As in the polyhedral approach, we have also applied the Raman compressibility approach to other perovskite-type titanates ATiO$_3$ (A = Ba, Pb, Sr, Ca), for which pressure-dependent Raman data are available in the literature [22–28]. The latter results are presented in table 2(B).

When the compressibility values deduced from Raman spectra are compared with the observed values and with the values estimated from the polyhedral approach, some observations can be made.

(i) The compressibilities estimated from the Raman approach match within 10% the values that have been reported in the literature, i.e. the Raman approach seems to reproduce the actual compressibility better than the polyhedral approach.

(ii) TiO$_6$ compressibilities deduced from Raman spectra are remarkably uniform among the different titanates ($(4.3 \pm 0.2) \times 10^{-3}$ GPa^{-1}) but are higher than those estimated from the polyhedral approach (2.5×10^{-3} GPa^{-1}).

For a discussion of this difference, in terms of comparative crystal chemistry [10], it is instructive to inspect the compressibility of TiO$_2$, whose structure can be described as a linked network of TiO$_6$ octahedra. For rutile-type TiO$_2$, Hazen and Finger [30] reported that the compressibility value predicted by the polyhedral approach (2.5×10^{-3} GPa^{-1}) is smaller than the one observed by means of x-ray diffraction (4.4×10^{-3} GPa^{-1}). This discrepancy between estimated and observed values is among the largest yet observed for the use of the polyhedral approach and has been attributed to a non-negligible covalent contribution to the Ti–O bonding. Supporting this interpretation, Kim *et al* [31] have shown for TiO$_2$ that a partially ionic model is necessary to model its elastic properties. Our Raman-deduced values for TiO$_6$ octahedra in ATiO$_3$ titanates (table 2) match very well with the observed compressibility value for rutile-type TiO$_2$, validating the Raman

Table 2. Compressibilities deduced from the Raman approach and the parameters used. Results are compared with the polyhedral approach and literature data. (A) $Na_{0.5}Bi_{0.5}TiO_3$. (B) Perovskite-type titanates $ATiO_3$ (A = Ca, Ba, Sr, Pb).

	Material	Entity	ν (cm^{-1})	$d\nu/dP$ (10^{-9} cm^{-1} Pa^{-1})	κ (10^{-3} GPa^{-1}) Raman	Polyhedral approach	Literature[a]
(A)	NBT[b]	NaO_{12}	120	3.2 ± 0.3	12.3	27.8	
		BiO_{12}				9.3	
		TiO_6	540	5.0 ± 0.3	4.3	2.5	
		Na^+TiO_3 cluster			9.4	10.3	
		$Bi^{3+}TiO_3$ cluster				6.4	
		$Na_{0.5}Bi_{0.5}TiO_3$				8.4	
(B)	$CaTiO_3$[c]	CaO_{12}	155	1.9 ± 0.2	5.7	10.0	
		TiO_6	500	4.7 ± 0.3	4.3	2.5	
		$CaTiO_3$			5.4	6.7	4.7, 5.6
	$BaTiO_3$[d]	BaO_{12}				14.8	
		TiO_6	550	5.4 ± 0.5	4.5	2.6	
		$BaTiO_3$				8.3	5.1, 6.4, 7.2
	$SrTiO_3$[e]	SrO_{12}	150	2.1 ± 0.2	6.5	13.9	
		TiO_6	500	5.7 ± 0.3	4.2	2.5	
		$SrTiO_3$			6.0	7.9	5.6, 5.8
	$PbTiO_3$[f]	PbO_{12}				10.6	
		TiO_6				2.6	
		$PbTiO_3$				7.0	4.9

[a] References are given in table 1.
[b] Raman data from [8] for the orthorhombic phase.
[c] Raman data from [27] for the orthorhombic phase.
[d] Raman data from [23]; up to 3 GPa, the evolution of Raman bands is mainly driven by a phase transition mechanism. Data are given for pressure-dependent evolution of Raman bands in the 3 to 8.5 GPa range, where $BaTiO_3$ is cubic. Pressure-dependent Raman data below 200 cm^{-1} (i.e. needed for BaO_{12}) have not been reported.
[e] In the cubic phase of $SrTiO_3$ (at 300 K), first-order Raman scattering is forbidden. At 6 GPa, $SrTiO_3$ undergoes a cubic-to-tetragonal phase transition; however, on the basis of the only available Raman data [26] it is not straightforward to attribute vibrational modes to TiO_6 and SrO_{12} polyhedra, and as a consequence the assignments are only tentative.
[f] The available pressure-dependent Raman bands [24, 25] for $PbTiO_3$ are mainly determined by a phase transition mechanism when approaching the tetragonal-to-cubic phase transition rather than being representative for bond shortening.

approach for perovskite-type titanates and implying a covalent contribution to the Ti–O bonding in perovskite-type titanates. This observation is in agreement with recent molecular dynamics simulations for $SrTiO_3$ by Katsumata *et al* [32] showing that a partially ionic model is necessary to reproduce experimental results on thermal expansion or compressibility coefficients.

