

Pressure and temperature-dependent structural studies of $\text{Ba}_2\text{BiTaO}_6$

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Abstract

The ordered double perovskite $\text{Ba}_2\text{BiTaO}_6$ is shown to undergo a first-order rhombohedral ($R\bar{3}$) to monoclinic ($I2/m$) phase transition, which can be induced by either lowering the temperature or through the application of pressure. The structures in both phases have been refined from high resolution neutron powder diffraction data at various temperatures, while the high pressure measurements utilised synchrotron X-ray diffraction data. The rhombohedral structure is characterised by out-of-phase tilts about the [111] axis. In the monoclinic structure the tilt axis has changed to be about the [110] axis; however, the magnitude of the tilts in the two structures is remarkably similar.

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1. Introduction

As is observed for the mineral perovskite (CaTiO_3) itself, many metal oxides described as having the ABO_3 perovskite structure do not, in fact, have the cubic aristotype [1]. Rather a combination of rotation or tilting of the corner shared BO_6 octahedra and/or cation ordering reduces the symmetry. These, sometimes very subtle, distortions are often the cause of the important physical, electronic and magnetic properties of perovskites. The array of different properties displayed by perovskites has resulted in considerable academic interest in these types of materials for over 50 years. The actual and potential industrial use of perovskites is enormous, for example in the electroceramics industry. The use of perovskites as ferroelectrics [2], ionic conductors [3], superconductors [4] and magnetoresistant materials, has prompted a new wave of interest in these fascinating materials in recent times.

The desirable properties of perovskites are optimized by careful control of the composition of the metal oxide. These substitutions can result in structural phase transitions as is well illustrated in the series $\text{Ba}_{1-x}\text{Sr}_x\text{ZrO}_3$ [5] where the change in the effective size of the A-type cation alters the magnitude and nature of the tilting of the ZrO_6 octahedra resulting in the formation of four crystalline phases. Substitutions can also occur on the perovskite B-site giving oxides of the form $\text{AB}_{1-x}\text{B}'_x\text{O}_3$. In situations where $x = \frac{1}{2}$ and the size and/or charge of the two B-type cations are sufficiently different the two B-type cations can display long-range order. These ordered oxides are referred to as double perovskites of the type $\text{A}_2\text{BB}'\text{O}_6$ [1,6]. This B-cation ordering can coexist with octahedral tilting.

A large number of double perovskites have a monoclinic rock-salt $P2_1/n$ type structure [1,6,7]. Fewer examples with a rhombohedral $R\bar{3}$ structure are known, an obvious example being K-doped $\text{Ba}_2\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}_6$ [8,9]. The $R\bar{3}$ phase only exists at elevated temperatures in pure $\text{Ba}_2\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}_6$, [9–11]. At room temperature it has a monoclinic structure in $I2/m$. Structural studies of

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$\text{Ba}_2\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}_6$ have demonstrated that the $R\bar{3} \rightarrow I2/m$ transition is first order [10,11]. This rhombohedral structure also occurs at room temperature when the Bi^{V} is replaced by other pentavalent cations, such as Ta^{V} , Nb^{V} and Sb^{V} [12,13]. Thornton et al. [14] have suggested that a monoclinic structure forms in $\text{Ba}_2\text{BiSbO}_6$ at low temperatures. By analogy with $\text{Ba}_2\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}_6$ it is reasonable to expect that the monoclinic structure will be stabilized by a reduction in the cell volume. This may be achieved in a number of ways, the most obvious being the application of pressure or a reduction in temperature. In the present paper, we describe the use of both methods in the study of a representative rhombohedral double perovskite, namely $\text{Ba}_2\text{BiTaO}_6$.

