Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

The tetragonal phase of $Na_{0.5}Bi_{0.5}TiO_3$ – a new variant of the perovskite structure

G. O. Jones* and P. A. Thomas

Department of Physics, University of Warwick, Coventry CV4 7AL, England

Correspondence e-mail: phrxg@csv.warwick.ac.uk

Received 4 November 1999
Accepted 18 January 2000

The structure of the tetragonal phase of the *A*-site-substituted perovskite sodium bismuth titanate, $Na_{0.5}Bi_{0.5}TiO_3$, has been determined by neutron powder diffraction at 698 K. The structure was refined in space group *P*4*bm* with a (= b) = 5.5191 (1), c = 3.9085 (1) Å, V = 119.055 (5) Å^3, Z = 2 and D_x = 5.91 Mg m^{-3}. The structure exhibits an unusual combination of in-phase ($a^0a^0c^+$) tilts and antiparallel cation displacements along the polar *c* axis, which results in a new variant of the perovskite structure.

1. Introduction

Sodium bismuth titanate ($Na_{0.5}Bi_{0.5}TiO_3$), NBT, is one of only a handful of perovskite (generic formula ABO_3) compounds, as opposed to solid solutions, which are substituted on the *A* site. The small number of examples includes, in addition to NBT, its analogue $Ag_{0.5}Bi_{0.5}TiO_3$ (Park *et al.*, 1999), $K_{0.5}Bi_{0.5}TiO_3$ (Smolenskii *et al.*, 1960), $Ag_{0.5}Nd_{0.5}TiO_3$ (Park *et al.*, 1998) and the rare-earth manganites typified by $La_{0.5}Sr_{0.5}MnO_3$ (Woodward *et al.*, 1998).

Since the early discovery of NBT (Smolenskii *et al.*, 1960), many of its characteristics, particularly optical and dielectric properties and structural phase transitions, have been studied (Suchanicz & Ptak, 1990; Tu *et al.*, 1994; Vakhruskev *et al.*, 1989). The findings of these investigations are partly in disagreement, and there remains considerable controversy concerning the number of different phases existing, their electric order and the temperature range over which they exist. The fundamental sequence of phase transitions from the high-temperature prototypic cubic structure to a tetragonal phase at a temperature within the range 783–813 K, and then a rhombohedral phase below a temperature of approximately 533 K was established by Suchanicz & Kwapulinski (1995). However, the phase transition temperatures, the development of regions of co-existence of rhombohedral–tetragonal and tetragonal–cubic phases and the symmetry and structures of all the phases have not been conclusively established.

In this paper, we report here for the first time the structure of the tetragonal phase of NBT. This work forms part of a comprehensive neutron powder diffraction study of NBT in the temperature range from 5–873 K. The results of the extended study will be reported in detail elsewhere (Jones & Thomas, 2000). In summary the structure in the temperature interval 5–528 K is purely rhombohedral and described by the polar space group *R*3*c*, with $a^-a^-a^-$ (Glazer, 1975) anti-phase tilts of the oxygen octahedra about the pseudo-cubic axes and parallel cation displacements (Jones & Thomas, 2000). The ideal cubic perovskite structure, space group $Pm\bar{3}m$, was

