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On the Crystal Structure of $BaTbO_3$

W. T. Fu,*[,1] D. Visser,† and D. J. W. IJdo*

**Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands; and*
†NWO-EW, ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, United Kingdom

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The structure of perovskite-like $BaTbO_3$ has been reinvestigated by high-resolution powder neutron diffraction at room temperature using HRPD at the ISIS Facility. It has been shown that neither the space group $R\bar{3}c$ nor *Pnma* describes correctly its structure. The profile refinement has demonstrated that $BaTbO_3$ is tetragonal, space group *I4/mcm*, with the cell parameters $a = 6.04832(4)$ Å and $c = 8.58569(10)$ Å. This result is in agreement with the conclusions of Woodward, that the space group $R\bar{3}c$ is unlikely adopted by the $A^{2+}B^{4+}O_3$-type perovskites.

Key Words: **perovskite; high-resolution powder neutron diffraction; crystal structure.**

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1. INTRODUCTION

Structures in the perovskite family ABX_3 have held the interest over many years. Depending on the tolerance factor, $t = (r_A + r_X)/2^{1/2}(r_B + r_X)$, the structure is simple cubic ($t \approx 1$), space group $Pm\bar{3}m$, or distorted ($t > 1$ or $t < 1$) with generally lower symmetry. Distortions from the ideally cubic perovskite structure can be attributed to three different mechanisms (1): distortion of the BX_6 octahedra, cation displacement within the octahedra, and tilting of the octahedra. The last type distortion is the most common one, and the majority of distorted perovskites can be derived from the cubic perovskite by tilting the normally rigid octahedral unit. Glazer (2, 3) developed a description of the different tilting patterns in terms of component tilts around the pseudo-cubic axes, and obtained, by inspection, 23 corresponding space groups. Recently, Howard and Stokes (4) undertook a group-theoretical analysis and found 15 possible structures as derived from the cubic aristotype by the simple tilting of rigid octahedra. The tilting results in a lower coordination number of the *A* cation, which is 12 in the cubic aristotype, so that the smaller *A* can accommodate in the ABX_3 structure ($t < 1$).

The tilting of the octahedra gives rise not only to the splittings of the main diffraction peaks but also to the possible appearance of additional superlattice peaks due to the enlargement of the unit cell. However, identification of the nature of octahedral tilt from the peak shapes is not always straightforward due mainly to the instrument resolution. Moreover, although the superlattice reflections of oxide perovskites may easily be revealed by neutron diffraction technique, the assignment of the space group could be mistaken without properly comparing the yet other possibilities.

$BaTbO_3$ is an apparently simple perovskite. The structure of this compound, both at room temperature and at 4 K, was first reported by Jacobson *et al.* (5, 6), derived from powder neutron diffraction data, to be rhombohedral (space group $R\bar{3}c$, tilting ($a^-a^-a^-$) in Glazer's notation). Banks *et al.* (7) achieved the same results from powder neutron diffraction data as well. Recently, Tezuka *et al.* (8) have reported an orthorhombic structure for $BaTbO_3$ [space group *Pnma*, tilting ($a^+b^-b^-$)], obtained from their high-resolution powder neutron diffraction data. However, they did not give any reason for choosing this space group nor mention whether the refinement in *Pnma* is superior to that in $R\bar{3}c$.

The continuing interest in the structural variations and phase transitions in perovskites (9) has led us to reexamine the structure of the title compound. In this communication, we report new result on $BaTbO_3$ obtained from the high-resolution powder neutron diffraction.

2. EXPERIMENTAL

$BaTbO_3$ was prepared from AR $BaCO_3$ and Tb_4O_7 (99.99%) in an alumina crucible in air at 1323 K for a week with repeated grindings, and furnace cooled to the room temperature. X-ray diffraction patterns were collected with a Philips PW1050 diffractometer using the monochromatic Cu$K\alpha$ radiation in steps of 0.02° (2θ) and 12 s counting time in the range $10° < 2\theta < 117°$. High-resolution powder neutron diffraction data were obtained from the ISIS facility,

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[1] To whom correspondence should be addressed. Fax: + 31-71-5274537. E-mail: w.fu@chem.leidenuniv.nl.