2. Experimental

The polycrystalline sample of $\text{Ba}_2\text{BiTaO}_6$ was prepared by heating stoichiometric quantities of BaCO_3 , Bi_2O_3 and Ta_2O_5 . A modified Merrill-Bassett diamond-anvil cell was used for the X-ray studies in the pressure range 1 Bar–6.0 GPa. The powdered sample, together with a few small ruby chips was loaded into a 200 μm hole in a steel gasket. A methanol–ethanol–water (16:3:1) mixture was used as the hydrostatic pressure transmitting medium. The pressure was calibrated by measuring the shift of the R_1 fluorescence line of ruby before and after each run. The X-ray diffraction data were collected using synchrotron radiation at the bending magnet beamline, X7A, of the National Synchrotron Light Source at Brookhaven National Laboratory [15]. A wavelength of 0.68405 \AA was selected using a bent Si 111 focusing crystal monochromator. Data were collected using a linear position sensitive detector mounted ca. 450 mm from the sample. Further information on the instrument configuration and data collection procedure can be found elsewhere [16]. Powder neutron diffraction data were collected at room temperature using 1.4938 \AA neutrons using the high resolution powder neutron diffractometer at ANSTO's HIFAR reactor [17]. The program RIETICA was employed to refine the crystal structures using the Rietveld method [18].

3. Results and discussion

That the structure of $\text{Ba}_2\text{BiTaO}_6$ is rhombohedral at room temperature was rapidly established from either the synchrotron X-ray or neutron diffraction measurements. The structure was refined in space group $R\bar{3}$, Fig. 1. The refined Ta–O distance of 2.003(2) \AA and Bi–O distance of 2.315(2) \AA obtained from the refinements using the powder neutron diffraction data are diagnostic of Ta^{V} and Bi^{III} , as are the bond valences.

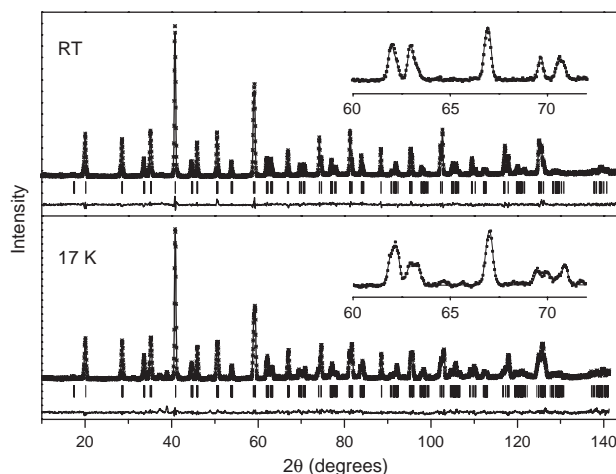


Fig. 1. Observed neutron, calculated and difference profile for $\text{Ba}_2\text{BiTaO}_6$ at room temperature, fitted in $R\bar{3}$ and at 17 K fitted in $I2/m$.

The rhombohedral structure is characterized by rock-salt like ordering of the Ta and Bi over alternate layers. The two BO_6 octahedra are rotated about the pseudocubic [111] axis with each successive octahedra rotating in an opposite sense, that is out-of-phase or ‘-’ in Glaziers notation [19,20].

Upon cooling the sample to 17 K we observe a clear change in the appearance of the neutron diffraction pattern. All the reflections can be indexed to a monoclinic cell. Importantly, no reflections indicative of M-point modes were observed, demonstrating the absence of any in-phase or +tilts [20]. This shows that the monoclinic structure is not in space group $P2_1/n$ ($a^+b^-b^-$). The structure was then refined in space group $I2/m$ ($a^+b^-b^-$), this having only out-of-phase tilts about the [110] axis. Again the average of the estimated Ta–O and Bi–O distances of 2.001(6) and 2.323(4) \AA are indicative of Ta^{V} and Bi^{III} , respectively.

The magnitude of the tilt angle, ϕ , in the two phases has been estimated from the refined atomic coordinates [9]. For the rhombohedral phase it is given by $\tan \phi = \sqrt{3}(y - x)$ where x and y refer to the atomic coordinates for the oxygen atom. For the monoclinic phase the appropriate expression is $\tan \phi = \frac{1}{3}(4x_1a/c - 8z_2c/a)$ where x_1 and z_2 refer to the atomic coordinates for O(1) and O(2) in Table 1. Despite the dramatic change in the orientation of the two structures we observe the tilt angles in the two phases to be approximately the same, 8.4° and 10.2°, respectively. The consistency of the tilt angles in the two phases is similar to the situation in $\text{Ba}_2\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}_6$ [10] and PrAlO_3 [21,22]. The latter compound is of particular interest as it also undergoes a first-order transition that involves a change in the tilt axis from [111] to [110]. The first-order rhombohedral ($a^-a^-a^-$) to orthorhombic ($a^+b^-b^-$) transition in