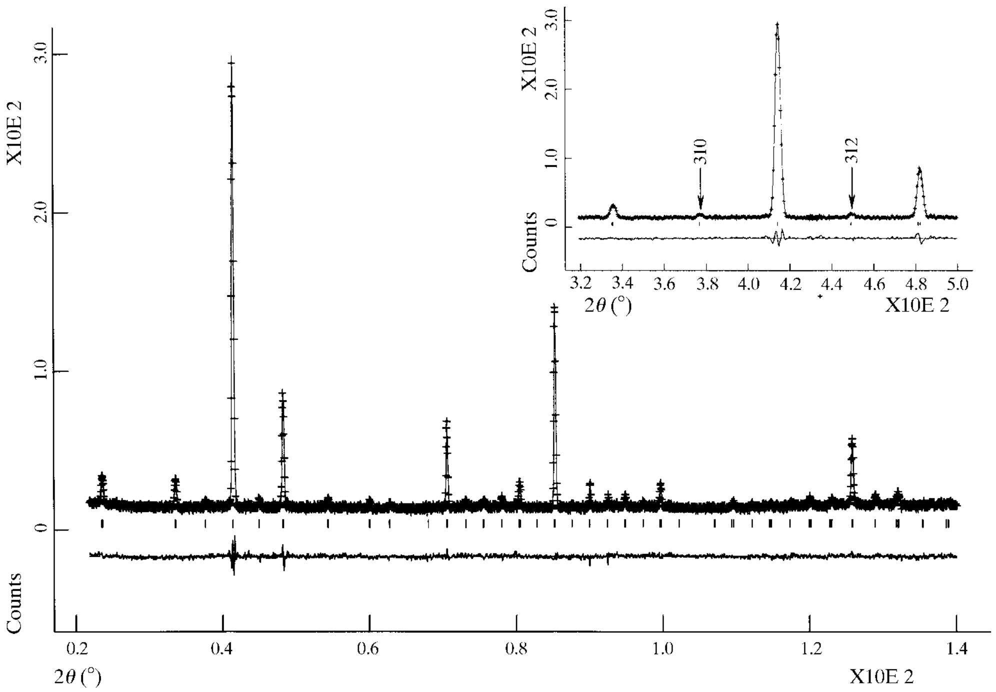

Figure 1
The observed, calculated and difference curves from the 698 K Rietveld refinement of $Na_{0.5}Bi_{0.5}TiO_3$. The marks indicate the positions of the reflections. The low-angle data ($32 < 2\theta < 50^\circ$), showing the first two superstructure peaks, are magnified in the insert.

found for the high-temperature phase (above 813 K). Co-existence of rhombohedral and tetragonal phases was evident in the temperature range 573–593 K and a purely tetragonal phase was seen at 673 K and above.

This paper concentrates on the purely tetragonal phase, which has been solved in the non-centrosymmetric, polar and potentially ferroelectric space group *P*4*bm*. The structure possesses an unusual combination of in-phase oxygen-octahedral tilts (Glazer notation $a^0a^0c^+$) and anti-parallel cation displacements along the polar axis. To our knowledge, this structure-type is unprecedented amongst the perovskites; hence, we report this finding separately here.

2. Experimental procedure

2.1. Sample preparation

NBT crystals were grown *via* spontaneous crystallization from the flux in closed platinum crucibles in air. The starting materials consisted of reagent-grade powders (99.9% purity) of Na_2CO_3, Bi_2O_3 and TiO_2. Stoichiometric amounts were weighed and thoroughly mixed. The ground powders were then calcined in closed platinum crucibles for 12 h at 1073 K, re-ground and calcined again under identical conditions. The pale yellow crystals were in the form of parallelepipeds of size ~1 mm^3. Phase characterization and composition were confirmed using X-ray powder diffraction with a Bruker D5005 diffractometer and chemical analysis. Powdered samples for neutron diffraction were obtained from ground crystals.

2.2. Neutron investigation

Powder neutron diffraction experiments were undertaken to obtain accurate information about the oxygen fractional coordinates in the presence of bismuth and to avoid the problems of twinning in single-crystal studies. Neutron powder data for the tetragonal phase were collected at 698 K on diffractometer D2B at the Institut Max von Laue–Paul Langevin (ILL). Table 1[1] lists the experimental details, data collection and refinement.

2.3. Refinements

Refinements by the Rietveld profile-fitting method with *GSAS* (Larson & Von Dreele, 1995) were carried out. Compared with the pseudo-cubic powder pattern referred to on the $2a \times 2b \times 2c$ ($8 \times 8 \times 8$ Å^3) unit cell, superstructure reflections of the type *h* odd, *k* odd, *l* even were observed. These are consistent with the tilt system $a^0a^0c^+$ (Glazer, 1975), and the tetragonal unit cell $2a^{1/2} \times 2b^{1/2} \times c$. Following the reported structure of $NaNbO_3$ (Glazer & Megaw, 1972), the space group *P*4/*mbm* was assigned and the structure was refined with the starting positions given in Table 2. Initially, Na and Bi, each with site occupation factor 0.5, were constrained to be at the same coordinates. The background was based on a linear function and peak shapes (based on earlier refinements of the room-temperature structure) were described by pseudo-Voigt profiles. Despite an initially encouraging degree of agreement between the calculated and observed data with $\chi^2 = 0.3062$, $R_p = 0.0914$ and $wR_p = 0.1361$, refinement in this space group was impossible as none of the free structural parameters could be refined. Relaxing the mirror plane restriction by choosing polar space group *P*4*bm* solved this difficulty. The refinement was stable and converged quickly, giving the profile parameters $\chi^2 = 0.069$, $R_p = 0.0501$, $wR_p = 0.0647$, $a (= b) = 5.5191\ (1)$ Å and $c = 3.9085\ (1)$ Å [$2 \times c^{1/2}/a = 1.0015\ (1)$].