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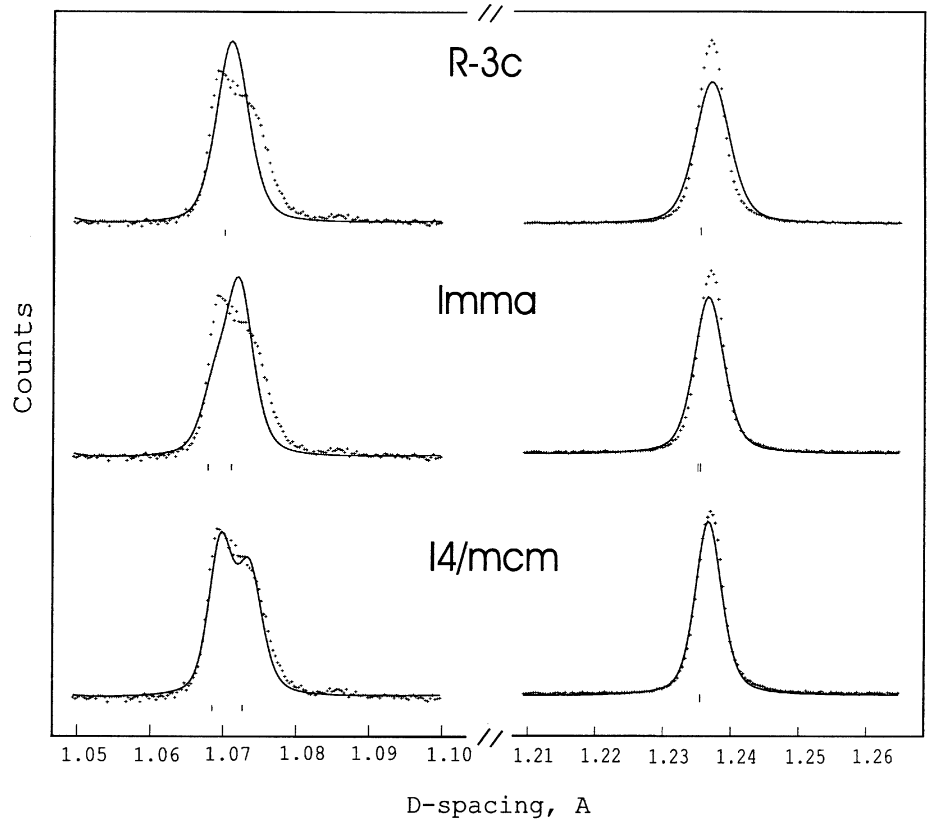

FIG. 1. A section of the observed high-resolution neutron diffraction pattern (crosses) of $BaTbO_3$, showing the basic (222) and (400) diffraction peaks. The continuous lines are the calculated profiles in the space groups $R\bar{3}c$, *Imma* and *I*4/*mcm*, respectively. Tick marks indicate the allowed diffractions by each space group. The significance of the splitting of the basic (400) diffraction is discussed in the text.

Rutherford Appleton Laboratories. The sample was loaded into an 11 mm diameter vanadium can. The diffraction patterns were recorded in both the backscattering detector bank and the 90° detector bank over the time-of-flight that ranged between 32–120 ms and 35–114 ms, corresponding to the *d*-spacings from 0.6 to 2.5 Å and 1.0 to 3.3 Å, respectively. The patterns were normalized to the incident beam spectrum as recorded in the upstream monitor, and corrected for detector efficiency according to prior calibration with a vanadium scan. The patterns were recorded to a total incident proton beam of about 300 μA h, for approximately 8 h. Calculations were performed simultaneously on both backscattering and 90° bank data by the Rietveld method using the GSAS computer program (10).

3. RESULTS

The X-ray diffraction pattern of $BaTbO_3$ showed typically the strong lines characteristic of pseudo-cubic perovskite cell. A few very weak additional lines at low 2θ angles and the splitting of main peaks at high angles part were visible. Although the X-ray diffraction pattern did not reveal any impurity, the neutron diffraction diagrams have shown a few very small peaks at the *d*-value of about 1.879, 1.605, 1.332 and 1.085 Å characteristics of a fluoride-like structure (Fig. 2). Careful analysis indicates that it is due to the trace of unreacted TbO_{2-x} (11). Therefore, all of the observed superlattice reflections can be indexed in terms of the double unit cell with odd integer indices, indicating the presence of only antiphase (−) tilting of the adjacent octahedra. In addition, we found no evidence in our data to adopt low-symmetry structure, such as monoclinic or triclinic, that results from non-equal tilts around the pseudo-

TABLE 1
Refined Atomic Positions and Thermal Parameters of $BaTbO_3$

Atoms	Site	*x*	*y*	*z*	*B* (Å^2)
Ba	4*b*	0.5	0	0.25	1.00(2)
Tb	4*c*	0	0	0	0.51(2)
O(1)	4*a*	0	0	0.25	1.74(5)
O(2)	8*h*	0.2810 (1)	$x + 0.5$	0	1.16(2)

Note. $R_{wp} = 4.48\%$, $R_p = 3.64\%$.

