Crystal structure and ionic conductivity of a new bismuth tungstate, $Bi_3W_2O_{10.5}$

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Abstract.   The compound $Bi_3W_2O_{10.5}$ was synthesized by the solid-state technique from Bi_2O_3 and WO_3 in stoichiometric quantities. Single crystals were grown by the melt-cooling technique and the crystal structure was solved in the tetragonal *I4/m* space group with $a = 3.839$ (1) Å, $c = 16.382$ (5) Å, $V = 241.4$ (1) Å^3, $Z = 4$ and was refined to an R index of 0.0672. The structure represents a modification of the Aurivillius phase and consists of $[Bi_2O_2]^{2+}$ units separated by WO_8 polyhedra. a.c. impedance studies indicate oxide ion conductivity of $2.91\ 10^{-5}$ Scm^{-1} at 600°C.

Keywords.   Bismuth tungstate; single crystal X-ray diffraction; a.c. impedance; oxide ion conductivity.

1. Introduction

The discovery of Aurivillius phases[1] has led to extensive studies on various bismuth-containing oxides for a wide range of applications. The family is represented by the general formula $Bi_2M_{n-1}R_nO_{3n+3}$, where M = Bi, Pb, Nb, K, Sr, Ca, Ba and rare earth ions, and R = Ti, Nb, Ta, W, Cr and V. The structure consists of $M_{n-1}R_nO_{3n+1}$ perovskite layers interleaved by sheets of $[Bi_2O_2]^{2+}$ units, where $n = 1, 2, 3, 4$ and 5. The Bi_2O_3–WO_3 system has been well investigated. Hey *et al*[2] isolated two other bismuth tungstates, Bi_2WO_6 and $Bi_2W_2O_9$. Bi_2WO_6[3] has a structure similar to that of the Aurivillius phases. The structure was described as a commensurate modulation of the *Fmmm* structure derived from an idealized parent *I4/mmm* structure. Electrical and optical properties of Bi_2WO_6 such as ferroelectricity, piezoelectricity, pyroelectricity and nonlinear dielectric susceptibility have been extensively studied.[4]

The structure of $Bi_2W_2O_9$[5] presents an entirely different layered arrangement with $[Bi_2O_2]^{2+}$ sheets interleaved by W_2O_7 sheets of double octahedral layers thickness. Ling *et al*[6] reported yet another modulated bismuth tungstate, $Bi_{14}WO_{24}$ with a structure related to that of fluorite type in the tetragonal *I4/m* space group. The structure was described to be a super structure of fluorite type *d*-Bi_2O_3. Crumpton *et al*[7] reported the polymorphic modifications of

$Bi_{14}WO_{24}$. The low temperature monoclinic *C2/m* phase is obtained by slow cooling of the high tetragonal temperature phase. A rotational disorder observed around the *c* axis in the tetragonal *I4/m* form is reduced in the polymorphic *C2/m* form.

The Bi_2O_3–WO_3 phase diagram appears to be fairly complicated. Solid solutions with very low content of WO_3 exhibit *b*-Bi_2O_3 type structure. In the composition type, $Bi_{2-x}W_xO_{3+1.5x}$, three solid solution ranging from $0.064 \leq x \leq 0.134$ (type Ia), $0.134 \leq x \leq 0.286$ (type Ib) and $0.286 \leq x \leq 0.364$ (type II) have been identified.[8] Further, ionic properties of solid solution of the type, $(Bi_2O_3)_{1-x}(WO_3)_x$[9] ($x = 0.05$–0.5) indicate ionic conductivity of the order of 10^{-1} Scm^{-1} at 880°C for $(Bi_2O_3)_{0.78}(WO_3)_{0.22}$. We are interested in the structural features of novel phases in the Bi_2O_3–WO_3 system, in particular to generate new structural types.

In this context we have synthesized $Bi_3W_2O_{10.5}$ by the solid-state technique and in this article we report the single crystal X-ray structure and preliminary studies on a.c. impedance of the compound.