(iii) Compressibilities estimated for TiO_6 estimated through the Raman approach are smaller than those for AO_{12}—however, to a smaller extent than would be expected from the intuitive inverse relationship between bond length and compressibility. Furthermore, AO_{12} compressibilities deduced from Raman spectra yield lower values (roughly by a factor of 2) than those from the polyhedral approach.

We have already discussed in section 2.2 the inaccurate bulk compressibilities arising from the polyhedral approach being most probably due to overestimated AO_{12}

compressibilities or to a simplification in the transition from polyhedron to bulk compressibilities. The fact that the Raman approach leads to lower AO$_{12}$ compressibility values appears to point rather to an overestimation of the AO$_{12}$ compressibilities, i.e. an inappropriate equation (3) for AO$_{12}$ polyhedra in perovskites.

To conclude for this section, we believe that the Raman approach allows a reliable estimation of the compressibility for perovskite-type titanates, provided that appropriate modes are identified in pressure-dependent Raman spectra. In particular, values derived from high-frequency Raman bands allow a very good estimation of the TiO$_6$ compressibility for titanates and we think that this is more generally true for BO$_6$ octahedra in perovskite oxides.

4. Concluding remarks

We have described a way to estimate the compressibility of Na$_{0.5}$Bi$_{0.5}$TiO$_3$, its constituent polyhedra (AO$_{12}$ and TiO$_6$) and the nano-clusters (Bi^{3+}TiO$_3$ and Na$^+$TiO$_3$) through two different approaches. For a discussion of the reliability of the chosen approaches we have extended the study to other perovskite-type titanates ATiO$_3$ (A = Ba, Pb, Sr, Ca) by using data available in the literature. We have shown that the polyhedral approach overestimates compressibilities of perovskite-type titanates by roughly 25%, which we propose to take into account by means of an empirical scaling factor. On the other hand, the Raman approach used here yields compressibilities within 10% of the experimental values, the compressibilities for TiO$_6$ octahedra in different titanates being remarkably uniform: $(4.3 \pm 0.2) \times 10^{-3}$ GPa^{-1}.

To the best of our knowledge, in the literature there is no clear picture of the impact of AO$_{12}$ and BO$_6$ polyhedra on the elasticity, i.e. compressibility and thermal expansion, of perovskites. Some authors suggest that the temperature-induced volume change is due to the change in B–O bond lengths and the tilting of the BO$_6$ octahedra framework [33, 34]. For the special case of perovskites with a cubic structure, i.e. no octahedra tilts, the contribution of the A cation to the thermal expansion has been suggested [34] to be negligible in comparison with that of the B cation. On the other hand, a more recent comparative thermal expansion study of cubic SrZrO$_3$ and SrTiO$_3$—in comparison to results on CaTiO$_3$—indicates that the influence of the A cation is not totally negligible [35]. Finally, on the basis of a study of different titanates, Fischer *et al* [17] propose that cation–anion displacements in perovskites have a large effect on elasticity, while they believe that the influence of the degree of polyhedra tilting is small. As a consequence, although the general understanding of the compressibility is rather poor, it appears that the A cation does not play the important role in the elasticity that one would expect in view of the weakly bonded large AO$_{12}$ polyhedra which fill approximately 5/6 of the cubic perovskite unit cell. Our study of the pressure-dependent evolution of particular Raman modes, i.e. of microscopic force constants, is further evidence for this. Nevertheless, as our study shows, in view of the different compressibility values for titanates (table 2), the influence of the A site is not negligible. Further studies, extended to other perovskites, are clearly needed to obtain a more precise picture of the compressibility of perovskites. In this study it has been demonstrated that Raman spectroscopy, through its access to microscopic forces, is a valuable alternative technique for the estimation of compressibilities of perovskites and it is hoped that this study will stimulate other studies. We believe that a full comparative study using the available literature data on compressibilities of perovskites will allow one to separate out the influences of bond-length change, polyhedron type, octahedra tilt, cation displacements etc; such work is currently in progress.

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