As a check on the stoichiometry, the occupancies of Na^+ and Bi^{3+} refined to values of 0.49 (1) and 0.51 (1), showing that any deviation from the ideal composition was small. The occupancies were subsequently fixed for the remaining refinements. The Na and Bi positions were then allowed to refine separately with the result that Bi became displaced by 0.02 Å along the polar axis (+*c*) with respect to Na. Introducing this

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM0024). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

Crystal data	
Chemical formula	$Na_{0.5}Bi_{0.5}TiO_3$
Chemical formula weight	211.88
Cell setting	Tetragonal
Space group	*P*4*bm*
a (Å)	5.5191 (1)
c (Å)	3.9085 (1)
V (Å^3)	119.055 (5)
Z	2
D_x (Mg m^{-3})	5.91
Radiation type	Neutron
Wavelength (Å)	1.595
Temperature (K)	698
Specimen shape	Random powder
Specimen cooling rate (K min^{-1})	0.6
Specimen preparation	Crystal growth from the flux; powder prepared from ground crystals
Specimen pressure (kPa)	Ambient
Specimen preparation temperature (K)	1573
Colour	Straw-coloured
Data collection	
Diffractometer	D2B (high resolution)
Data collection method	Static sample, 2θ scan
Detectors	63 ^{3}He counting tubes
Instrument location	Institut Laue–Langevin, Grenoble, France
Specimen mounting	Vanadium can
Specimen environment	Furnace (200–1000 K)
Temperature (K)	698
Scan time	1 h per pattern; four patterns taken and averaged
Absorption correction	None
Refinement	
Starting model	$NaNbO_3$, space group *P*4/*mbm* followed by relaxation of the centre of symmetry to give *P*4*bm*
Initial peak-shape parameters	Parameters for pseudo-Voigt peak-shape† from refinement of rhombohedral phase of NBT
Background fitting and refinement	By linear interpolation: eight coefficients refined
Refined overall parameters:	
Scale	1588 (7)
2θ zero error	−1.3 (1)
Refined peak-shape parameters:	
u,v,w,P	96 (6), −244 (9), 233 (5)
L_X, L_Y	0.13 (1), 2.4 (1)
A_s	−0.03 (1)
Treatment of floating origin	Ti z-coordinate fixed at 0
Refinement strategy	Alternating cycles of profile and structural parameters; displacement parameters refined individually at first to avoid correlations – ultimately all refined together
Goodness-of-fit indicator for Bragg intensities, χ^2	0.069
R_p	0.050
wR_p	0.065
$2\theta_{\min}$ (°)	21.815
$2\theta_{\max}$ (°)	140.015
Increment in 2θ (°)	0.05
Wavelength of incident radiation (Å)	1.595
Excluded region(s)	None
No. of parameters used	39
Preferred orientation correction	None
Source of atomic scattering factors	*GSAS* (Larson & Von Dreele, 1995)
Computer programs	
Structure refinement	*GSAS* (Larson & Von Dreele, 1995)

† The pseudo-Voigt function as defined in the *GSAS* manual is $F(\Delta 2\theta) = \eta L(\Delta 2\theta', \Gamma) + (1-\eta)G(\Delta 2\theta', \Gamma)$, where η is the mixing coeffficient and Γ the full-width at half maximum. The 2θ difference is given by $\Delta 2\theta' = \Delta 2\theta + f_i A_s/\tan 2\theta + S_s \cos\theta + T_s \sin 2\theta$, where A_s is the asymmetry correction, S_s and T_s are sample shift and transparency corrections (not refined for the is geometry – set to zero. The variance of the peak varies as $\sigma^2 = U\tan 2\theta + V\tan\theta + W + P/\cos^2\theta$.

freedom had a negligible effect on the profile parameters and no effect on the anisotropic displacement factors.

It should be noted that the tetragonal phase of NBT was previously reported in space group *P*4*mm* (Zvirgzds *et al.*, 1982). Refinement of the present data for NBT in *P*4*mm* (a non-centrosymmetric space group that allows cation displacements) was tried with similar cation displacements to the *P*4*bm* model resulting. However, since the superstructure reflections arising from the octahedral tilts are absent in *P*4*mm*, this space group can be rejected on these grounds alone. Nevertheless, the observation that the structure can be refined in *P*4*mm*, whereas it cannot be refined at all in *P*4/*mbm* (a centrosymmetric space group that allows superstructure reflections but does not allow cation displacements), reinforces the conclusion that the choice of polar space group for this phase is correct. The observed, calculated and difference profiles from the final Rietveld refinement in *P*4*bm* are shown in Fig. 1.