2. Experimental section

2.1 *Preparation*

Bi_2O_3 (Fluka, 99.99%) was dried at 600°C before use and WO_3 (Fluka, 99.99%) was used as such. A polycrystalline sample of $Bi_3W_2O_{10.5}$ was synthesized by the solid-state method using Bi_2O_3 and WO_3 in stoichiometric quantities. The starting materials

were ground well in an agate mortar and fired at 850°C for 24 h in a platinum crucible. Preliminary powder X-ray patterns confirm the formation of a single phase. Single crystals of $Bi_3W_2O_{10.5}$ were obtained by melting the polycrystalline sample at 1000°C and slow cooled at the rate of 1°C/min up to 935°C and then furnace-cooled to room temperature to yield transparent, pale yellow single crystals of $Bi_3W_2O_{10.5}$. Powder pattern of a crushed sample of single crystals was recorded to confirm the purity of the phase of the single crystals.

2.2 *Characterization*

2.2a *Single crystal X-ray diffraction:* Single crystal X-ray diffraction data were collected on a Bruker Axs SMART APEX CCD diffractometer[10] with a crystal to detector distance of 6·06 cm. The data were collected based on 3 sets of runs covering a complete sphere of reciprocal space with each set at different *j* angles (*j* = 0, 90, 180°). Each frame covered 0·3 degrees in *w*. The data were reduced using SAINT PLUS[11] and the structure was solved by direct methods using SHELXS97 and refined using SHELXL97.[12] Crystallographic data and the details of the single crystal data collection are given in table 1.

Table 1. Crystallographic data for $Bi_3W_2O_{10.5}$.

Crystal data	
Empirical formula	$Bi_3W_2O_{10.5}$
Crystal habit, colour	Cylindrical, yellow
Crystal size	$0·086 \times 0·131 \times 0·248$
Crystal system	Tetragonal
Space group	$I\,4/m$
Cell dimensions (Å/°) $a =$	3·839 (1)
$b =$	16·382 (5)
Volume (Å^3)	241·4 (1)
Formula weight	1162·64
Density (calculated) (g/cm^3)	7·997
Z	4
$F(000)$	481
Scan mode	*w* scan
q range (deg)	2·49–25·91
Recording reciprocal space	$-4 \leq h \leq 4, -4 \leq k \leq 4,$ $-20 \leq l \leq 20$
Number of measured reflections	875
Number of independent reflections	134 [R(int) = 0·0243]
m (mm^{-1})	78·267
Number of refined parameters	9
$R[I > 4\mathbf{s}I]/R$[all data]	0·0692/0·0692
$WR[I > 4\mathbf{s}I]/R$[all data]	0·1841/0·1841
GoF	1·088
Max/min $\Delta\rho e/\text{Å}^3$	5·481/–3·293

2.2b *a.c. Impedance:* A circular pellet of $Bi_3W_2O_{10.5}$ of about 10 mm diameter was sintered at 700°C. The sintered sample was sputtered with gold. The sample was then mounted in an impedance jig and placed in a tube furnace where the temperature was controlled to ±3°C over the range 30–600°C. a.c Impedance measurements were carried out between 5 Hz and 13 MHz on a Hewlett–Packard HP4192A impedance gain phase analyzer. A home built cell assembly with a 2-terminal capacitor configuration and stainless steel electrodes were used for the experiment. The sample temperature was measured using a Pt–Rh thermocouple positioned very close to the sample. The frequency dependence of the impedance was measured between 30° and 600°C in a heating–cooling cycle. The samples were equilibrated for half an hour at every temperature. The ionic conductivity was calculated from the intercept of the single semicircular arcs obtained in the complex impedance plots.

