Crystal structure of the 'mixed-layer' Aurivillius phase $Bi_5TiNbWO_{15}$

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Abstract

The crystal structure of the Aurivillius phase $Bi_5TiNbWO_{15}$ has been analyzed in detail using powder X-ray and neutron diffraction. The structure can be described as a regular intergrowth of alternating single and double perovskite-like layers sandwiched between fluorite-like bismuth oxide layers, such that the layer sequence is … $[WO_4]$–$[Bi_2O_2]$–$[BiTiNbO_7]$–$[Bi_2O_2]$ …. There is complete ordering of tungsten within the B sites of the single perovskite layer, so that the structure can be described as a direct intergrowth of the 'component' Aurivillius phases Bi_2WO_6 and Bi_3TiNbO_9. At 25 °C the structure adopts the polar orthorhombic space group $I2cm$, $a = 5.4231(2)$ Å, $b = 5.4027(2)$ Å, $c = 41.744(1)$ Å.
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1. Introduction

The Aurivillius family of layered bismuth oxides is currently one of the most important classes of ferroelectric material, being studied in particular for their potential in information storage systems [1,2]. Structurally they may be described as regular intergrowths of alternating perovskite-like and fluorite-like layers, with general composition $[A_{n-1}B_nO_{3n+1}]$ and $[Bi_2O_2]$, respectively [3,4]. Archetypal members of this series are therefore Bi_2WO_6 ($n = 1$), $SrBi_2Ta_2O_9$ ($n = 2$) and $Bi_4Ti_3O_{12}$ ($n = 3$). The crystallographic characteristics of various members of this series with layer thicknesses (n) up to four perovskite layers are now fairly well established [5–10]. However, there remains an important subset of this family whose structural nature is still not established in detail. These are the 'mixed layer' phases, which correspond to a regular intergrowth having alternating even and odd perovskite layer thicknesses, n and $n+1$.

Evidence of irregular intergrowths consisting of blocks of differing layer thickness has been known for a long time, through the high-resolution TEM work of Rao and co-workers [11]. Isolation of macroscopically pure phases such as $Bi_5TiNbWO_{15}$ ($n = 1, 2$), $Bi_7Ti_4NbO_{21}$ ($n = 2, 3$) and $SrBi_8Ti_7O_{27}$ ($n = 3, 4$) had also been suggested as long ago as 1977 by Kikuchi et al. [12] based on indexing of powder X-ray diffraction data. However, no detailed structural refinements of any of these mixed intergrowths have been reported until the work of Mercurio et al. on $Bi_7Ti_4NbO_{21}$ [13]. These authors used a combined X-ray and neutron single crystal diffraction study to provide the most reliable structure to date of a mixed layer Aurivillius phase. In the case of the simpler ($n = 1, 2$) archetype $Bi_5TiNbWO_{15}$, previous reports have suggested conflicting unit cell data (for example, Kikuchi [12] originally suggested orthorhombic symmetry, with $a \sim b \sim 5.4$ Å, $c \sim 20.9$ Å, whereas Lisinska-Czekaj et al. [14] have recently proposed tetragonal symmetry, $a \sim 3.84$ Å, $c \sim 20.9$ Å). $Bi_5TiNbWO_{15}$ is known to be ferroelectric at ambient temperature (for example, a dielectric maximum, T_m, of 475 °C is given in Ref. [14]), which might suggest a

maximum of orthorhombic symmetry, in the light of the known behavior of other Aurivillius phases. In this paper we present the first detailed structural study of an $(n = 1, 2)$ Aurivillius phase, $Bi_5TiNbWO_{15}$, using a combination of X-ray and neutron powder diffraction and Rietveld refinement.

2. Experimental

Pure polycrystalline $Bi_5TiNbWO_{15}$ was prepared by conventional solid state reaction of stoichiometric quantities of the component binary oxides, which were thoroughly ground and heated in air at 800 °C for 24 h, 900 °C for 24 h and 1000 °C for 72 h, with intermediate regrindings. The product was judged to be phase-pure on the basis of successful indexing of the powder X-ray diffraction data (Stoe STADI/P diffractometer, $CuK\alpha_1$ radiation, operating in transmission mode). Powder neutron diffraction data were collected at 25 °C on the high-flux diffractometer Polaris at the ISIS Facility, UK, with an approximately 10 g sample packed in a thin-walled vanadium can. Data from both the 145° and 90° detector banks were used in the subsequent Rietveld analyses (GSAS [15]).

