

Rapid communication

$\text{Bi}_{2-x}\text{Ln}_x\text{WO}_6$: a novel layered structure type related to the Aurivillius phases

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Abstract

The crystal structure of $\text{Bi}_{0.7}\text{Yb}_{1.3}\text{WO}_6$ (a representative of the isomorphous series $\text{Bi}_{2-x}\text{Ln}_x\text{WO}_6$; $0.3 < x < 1.3$, for most lanthanides) has been determined. Contrary to previous suggestions, this structure type (space group $A2$; $a = 8.1070(3) \text{ \AA}$, $b = 3.7048(2) \text{ \AA}$, $c = 15.8379(8) \text{ \AA}$, $\beta = 103.548(4)^\circ$) contains layers of stoichiometry WO_4 , containing WO_6 octahedra sharing both edges and corners. These layers alternate with fluorite-like $(\text{Bi}/\text{Yb})_2\text{O}_2$ sheets; this is a novel and unexpected arrangement and contrasts dramatically with the purely corner-sharing octahedral WO_4 -layer in the parent Aurivillius phase Bi_2WO_6 .

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1. Introduction

Bi_2WO_6 is a well-known ferroelectric, with a high T_C of around 950°C [1], and the simplest member of the Aurivillius family of layered perovskites, which are structurally comprised of alternating perovskite-like and fluorite-like blocks [2,3], of general formula $[\text{Bi}_2\text{O}_2][\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$. For Bi_2WO_6 , $n = 1$ and the perovskite block consists of an infinite two-dimensional array of corner-linked WO_6 octahedra. It has previously been established that a certain degree of oxide ion vacancies can be accommodated in the perovskite layers, which often gives rise to high oxide ion conductivity, for example in the well-known BIMEVOX series based on $\text{Bi}_2\text{VO}_{5.5}$ [4]. Other structural variants on this basic structural family include phases containing alternating ‘widths’ of perovskite slab (e.g., the $n = 1/n = 2$ phase $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ [5]) and more complex intergrowth structures formed by replacement of alternate perovskite layers by other anionic blocks, for example halide layers, in $\text{Bi}_4\text{NbO}_8\text{Cl}$ [6]. However, in all of these variants the

essential structural features of ‘fluorite’ and ‘perovskite’ (i.e., corner-linked octahedral) layers remain intact. Previously, Watanabe and co-workers [7–9] have proposed an unusual variant of this family, $\text{Bi}_{2-x}\text{Ln}_x\text{WO}_6$ (approximate limits $0.3 < x < 1.3$ for most lanthanides), which they postulated, based on high-resolution electron microscopy (HREM) and Raman spectra, comprised a layer of WO_4 stoichiometry, analogous to Bi_2WO_6 , but consisting of isolated WO_4 tetrahedral units. Although this structure type seems plausible in essence and, indeed, a closely related structure has been seen in La_2MoO_6 [10], the details were never fully established, and the postulated model contained several unacceptably short bond distances. We have now re-analyzed this structure type using powder X-ray and neutron diffraction, and show that the postulated structure is indeed incorrect in a significant way. The true structure contains the expected fluorite-like $[(\text{Bi}/\text{Ln})_2\text{O}_2]$ layers, but intergrown with WO_4 layers which contain both edge-sharing and corner sharing WO_6 octahedra, a feature which is unprecedented in layered oxides of this family.

Due to the favorable neutron scattering contrast ($b(\text{Bi}) = 8.5$, $b(\text{Yb}) = 12.4 \text{ fm}$) the Yb-containing

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Table 1
Final refined atomic parameters for $\text{Bi}_{0.7}\text{Yb}_{1.3}\text{WO}_6$, space group $A2$

Name	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}} \times 100$	Occ.
Bi1	0.9167(3)	0.000000	0.3289(2)	0.36(3)	0.44(2)
Yb1	0.9167(3)	0.000000	0.3289(2)	0.36(3)	0.56(2)
Bi2	0.4028(4)	−0.0106(17)	0.3201(2)	0.36(3)	0.26(2)
Yb2	0.4028(4)	−0.0106(17)	0.3201(2)	0.36(3)	0.74(2)
W	0.2972(6)	0.498(3)	0.4991(4)	0.51(9)	1
O1	0.1228(7)	−0.020(3)	0.2514(4)	0.48(10)	1
O2	0.3646(6)	0.479(2)	0.2341(4)	0.22(7)	1
O3a	0.3276(10)	0.026(4)	0.5354(6)	0.30(11)	0.56(1)
O4	0.5265(7)	0.422(2)	0.5804(4)	0.53(10)	1
O5	0.1859(8)	0.376(2)	0.5759(5)	0.69(11)	1
O6	0.1440(10)	0.629(2)	0.4079(7)	2.09(15)	1
O3b	0.2934(12)	0.002(6)	0.4504(7)	0.30(11)	0.44(1)