Table 1

Structural parameters for the two phases of $\text{Ba}_2\text{BiTaO}_6$ obtained from Rietveld refinement. Note the large uncertainties for the refined atomic coordinates for the high-pressure cell demonstrating as a consequence of the effects of absorption and the limited angular range

$R\bar{3}$	$a = 6.0513(2) \text{ \AA}$	$\alpha = 60.285(1)^\circ$		R_p 5.48	R_{wp} 6.80
Atom	Site	x	y	z	$B (\text{\AA}^2)$
<i>T = 298 K neutron</i>					
Ba	$2c$	0.2498(2)	0.2498(2)	0.2498(2)	0.84(2)
Bi	$1a$	0	0	0	0.70(5)
Ta	$1b$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.29(5)
O	$6f$	0.2258(3)	0.3108(12)	0.7312(5)	2.16(2)
$R\bar{3}$	$a = 6.0348(2) \text{ \AA}$	$\alpha = 60.276(3)^\circ$		R_p 4.33	R_{wp} 5.42
Atom	Site	x	y	z	$B (\text{\AA}^2)$
<i>Pressure = 0.83 GPa X-ray</i>					
Ba	$2c$	0.250(2)	0.250(2)	0.250(2)	0.3(2)
Bi	$1a$	0	0	0	3.6(2)
Ta	$1b$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	3.6(2)
O	$6f$	0.250(5)	0.346(6)	0.791(6)	1.9(8)
$I2/m$	$a = 6.0803(3) \text{ \AA}$ $b = 6.0280(3) \text{ \AA}$ $c = 8.5563(4) \text{ \AA}$	$\beta = 90.286(2)^\circ$		R_p 6.51	R_{wp} 8.28
Atom	Site	x	y	z	$B (\text{\AA}^2)$
<i>T = 17 K neutron</i>					
Ba	$4i$	0.5036(9)	0	0.2493(8)	0.40(4)
Bi	$2a$	0	0	0	0.46(6)
Ta	$2d$	0	0	$\frac{1}{2}$	0.14(6)
O1	$4i$	0.0590(9)	0	0.2685(7)	1.69(8)
O2	$8j$	0.2719(5)	0.2665(7)	-0.0329(3)	1.55(5)

PrAlO_3 can be induced by either lowering the temperature to near 220 K [23] or by increasing the pressure to above 8 GPa [24].

As noted above $\text{Ba}_2\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}_6$ adopts a monoclinic $I2/m$ structure at room temperature and undergoes a first-order transition to the rhombohedral $R\bar{3}$ structure near 400 K [10,11]. We have not sought to demonstrate that the $R\bar{3} \rightarrow I2/m$ transition in $\text{Ba}_2\text{BiTaO}_6$ is first order, but rather note that group theory shows this must be first order [20].

Application of pressure results in a progressive reduction in the size of the rhombohedral cell as evident from the shift in the diffraction peaks, Fig. 2. At pressures of up to 3.9 GPa the structure remains rhombohedral and there is an approximately linear decrease in the cell parameters, Fig. 4. Near 4 GPa the diffraction patterns show a distinct change. This is illustrated in Fig. 2 by the sudden onset of a large splitting of the (cubic) 110 reflection near $2\theta = 13^\circ$ and an apparent reversal of the intensities of the peaks of the (cubic) 211 and 220 reflections near $2\theta = 22.5^\circ$ and 26° , respectively. These changes indicate a structural phase transition near 4 GPa. Examination of the diffraction profiles showed no evidence for any reflections indicative of in-phase tilting of the BO_6 octahedra and it was

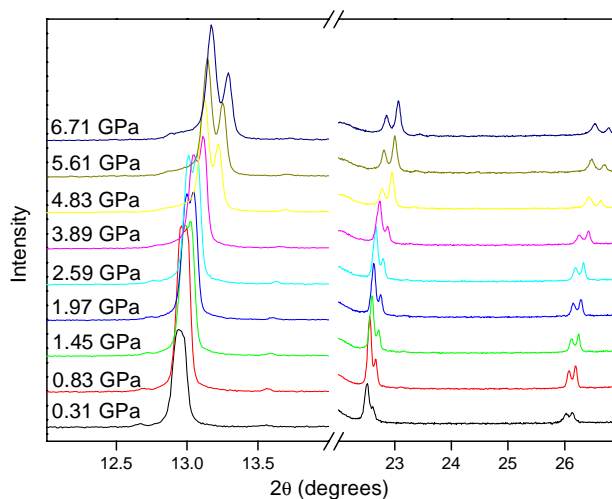


Fig. 2. Portions of the observed synchrotron X-ray diffraction profiles showing the diagnostic splitting of the pseudocubic $110 \approx 13^\circ$, $211 \approx 22.5^\circ$ and $220 \approx 26^\circ$ reflections. The patterns were recorded at the indicated pressure, with the pattern at 0.31 GPa recorded at the conclusion of the experiment, following pressure release.