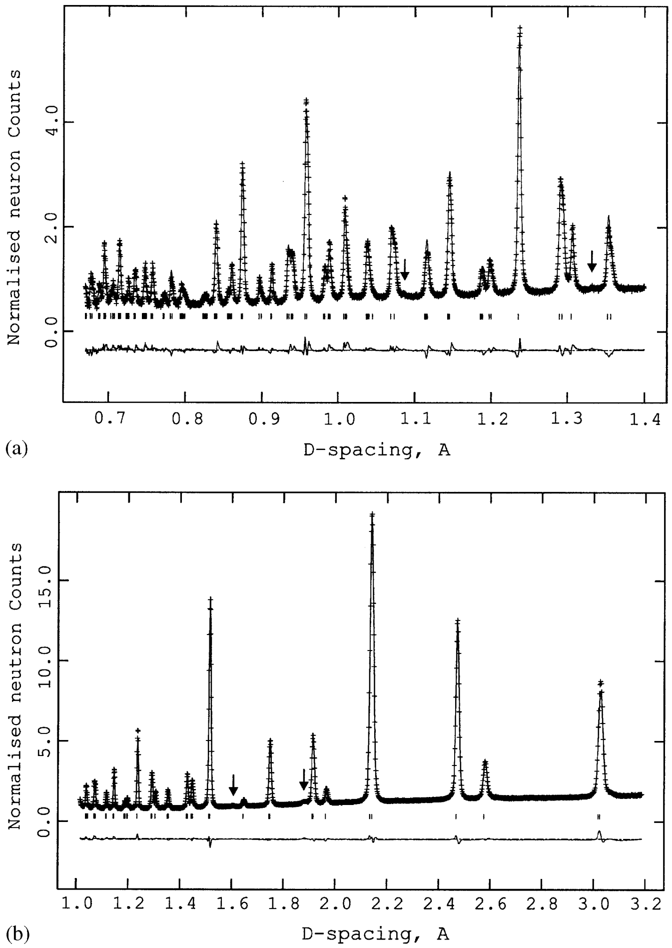

FIG. 2. Observed (crosses) and calculated (continuous line) profiles of $BaTbO_3$ in the space group $I4/mcm$. (a) and (b) denote the backscattering bank data (only the low d-value that range from 0.66 to 1.4 Å is shown) and 90° bank data, respectively. Tick marks indicate the positions of allowed reflections. A difference curve ($I_{obs.} - I_{cal.}$) is shown at the bottom. The arrows indicate a small contamination of TbO_{2-x}.

cubic axes. This leads to the three possible space groups: $I4/mcm$ ($a^0a^0c^-$), $Imma$ ($a^0b^-b^-$) and $R\bar{3}c$ ($a^-a^-a^-$), of which $R\bar{3}c$ has been reported previously (5–7). Close inspection of the high-resolution backscattering bank data has, however, ruled out the space group $R\bar{3}c$, because some basic diffraction peaks, e.g. (200) ($d \approx 2.14$ Å) and (400) ($d \approx 1.07$ Å), are asymmetric due to splitting (Fig. 1), where the space group $R\bar{3}c$ permit only single line, i.e. (220) and (440), respectively. Further, the basic (222) diffraction ($d \approx 1.236$ Å) does not split within the instrument resolution indicating a tetragonal or a pseudo-tetragonal structure (Fig. 1). Refinement carried out in both tetragonal and orthorhombic models has confirmed the space group $I4/mcm$; the weighted profile R values are $R_{wp}(I4/mcm) = 4.48\%$ and $R_{wp}(Imma) = 6.08\%$, respectively. The refined cell parameters are $a = 6.04832(4)$ Å and $c = 8.58569(10)$ Å.

TABLE 2
Selected Interatomic Distances (Å)

Tb–O(1)	2.14642(3)	×2
Tb–O(2)	2.1548(1)	×4
Ba–O(1)	3.02416(2)	×4
Ba–O(2)	2.8489(6)	×4
Ba–O(2)	3.2225(7)	×4

Table 1 lists the refined structural and thermal parameters. The plots of the observed and calculated profiles are shown in Fig. 2. Some selected interatomic distances are given in Table 2.