3. Results and discussion

Careful inspection of the preliminary powder X-ray data clearly revealed that the previously suggested unit cells could not fully account for all the observed peaks. An I-centred orthorhombic cell, with $a \sim b \sim 5.4$ Å, $c \sim 41.7$ Å (i.e. a 'doubled' c-axis) was required. Systematic absences were compatible with $Imcm$ (No. 74) or $I2cm$ (No. 46); since this material is known to be ferro-electric at room temperature, the latter (polar) space group was assumed in subsequent analysis. In fact, two teams had previously predicted this space group for an Aurivillius phase of the $(n = 1, 2)$ type, using quite different approaches [10,16]. The $(n = 2, 3)$ phase $Bi_7Ti_4NbO_{21}$ was also found to adopt this space group (with $c \sim 58$ Å), and a starting model for the present structure could easily be derived from this, by appropriate adjustments. As neutron diffraction is somewhat ambiguous to possible ordering of the B-site cations (neutron scattering lengths, $b(W) = 0.477$, $b(Nb) = 0.7054$, $b(Ti) = -0.3438 \times 10^{-12}$ cm) a preliminary, approximate refinement was carried out using the X-ray data alone. This clearly revealed complete ordering of the B-cations, viz. W in the $n = 1$ block and Ti/Nb disordered over the $n = 2$ block. These occupancies were therefore fixed during subsequent analysis of the neutron data. Rietveld analysis proceeded straightfor-wardly, with the final refinement treating all atoms

Table 1
Final refined atomic parameters for neutron Rietveld refinement of $Bi_5TiNbWO_{15}$, space group $I2cm$, $a = 5.4231(2)$ Å, $b = 5.4027(2)$ Å, $c = 41.744(1)$ Å. $R_{wp} = 0.041$, $\chi^2 = 19.5$, for 7792 data points and 5079 contributing reflections, $0.43 < d < 4.16$ Å

Atom	x	y	z	U_{iso} (Å^2)
Bi1	0.543(1)	0.016(1)	0.0671(1)	1.1(1)
Bi2	0.027(1)	−0.009(1)	0.1286(1)	1.4(1)
Bi3	0.035(2)	0.010(1)	0.25	3.4(1)
W1	0.014(2)	0	0	0.1(1)
Nb/Ti2	0.502(3)	−0.035(2)	0.1983(2)	0.1(1)
O1	0.270(2)	0.231(3)	−0.0059(2)	5.7(2)
O2	−0.057(1)	0.057(1)	0.0440(2)	1.8(1)
O3	0.261(2)	0.241(1)	0.0992(1)	0.32(9)
O4	0.753(2)	0.755(1)	0.0975(1)	0.1(1)
O5	0.480(2)	−0.042(1)	0.1543(1)	1.2(1)
O6	0.180(1)	0.204(1)	0.1979(1)	0.3(1)
O7	0.774(1)	0.787(1)	0.2074(1)	−0.1(1)
O8	0.460(2)	0.060(2)	0.25	1.7(2)

Table 2
Selected bond lengths (Å) and bond valence sums (Σ, valence units) for $Bi_5TiNbWO_{15}$

Bi1–O2	3.397(7)	Bi2–O3	2.229(5)	Bi3–O6	2.537(6) × 2
Bi1–O2	2.385(8)	Bi2–O3	2.383(6)	Bi3–O6	3.270(7) × 2
Bi1–O2	3.275(8)	Bi2–O4	2.347(6)	Bi3–O7	2.569(6) × 2
Bi1–O2	2.568(9)	Bi2–O4	2.223(5)	Bi3–O7	2.736(8) × 2
Bi1–O3	2.360(6)	Bi2–O5	3.171(8)	Bi3–O8	3.12(1)
Bi1–O3	2.228(7)	Bi2–O5	2.672(8)	Bi3–O8	2.34(1)
Bi1–O4	2.219(7)	Bi2–O5	2.662(8)	Bi3–O8	3.13(1)
Bi1–O4	2.492(6)	Bi2–O5	3.177(8)	Bi3–O8	2.33(1)
Σ (Bi1)	3.05	Σ (Bi2)	2.89	Σ (Bi3)	2.76
W1–O1	1.90(1) × 2	Nb2–O5	1.85(1)		
		Nb2–O6	2.17(2)		
W1–O1	1.99(1) × 2	Nb2–O6	1.99(2)		
		Nb2–O7	1.79(2)		
W1–O2	1.895(6) × 2	Nb2–O7	1.93(2)		
		Nb2–O8	2.23(1)		
Σ (W1)	5.84	Σ (Ti/Nb2)	4.64		