3. Results and discussion

3.1 *Crystal structure*

The yellow compound, $Bi_3W_2O_{105}$ crystallized into the tetragonal *I4/m* system with $a = 3·839$ (1) Å, $c = 16·382$ (5) Å, $V = 241·4$ (1) Å^3 and $Z = 4$. Table 1 lists the crystallographic details. The positions of the Bi and W atoms were obtained by direct methods and all the remaining oxygen atoms in the structure were located by difference Fourier synthesis. Initial isotropic thermal parameters indicate that the occupancy of the bismuth atom at the 4*e* site needs to be re-refined. On refining the occupancy and isotropic thermal parameter of the Bi(1) atom alternately, the occupancy factor converged to a value of Bi(1) was located at the 4*e* site with a large thermal parameter. So the occupancy of Bi(1) was refined with fixed isotropic thermal factor. The refinements converged for an occupancy factor of 0·187(2). This amounts to 75% occupancy at the 4*e* site by the Bi(1) atom resulting in 3 Bi atoms in the unit cell. The oxygen atoms located by the difference Fourier also revealed large thermal parameters with O(1) and O(2) occupying the 4*d* and 8*g* sites respectively. In order to balance the stoichiometry and also investigate the high thermal parameters of oxygen atoms, the occupancy of oxygen atoms were also refined in the same way as that of Bi(1) atom. The final cycles of refinement converge to an $R = 0·0692$ with O(1)

Table 2. Fractional atomic co-ordinates and equivalent thermal parameters (U_{eq}) for Bi$_3$W$_2$O$_{10.5}$.

Atom	x	y	z	Occupancy	Wyckoff position	$U_{(eq)}$ Å^2
Bi1	–0·5	–0·5	–0·16763(18)	0·75	4e	0·0404(12)
W1	0	0	0	1	2a	0·0165(11)
O1	–0·5	–1·0	–0·25	1	4d	0·11(5)
O2	0	–0·5	0·068(3)	0·81	8g	0·10(2)
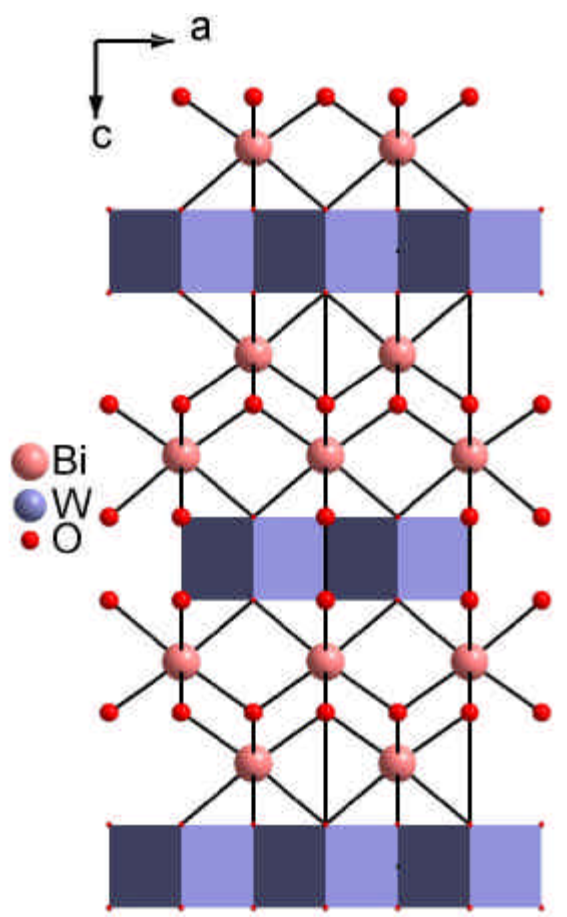
Figure 1. Crystal structure of Bi$_3$W$_2$O$_{10.5}$ along the *b* axis.
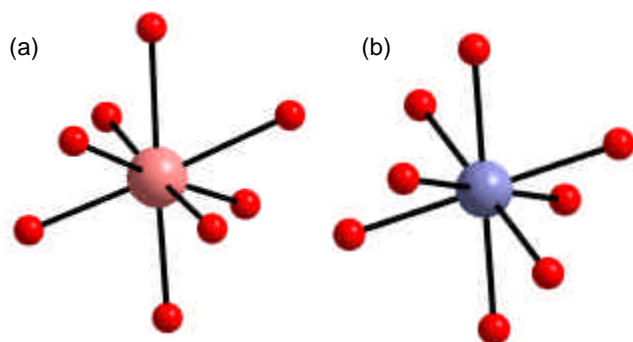
Figure 2. Co-ordination around (**a**) Bi and (**b**) W atoms.

fully occupied at the 4d site and O(2) at the 8g site with an occupancy of 0·40 (2). Hence the final stoichiometry is Bi$_3$W$_2$O$_{10.5}$. The fractional atomic co-ordinates for all the atoms are listed in table 2.