3. Discussion

The tetragonal structure of NBT is distorted from cubic by in-phase rotations of the TiO_6 octahedra about the c axis, combined with a 0.09 (1) Å displacement of the anti-parallel cations along the polar c axis. A view of the structure along [001] is shown in Fig. 2. This is an unprecedented combination as the $a^0a^0c^+$ tilts produce an environment for the A cation, which is identical when viewed (from the cation), along $+\mathbf{c}$ and $-\mathbf{c}$. Therefore, from the geometry of the framework alone, there is no incentive for the A cation to move off-centre. Since Bi^{3+} and Na^+ are relatively small cations in the A site, both having ionic radii of 1.32 Å (Shannon, 1976), the presence of octahedral tilts is expected. For example, the $a^0a^0c^+$ tilt system occurs in $NaNbO_3$ (Glazer & Megaw, 1972).

Although it has been widely accepted that the tetragonal phase of NBT is nonpolar from pyroelectric studies (Sakata & Masuda, 1974), Zvirgzds *et al.* (1982) have observed a second maximum in the ε_r *versus* T curve at around 723 K, suggesting the phase may in fact be polar. Since A-cation displacements along [001] are not driven by the octahedral tilts, we contend that they result from the need to accommodate the stereochemically active lone pair on Bi^{3+}.

Table 2
Fractional atomic coordinates and equivalent anisotropic displacement parameters (Å^2).

	Starting position	x	y	z	Occupancy	U^{11}	U^{12}	U^{13}	U^{22}	U^{33}	U^{23}
Na1	0,1/2,1/2	0.0	1/2	0.523 (4)	0.5	0.048 (5)	−0.003 (2)	0.0	0.048 (5)	0.058 (5)	0.0
Bi2	0,1/2,1/2	0.0	1/2	0.523 (4)	0.5	0.076 (4)	−0.003 (2)	0.0	0.076 (4)	0.064 (8)	0.0
Ti3	0,0,0	0.0	0.0	0.0	1.0	0.021 (2)	0.0	0.0	0.021 (2)	0.006 (4)	0.0
O4	0,0,1/2	0.0	0.0	0.515 (4)	1.0	0.068 (2)	0.0	0.0	0.068 (2)	0.008 (4)	0.0
O5	0.26,0.24,0	0.270 (3)	0.230 (3)	0.026 (4)	1.0	0.026 (1)	−0.012 (2)	0.009 (4)	0.026 (1)	0.061 (2)	−0.009 (4)

The electronic configuration of Bi^{3+} is the same as that of Pb^{2+} (both having a completed outer 6*s* shell), which is likewise a lone-pair cation. Thomann (1987) noted the tendency of Bi^{3+} to behave similarly to Pb^{2+} in perovskites and identified Bi^{3+} as a cation likely to promote ferroelectric structures. The tetragonal phase of $PbTiO_3$ (space group *P*4*mm*) has Pb^{2+} cations displaced along the *c* axis, although the framework is not tilted as expected for the larger Pb^{2+} ion. Within the tilted framework, even though there is no geometric impetus for the cations to move off-centre, the inherent properties of Bi^{3+} promote movement along the polar axis, thus generating this unusual structure.

Bond-valence calculations using the program *VaList* (Willis & Brown, 1999), with the cations at their refined positions, give values for Na^+ and Ti^{4+} only 8% and 2% different, respectively, from their ideal values. However, the bond-valence sum calculated for Bi^{3+} shows a 32% deficiency from its ideal value of 3.0. In the rhombohedral (*R*3*c*) phase of $BiFeO_3$, Bi^{3+} has a valence deficiency of 19% despite a displacement as large as 0.55 Å along the polar axis to distort its coordination.. Displacement of Bi^{3+} and valence deficiency were also seen in the orthorhombic phase of $Ag_{0.5}Bi_{0.5}TiO_3$ (Park *et al.*, 1999) and in the *R*3*c* phase of NBT (Jones & Thomas, 1999). Thus, even though Bi^{3+} moves off-centre in order to satisfy its own stereo-chemical preferences, on the *A* site of perovskite structures in rhombohedral, tetragonal and orthorhombic polar phases, it seems that it is unable to achieve a perfect match to its ideal valency.