isotropically, producing the final atomic parameters given in Table 1. A total of 71 parameters were refined, including 47 structural parameters, together with lattice parameters, scale, background, peak-shape (two para-meters for each histogram, describing the Gaussian and Lorentzian half-widths) and preferred orientation ([001] zone). Selected bond lengths are given in Table 2, and the final Rietveld plot for the $2\theta = 145°$ detector bank is shown in Fig. 1.

The derived structure is shown in Fig. 2, and represents the anticipated regular intergrowth of $n = 1$ and $n = 2$ Aurivillius blocks. Table 1 reveals slightly large displacements parameters for atoms Bi(3) and O(1). These may be rationalized in the former case by assuming a small amount of disorder away from the
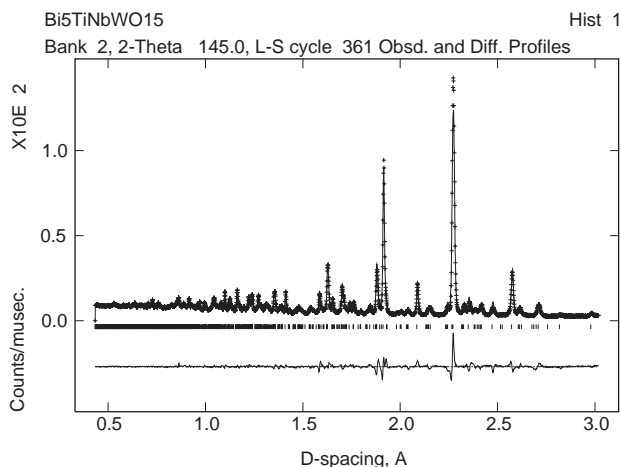
Bi5TiNbWO15　　　　　　　　　　　　　　　　　　　　　　Hist 1
Bank 2, 2-Theta　145.0, L-S cycle　361 Obsd. and Diff. Profiles

Fig. 1. Final Rietveld plot for Polaris refinement (145° bank) of $Bi_5TiNbWO_{15}$.
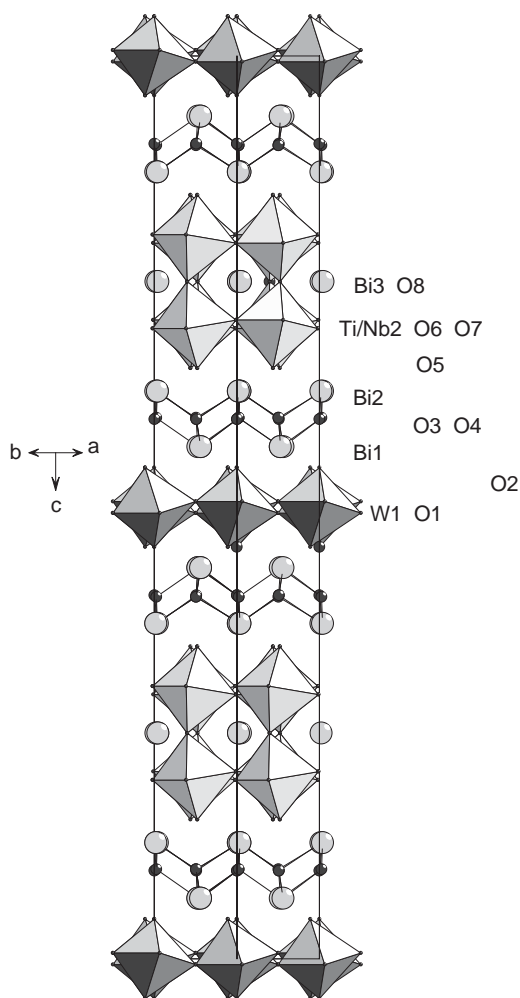
Fig. 2. Crystal structure of $Bi_5TiNbWO_{15}$ viewed along [110].