The crystal structure of Bi$_3$W$_2$O$_{10.5}$ along the *b* axis is shown in figure 1. Layers of [Bi$_2$O$_2$]$^{2+}$ units are interlinked by WO$_8$ polyhedra with Bi(1) atom surrounded by eight oxygen atoms resulting in a BiO$_8$ polyhedra. The BiO$_8$ polyhedra is formed by linking Bi(1) to four each of symmetrically related O(1) and O(2) atoms. The Bi(1)–O(1) and Bi(1)–O(2) distances are 2·346 (1) Å and 2·52 (4) Å respectively. The co-ordination of Bi(1) and W(1) atoms are shown in figure 2. Bi(1) is connected to W(1) by edge sharing of O(2) atoms through the long Bi(1)–O(2) contacts. W(1) is connected to symmetrically related O2 atoms at distances 2·22 (3) Å. Further, the WO$_8$ polyhedra are linked to one another by edge sharing along the *a* and *c* axes.

The main structural difference between Bi$_3$W$_2$O$_{10.5}$ and the Aurivillius phase lies in the fact that the layers of [Bi$_2$O$_2$]$^{2+}$ units are connected to the WO$_8$ polyhedra by edge sharing whereas in the Aurivillius phases the layers of [Bi$_2$O$_2$]$^{2+}$ units occur separately. This is the first example of an eight co-ordinated W atom in a bismuth tungstate.

3.2 *a.c. impedance*

a. c. Impedance studies suggest a conductivity value of 2·91 × 10^{-5} Scm^{-1} at 600°C. The X-ray powder pattern of the sample indicates no change after the conductivity measurements. The heating and the cooling cycles show no changes in the Arrhenius plot. The reported results correspond to the heating cycle. Figure 3 shows the Arrhenius plot of conductivity. The variation of log s with $1/T$ indicates linear behaviour, thus indicating the absence of any phase transition. This feature is further confirmed by DTA data recorded up to 700°C, which shows no phase transition in the whole range. The moderate conductivity is via oxygen ions.
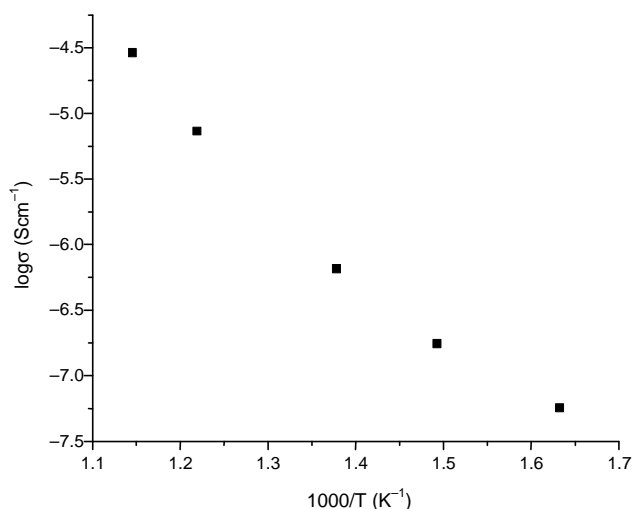
Figure 3.   Conductivity Arrhenius plot of $Bi_3W_2O_{10.5}$.

4. Summary

A new bismuth tungstate, $Bi_3W_2O_{10.5}$ was synthesized and characterized by single-crystal X-ray diffraction. The structure shows deviation from an ideal Aurivillius phase in terms of the arrangement of Bi and W atoms. Unlike in the regular Aurivillius phases, where W atom is octahedrally co-ordinated, $Bi_3W_2O_{10.5}$ depicts an unusual co-ordination for W atom and is linked to eight oxygen atoms at equal distances. The ionic conductivity of the order of 10^{-5} Scm^{-1} indicates moderate oxygen ion conductivity.

Supporting information available

CIF crystal data have been deposited at the Fachinformationszentrum Karlsruhe (FIZ) with the number CSD 415848.

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