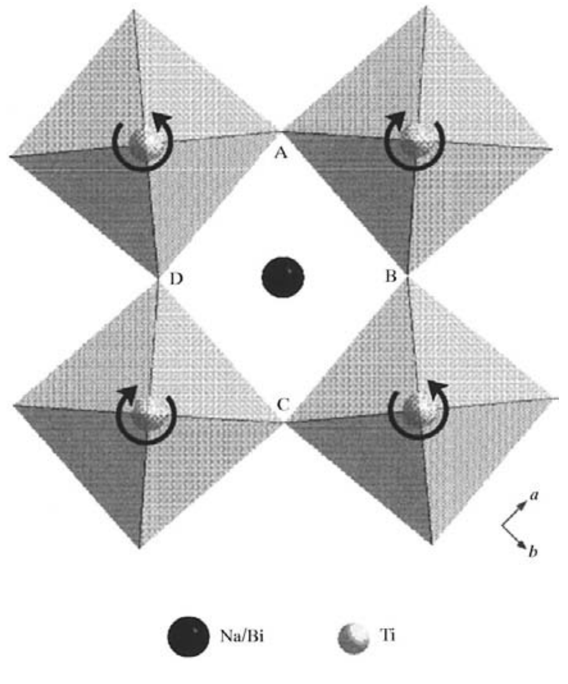

Figure 2
A view of the structure along [001], showing the octahedral tilting about the polar *c* axis. The Na/Bi cation is displaced along the +*c* axis (out of the plane, defined by the O atoms *A, B, C* and *D*).

The anisotropic displacement factors are given in Table 2. The generally large values reflect the temperature at which these data were collected. The displacement parameters of Na^+ and Bi^{3+} were allowed to refine separately throughout. Considerably larger parameters were found for Bi^{3+}. For both Na and O5, there was pronounced anisotropy with a larger apparent amplitude of motion along [001], the polar axis.

The bond distances and angles determined in this study were all reasonable, with the average Ti—O bond distance within the octahedra being 1.9852 (5), in agreement with previous studies.

4. Concluding remarks

The tetragonal phase of NBT is a perovskite structure in space group *P*4*bm*. The structure combines in-phase ($a^0a^0c^+$) tilts of oxygen octahedra with anti-parallel cation displacements along the polar axis. To our knowledge, this is a completely new variant in the field of perovskite structures.

The authors wish to thank A. W. Hewat for his help at the Institut Max von Laue–Paul Langevin with the neutron experiments. This research has been funded by an EPSRC Studentship award.

References

Glazer, A. M. (1975). *Acta Cryst.* A**31**, 756–762.
Glazer, A. M. & Megaw, H. D. (1972). *Philos. Mag.* **25**, 1119–1135.
Jones, G. O. & Thomas, P. A. (1999). XVIIIth IUCr Congress, Glasgow, Scotland. Abstract P11.10.027.
Jones, G. O. & Thomas, P. A. (2000). *Acta Cryst.* In preparation.
Larson, A. C. & Von Dreele, R. B. (1995). *GSAS*. General Structure Analysis System. Los Alamos National Laboratory, NM, USA.
Park, J. H., Woodward, P. M. & Parize, J. B. (1998). *Chem. Mater.* **10**, 3092–3100.
Park, J. H., Woodward, P. M., Parize, J. B., Reeder, R. J., Lubomirsky, I. & Stafsudd, O. (1999). *Chem. Mater.* **11**, 177–183.
Sakata, K. & Masuda, Y. (1974). *Ferroelectrics*, **7**, 347–349.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.
Smolenskii, G. A., Isupov, V. A., Agranovskaya, A. I. & Krainik, N. N. (1960). *Sov. Phys. Solid State*, **2**, 2982–2985.
Suchanicz, J. & Kwapulinski, J. (1995). *Ferroelectrics*, **165**, 249–253.
Suchanicz, J. & Ptak, W. S. (1990). *Ferroelectr. Lett.* **12**, 71–78.
Thomann, H. (1987). *Ferroelectrics*, **73**, 183–199.
Tu, C., Siny, I. & Schmidt, V. (1994). *Phys. Rev. B*, **49**, 11550–11559.
Vakhruskev, S. B., Kvyatkovskii, B. E., Malysheva, R. S., Okuneva, N. M. & Syrnikov, P. P. (1989). *Kristallografiya*, **34**, 154–158.
Willis, A. S. & Brown, I. D. (1999). *VaList*. CEA, France.
Woodward, P. M., Vogt, T., Cox, D. E., Arulraj, A., Rao, C. N. R., Karen, P. & Cheetham, A. K. (1998). *Chem Mater*. **10**, 3652–3665.
Zvirgzds, J. A., Kapostins, P. P., Zvirgzde, J. V. & Kruzina, T. V. (1982). *Ferroelectrics*, **40**, 75–77.