$$a = 8.1070(3) \text{ \AA}, b = 3.7048(2) \text{ \AA}, c = 15.8379(8) \text{ \AA}, \beta = 103.548(4)^\circ.$$

representative $\text{Bi}_{0.7}\text{Yb}_{1.3}\text{WO}_6$ was studied. All the analogues previously reported by Watanabe [8] are suggested to adopt the same structure type on the basis of powder X-ray diffraction. $\text{Bi}_{0.7}\text{Yb}_{1.3}\text{WO}_6$ was prepared by heating a thoroughly ground stoichiometric mixture of Bi_2O_3 , Yb_2O_3 and WO_3 at 1100°C for 100 h, with one intermediate regrinding. Neutron diffraction data were collected from ~ 10 g of polycrystalline sample at room temperature on the Polaris medium resolution time-of-flight powder diffractometer at ISIS, Rutherford Appleton Laboratory, UK. It was found that the powder X-ray diffraction pattern could be indexed using a simpler monoclinic unit cell than that suggested previously,¹ and this cell was then used to analyze the neutron data. Systematic absences for both data sets were consistent with space groups $A2/m$ (no. 12), Am (no. 8) and $A2$ (no. 5), with the former, centrosymmetric space group being adopted initially. The model was derived from that of Watanabe [9], which included the isolated WO_4 tetrahedral units. A poor fit was obtained to the neutron data. Recourse was then made to a partial model, viz. the fluorite-like layers were assumed intact, and the W position was assumed correct, based on the fit to the X-ray data. Completion of the structure was then achieved, making no assumptions about the remaining oxygen positions, using difference Fourier methods and Rietveld refinement with the neutron data. The resultant refinement was still unsatisfactory, and the final model was derived by lowering the symmetry to $A2$, with a significant improvement in the Rietveld fit.² This model (Table 1)

¹Watanabe suggested $a_{\text{W}} \sim 15.94 \text{ \AA}$, $b_{\text{W}} \sim 7.46 \text{ \AA}$, $c_{\text{W}} \sim 8.09 \text{ \AA}$, $\beta_{\text{W}} \sim 102.5^\circ$, space group $P2_1/a$ for BiYbWO_6 . Our cell represents $a \sim c_{\text{W}}$, $b \sim b_{\text{W}}/2$, $c \sim a_{\text{W}}$, $\beta \sim \beta_{\text{W}}$.

²Neutron Rietveld refinement used the GSAS suite. $A2/m$ model: final $R_{\text{wp}} = 0.062$, $R(F^2) = 0.093$ for 44 variables. $A2$ model: final $R_{\text{wp}} = 0.042$, $R(F^2) = 0.059$ for 57 variables. Both refinements: total d -spacing range $0.45\text{--}3.1 \text{ \AA}$. In the final model the O(3) site was disordered over two positions.

reveals the novel features of the structure, together with the similarities to the parent Bi_2WO_6 phase (Fig. 1). The effective ‘doubling’ of the a -axis (relative to the parent ‘perovskite-like’ cell) is caused by condensation of the WO_6 octahedra into dimeric chains (W–W distances: *intra*-dimer— 3.29 \AA , *inter*-dimer— 4.82 \AA) which run parallel to the b -axis (Fig. 2). These chains are then stacked alternately with the anticipated fluorite-like layers along the c -direction. It is noteworthy that the necessary presence of edge-sharing octahedra, rather than isolated tetrahedra (as suggested by Watanabe) can even be clearly inferred purely from the X-ray data, due to the short, well-determined W–W distances (in La_2MoO_6 the Mo–Mo distance between adjacent isolated tetrahedra is 4.10 \AA).

Whilst the edge-sharing of octahedral units is a well-established method of accommodating reduced oxygen stoichiometry in early transition metal oxides (e.g., crystallographic shear structures) we are unaware of any similar features in a layered perovskite-related structure. The driving force for the abrupt change of coordination from purely corner sharing to mixed corner- and edge-sharing in $\text{Bi}_{2-x}\text{Ln}_x\text{WO}_6$ (at $x \sim 0.3$) is unclear, but is presumably related to the tendency towards ordering of the Bi/Ln cations onto different crystallographic sites. It is known that higher n members of the Aurivillius family such as $\text{Bi}_{4-x}\text{Ln}_x\text{Ti}_3\text{O}_{12}$ can tolerate Bi/Ln cation disorder in the $[\text{Bi}_2\text{O}_2]$ layers up to a similar limit [11,12]. We have now discovered a novel means of accommodating much higher levels of Ln in the $[\text{Bi}_2\text{O}_2]$ layer in the $n = 1$ case. Indeed some degree of ordering is observed in the title compound, with Yb preferring the Bi(2) site adjacent to the ‘edge-shared’ O(4) sites in Fig. 1 (site occupancies, Bi(1): Bi/Yb = $0.44(3)/0.56(3)$; Bi(2): Bi/Yb = $0.26(3)/0.74(3)$). The combination of this cation-ordering, together with the distortion imposed by edge-sharing, may be responsible for the apparent lowering of symmetry from the ideal $A2/m$ to the polar $A2$ (SHG measurements reveal a modest signal of around 0.2 times that of quartz). These effects also give rise to a considerable distortion of the WO_6 octahedron. W–O bond lengths range from 1.73 to 2.13 \AA , which may be compared with $1.80\text{--}2.15 \text{ \AA}$ in Bi_2WO_6 itself [1]; although the nature of the distortion (i.e., W displaced towards one octahedral edge) is the same in these two structures, in the present case the magnitude of the distortion is increased due to the short, repulsive W–W interaction.