concluded that the structure only has out-of-phase tilts. Consequently the profile was analyzed assuming the space group to be $I2/m$ and this provided a much better

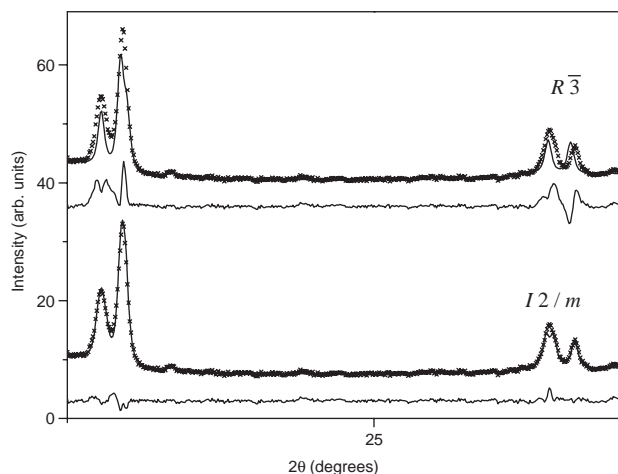


Fig. 3. Portion of the observed synchrotron X-ray calculated and difference profiles for $\text{Ba}_2\text{BiTaO}_6$ at 4.83 GPa, fitted in both $I2/m$ and $R\bar{3}$ illustrating the inability of the rhombohedral model to fit the observed profiles.

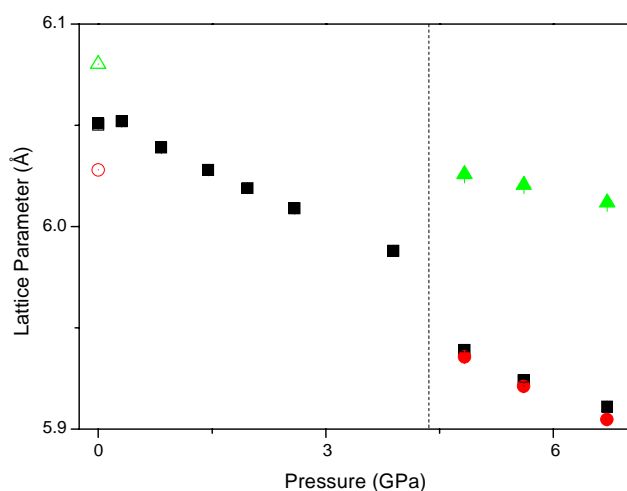


Fig. 4. Pressure dependence of the lattice parameters in $\text{Ba}_2\text{BiTaO}_6$. In the high pressure monoclinic phase the c -parameter has been reduced by $\sqrt{2}$ for ease of comparison. The point at 0.31 GPa is upon the release of the pressure and the point at “zero” pressure is from the neutron diffraction study. The open symbols at 0 GPa are for the low-temperature monoclinic phase.

fit to that available using models in $R\bar{3}$, Fig. 3. In refining the lattice parameters it was noted that the a parameter was always approximately equal to b , Fig. 4, suggesting the structure may in fact be tetragonal. An attempt to fit the pattern using a model in $I4/m$ ($a^0a^0b^-$) was only partially successful. The monoclinic model fitted the data better, and although it showed $a \approx b$ the monoclinic angle was clearly greater than 90° , $\beta \approx 90.2^\circ$. This value of the monoclinic angle is similar to that seen in the low temperature monoclinic structure refined using neutron diffraction data. It was concluded that the most appropriate space group for the high-pressure

structure was the monoclinic $I2/m$ and the structural analysis proceeded on this assumption.