plane of the ($n = 1$) block, an anisotropic refinement reveals quite large displacement parameters U_{11} and U_{22}, which, again, may suggest some disorder around this site; 'rotational' disorder of octahedral units around the c-axis in layered perovskites is quite common, and reflects a degree of compromise in accommodating intergrown block of differing 'width'. In this case, it is apparent from the relative a/b cell dimensions reported for Bi_2WO_6 (5.458 Å, 5.437 Å [17]), Bi_3TiNbO_9 (5.440 Å, 5.394 Å [6]) and $Bi_5TiNbWO_{15}$ (5.423 Å, 5.403 Å (this work)) that the [WO_4] block is under compressive stress compared to the [$BiTiNbO_7$] block, which naturally leads to such a rotational disorder. The relative mismatch of the two perovskite blocks may also be seen directly in the relative degrees of distortion of the two B-sites in $Bi_5TiNbWO_{15}$ versus the corresponding sites in Bi_2WO_6 and Bi_3TiNbO_9 (Figs. 3 and 4). The WO_6 octahedron in $Bi_5TiNbWO_{15}$ is *less* distorted than that in Bi_2WO_6, whereas the $(Ti,Nb)O_6$ octahedron is *more* distorted than that in Bi_3TiNbO_9. The nature of the distortions within each site does, however, remain the same, as does the nature of the tilt system within the ($n = 2$) block in the present case: this adopts the Glazer $a^-a^-c^+$ system [18] as seen in all ($n = 2$) Aurivillius structures which crystallize in space group $A2_1am$ in the ferroelectric phase.

In both $Bi_5TiNbWO_{15}$ and $Bi_7Ti_4NbO_{21}$ [13] the B-site ordering follows the pattern of the constituent, pure $n = 1$, 2 and 3 phases, i.e. the [WO_4], [$BiTiNbO_7$] and [$Bi_2Ti_3O_{10}$] blocks remain intact. This may be rationalized on electrostatic grounds, as this scheme leads naturally to 'neutral' intergrown Aurivillius blocks [Bi_2WO_6], [Bi_3TiNbO_9] and [$Bi_4Ti_3O_{12}$]. Zhou [19,20] has suggested a theory, based on high resolution TEM studies, that 'charged' blocks of this type would be inherently less stable than neutral blocks, and would lead to 'stepped' defects being formed, in order to self-compensate charge differences. An example of this could occur in the mixed ($n = 1, 2$) phase $Bi_5Nb_3O_{15}$, which must consist of 'charged' $[Bi_2NbO_6]^-$ ($n = 1$) and $[Bi_3Nb_2O_9]^+$ ($n = 2$) blocks. Our own powder diffraction studies support this idea—Rietveld refinements of $Bi_5Nb_3O_{15}$ using the model presented above for $Bi_5TiNbWO_{15}$ lead to comparatively poor fits, suggestive of complex microstructure; moreover, our preliminary TEM studies [21] suggest that the 'stepped' defects are much more prevalent in $Bi_5Nb_3O_{15}$ than in $Bi_5TiNbWO_{15}$.

4. Conclusions

The crystal structure of the ($n = 1, 2$) 'mixed layer' Aurivillius phase $Bi_5TiNbWO_{15}$ has been refined using combined X-ray and neutron powder diffraction data.

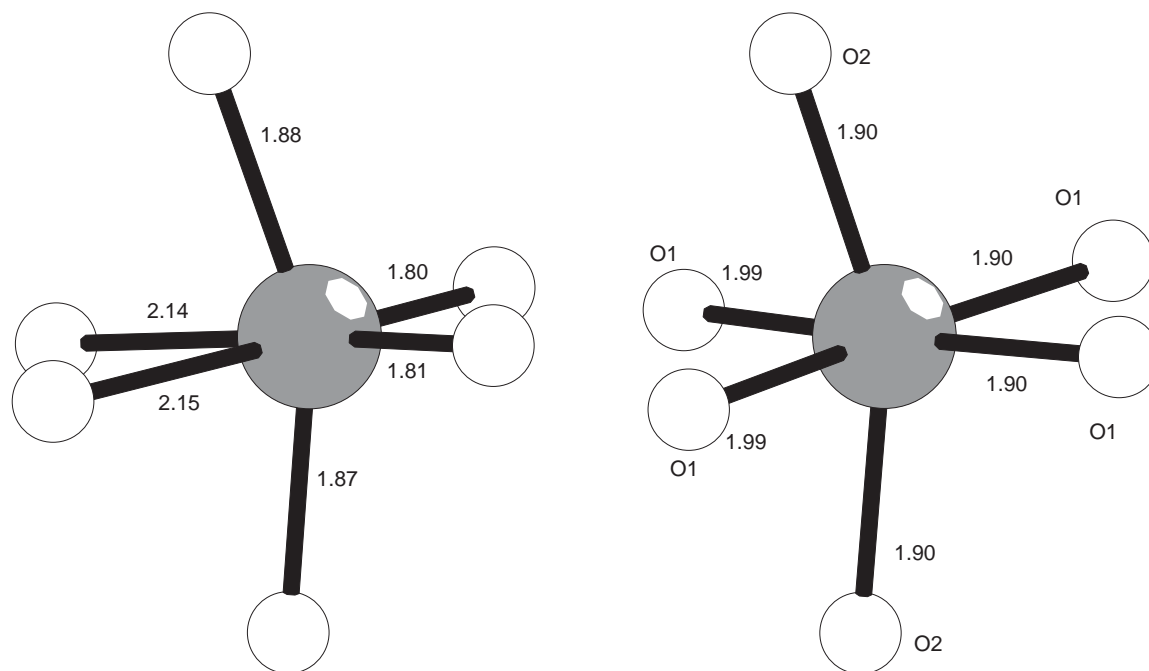mirror plane at $z = 0.25$, the possibility of which is revealed in the somewhat low bond valence sum of 2.76 at this site (see Table 2). For the O(1) atom, in the W–O