In summary, we have shown that the solid solutions $\text{Bi}_{2-x}\text{Ln}_x\text{WO}_6$ (approx. $0.3 < x < 1.3$) represent a novel structure type with the unusual feature of edge-sharing octahedral units, unique in this family. Further work is merited to ascertain whether these phases display ferroelectric properties or whether they may be doped aliovalently in order to produce a novel series of oxide ion conductors, for example.

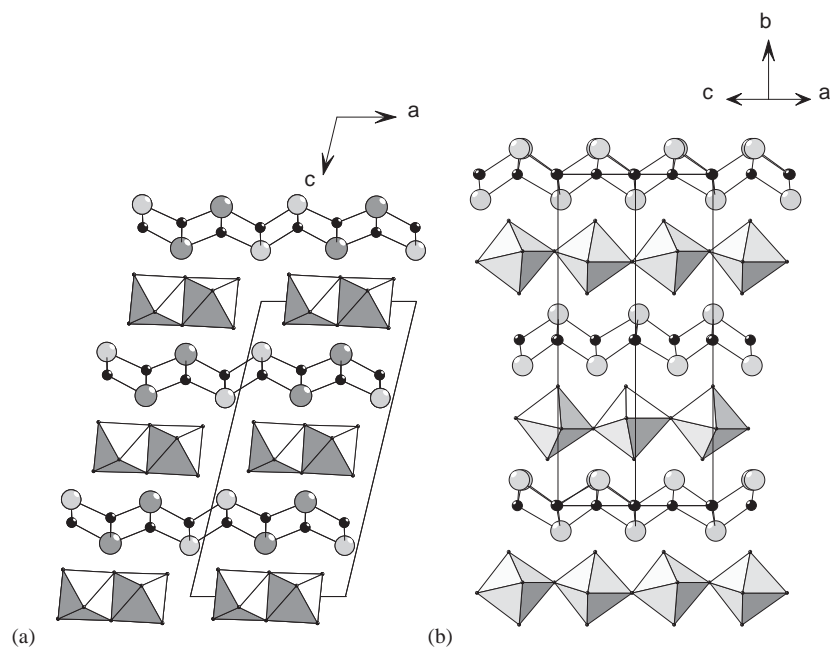


Fig. 1. (a) $\text{Bi}_{0.7}\text{Yb}_{1.3}\text{WO}_6$, showing alternating $[(\text{Bi},\text{Yb})_2\text{O}_2]$ layers and $[\text{WO}_4]$ edge-sharing octahedral layers. Bi1 and Bi2 sites are shown as light and dark gray, respectively (b) Bi_2WO_6 , showing corner-linked $[\text{WO}_4]$ layers.

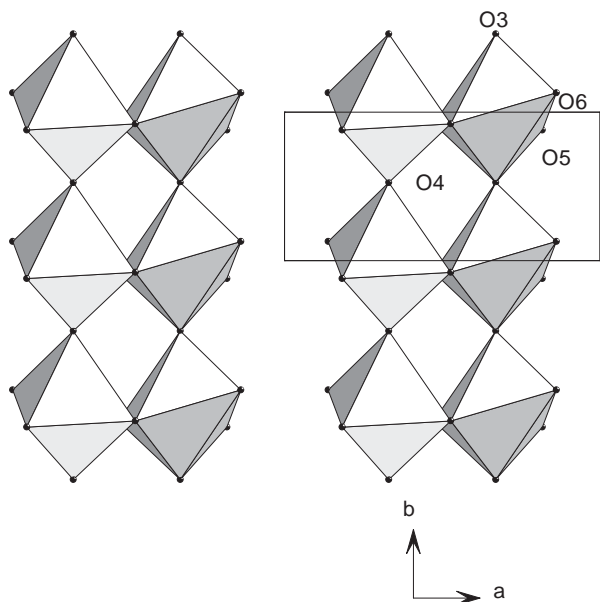


Fig. 2. Plan view of a single $[\text{WO}_4]$ sheet, showing continuous corner-linked chains of edge-shared octahedral dimers.

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