Whereas full structural refinements were possible using the neutron diffraction data it was not possible to refine the high-pressure structures using the synchrotron X-ray diffraction data. This is a consequence of the relatively small number of observed reflections, and the significant attenuation of the beam by the diamond anvils. This results in both unusual displacement parameters and large uncertainties in the atomic coordinates (see Table 1). Clearly it is not possible to monitor subtle changes in the MO_6 polyhedra from such data. Precise lattice parameters were obtained using either a Le Bail analysis or a Rietveld-type refinement where the fractional coordinates of the atoms were not varied. The results of these two analyses were in excellent agreement with each other. The pressure dependence of the lattice parameters and cell volumes using the latter approach are illustrated in Figs. 4 and 5.

It is evident from Fig. 5 that the volume of the monoclinic cell is noticeably smaller than that estimated by extrapolation from the values for the rhombohedral cell. Clearly, the change in the tilt axis from $[111]$ to $[110]$ reduces the volume of the cell despite the fact that the tilt angles in the two phases, estimated from the neutron diffraction study, are similar. Fig. 2 strongly suggests that the $R\bar{3} \rightarrow I2/m$ transition is first order as required by group theory [20].

Here, and in the studies of structural phase transitions in PrAlO_3 [23,24] and $\text{Ba}_2\text{PrRu}_{0.8}\text{Ir}_{0.2}\text{O}_6$ [25], we have used decreasing temperature and applied pressure as analogous perturbations on the system. This is possible since the low-temperature structure has the smaller volume. In other perovskites, including LaGaO_3 [26] and LaCrO_3 [27], a volume reducing first-order transition is observed above room temperature. In these cases

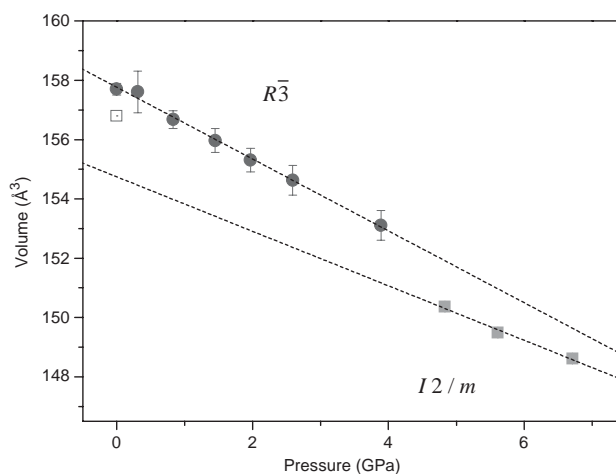


Fig. 5. Pressure dependence of the volume in $\text{Ba}_2\text{BiTaO}_6$. For clarity the volume of the monoclinic cell has been halved. The two points at zero pressure are from the neutron diffraction study. The dashed lines are the fits to the second-order Birch–Murnaghan equation of state.

the application of pressure can induce the same transition.

The bulk modulus, B_0 , of 126(10) GPa obtained by fitting a second-order Birch–Murnaghan [28] equation of state to the pressure dependence of the rhombohedral phase is comparable to that found for $\text{Ba}_2\text{PrRu}_{0.8}\text{Ir}_{0.2}\text{O}_6$ (139 GPa) [25]. It was previously suggested that the value of the bulk modulus for $\text{Ba}_2\text{PrRu}_{0.8}\text{Ir}_{0.2}\text{O}_6$ is reduced from that expected for a simple perovskite-type oxide as a consequence of a $\text{Pr}^{\text{III}}\text{--Pr}^{\text{IV}}$ valence state change; LaAlO_3 (28) and PrAlO_3 (24) have values of 190(5) and 205(8) GPa, respectively. However, the neutron diffraction data collected in this study shows the valence to be the same in both phases of $\text{Ba}_2\text{TaBiO}_6$ thus the origin of this low bulk modulus is worthy of further study.

In conclusion we have demonstrated that $\text{Ba}_2\text{BiTaO}_6$ adopts a rock-salt ordered double perovskite structure. Under ambient conditions the space group is $R\bar{3}$ and is characterized by out-of-phase tilts about the [111] axis. Cooling the sample to 17 K or applying pressures greater than ca. 4.0 GPa induces an, apparently, first-order transition to a monoclinic structure in space group $I2/m$. In the monoclinic structure the tilt axis has changed to be about the [110] axis; however, the magnitude of the tilts in the two structures is remarkably similar.

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