4. DISCUSSION

As was mentioned above, the rhombohedral space group $R\bar{3}c$ is not consistent with the observed high-resolution powder neutron diffraction data. This can also be seen from the rather poor agreement factor of the profile refinement ($R_{wp}(R\bar{3}c) = 7.59\%$). Tezuka *et al.* have reported an orthorhombic $Pnma$ structure for $BaTbO_3$ (8). However, we were unable to detect any reflection resulted from the coupled inphase (+) tilting around the pseudo-cubic $[100]_p$ axis. Doubt on this space group is also cast by considering the tolerance factor. In an earlier investigation (9), we have shown that while $SrPbO_3$, whose tolerance factor largely deviates from the unit ($t = 0.923$), does adopt $Pnma$ structure, the space group of $BaPbO_3$ ($t = 0.979$) is found to be $Imma$. Since the ionic radius of Tb^{IV} (0.76 Å) is quite similar to that of Pb^{IV} (0.775 Å) (11), it is not expected that $BaTbO_3$ ($t = 0.985$) would adopt the same structure as $SrTbO_3$ ($t = 0.930$) (7). In fact, the powder neutron diffraction diagram of Tezuka *et al.* (7) is basically identical to that of Jacobson *et al.* (5), and their refined oxygen positions suggest rather the space group $Imma$ than the space group $Pnma$ (the shifts of O(2) atoms due to inphase tilt around the $[100]_p$ axis are insignificant). In the light of the present investigation, refinement in the space group $I4/mcm$ would lead to a better result with lower weighted agreement factor.

In $BaTbO_3$ the octahedra are tilted 7.07° around the pseudo-cubic $[001]_p$ axis (Fig. 3), resulting in three different Ba–O distances ranging from 2.8489 to 3.2225 Å (Table 2). The Tb–O distances (2.1500 Å in average) are in good agreement with the ionic radii sum (12). The similar tilting pattern is also found for $SrTiO_3$ ($T < 110$ K) (13), $SrZrO_3$ ($T > 1103$ K) (14, 15), $BaBi_{0.5}In_{0.5}O_3$ (16), and some superconducting phases in the $BaPb_{1-x}Bi_xO_3$ (17, 18) and $BaPb_{1-x}Bi_{x/2}Sb_{x/2}O_3$ systems (19).

The present results support the conclusions, recently made by Woodward (20), that the energy stabilization attributable to the Coulomb term in $R\bar{3}c$ with respect to the other tilt systems decreases with decreasing the charge of

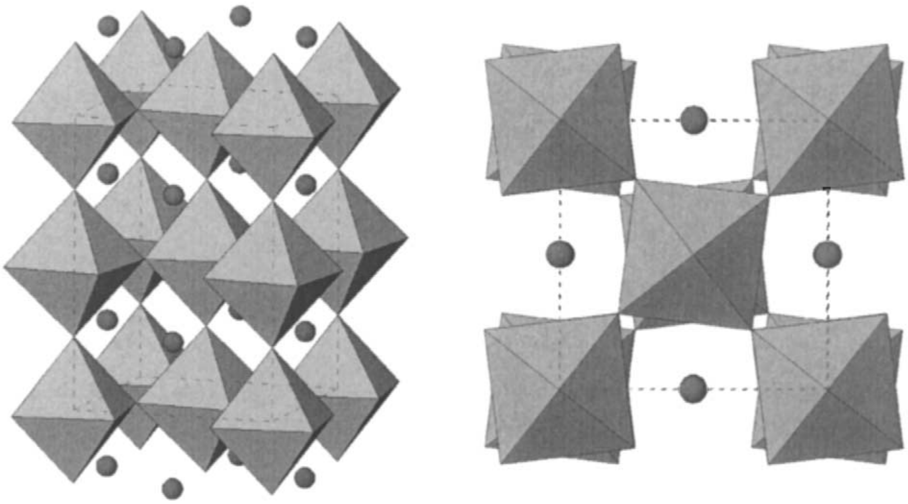

FIG. 3. (a) Schematic representation of the crystal structure of $BaTbO_3$ showing the TbO_6 octahedra and the Ba atoms. (b) A projected view of $BaTbO_3$ along the c-axis. The antiphase (-) tilting of the adjacent TbO_6 octahedral layers can clearly be seen.

A cation in the ABO_3 perovskites. This might explain why the rhombohedral distortion is commonly observed in the $A^{3+}B^{3+}O_3$-type perovskites but rarely observed in the $A^{2+}B^{4+}O_3$-type. In his list of rhombohedrally-distorted perovskites (20), $BaTbO_3$ was once the only example of the $A^{2+}B^{4+}O_3$-type. On the other hand, we noted that the phase sequence $Pnma \rightarrow Imma \rightarrow R\bar{3}c \rightarrow Pm\bar{3}m$ has been found for $BaCeO_3$ (21). The question that whether the $R\bar{3}c$ structure might also occur at high temperature in other related perovskites (e.g. $BaPbO_3$ and $BaTbO_3$) necessitates the further investigations.

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