Fig. 3. Comparison of local distortion within the WO_6 octahedron in Bi_2WO_6 (left) and $Bi_5TiNbWO_{15}$ (right). Bond lengths given in Å.
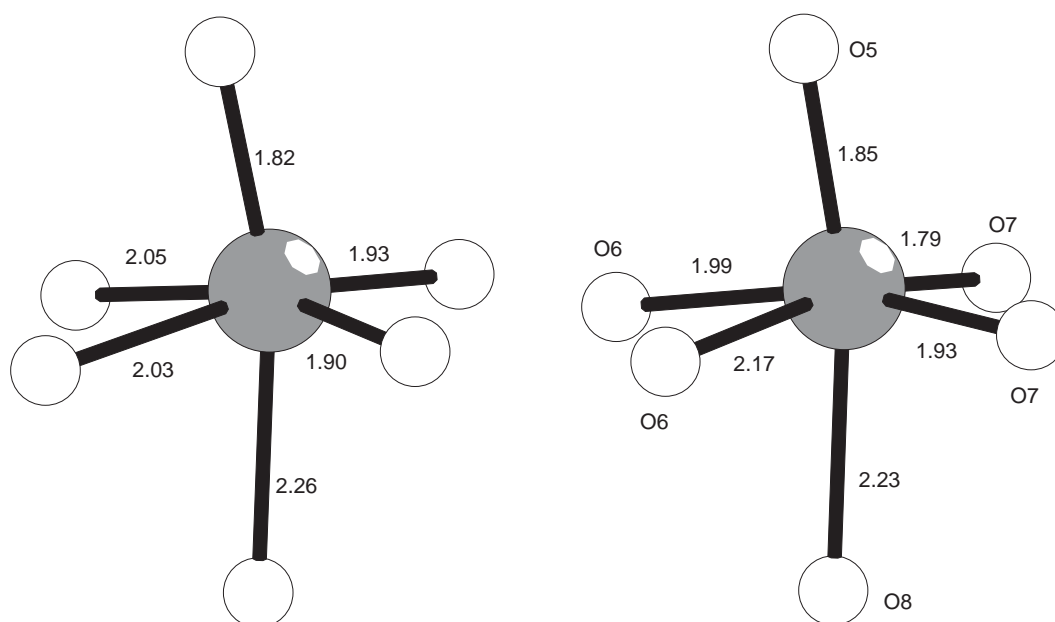

Fig. 4. Comparison of local distortion within the $(Ti/Nb)O_6$ octahedron in Bi_3TiNbO_9 (left) and $Bi_5TiNbWO_{15}$ (right). Bond lengths given in Å.

The structure displays a regular, well-ordered intergrowth of 'neutral' $[Bi_2WO_6]$ and $[Bi_3TiNbO_9]$ blocks, which is in accord with previous studies of the mixed $(n = 2, 3)$ phase $Bi_7Ti_4NbO_{21}$. It is probable that in similar intergrowths where 'charge-neutrality' is not possible within the component Aurivillius blocks, a more complex crystallographic structure and microstructure may occur. Further work on both the structure

and microstructure of these complex intergrowth phases are merited.

Acknowledgements

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