



Structure and conductivity in tungsten doped δ -Bi₃YO₆



A. Borowska-Centkowska^{a,*}, M. Leszczynska^a, W. Wrobel^a, M. Malys^a, M. Krynski^a, S. Hull^b, F. Krok^a, I. Abrahams^{c,*}

^a Faculty of Physics, Warsaw University of Technology, ul. Koszykowa 75, 00-662 Warsaw, Poland

^b ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom

^c Materials Research Institute, School of Biological and Chemical Sciences, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom

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ABSTRACT

Solid solution formation in the system Bi₃Y_{1-x}W_xO_{6+3x/2} has been studied using a combination of X-ray and neutron powder diffraction and a.c. impedance spectroscopy. Compositions in the solid solution adopt the δ -Bi₂O₃ type structure, with single phases evident from $x = 0.00$ to $x = 0.20$. Evidence for dopant clustering is presented and discussed. Models for the defect structure derived from diffraction studies are presented. Tungsten is proposed to adopt a tetrahedral coordination geometry, with a distorted octahedral geometry adopted by yttrium. Calculated coordination numbers for bismuth of around five are consistent with stereochemical activity of the Bi 6s² lone pairs of electrons. Despite a significant lowering of the nominal vacancy concentration with respect to δ -Bi₃YO₆, as well as enhanced vacancy trapping by W⁶⁺, tungsten doping is found to have very little influence on the total conductivity of δ -Bi₃YO₆. This is attributed to the compensating effect of enhanced oxide ion mobility caused by lattice expansion.

1. Introduction

Solid electrolytes based on bismuth oxide show exceptionally high conductivity at significantly lower temperatures than other oxide ion conducting solids. However, their application to date has been limited due to questions over their stability, particularly in reducing atmospheres. Nevertheless, their use in intermediate temperature solid oxide fuel cells has been successfully demonstrated [1,2]. The highly conducting δ -phase of bismuth oxide is only stable at high temperatures, above ca. 730 °C [3], but is readily preserved to room temperature, by partial substitution of Bi³⁺ by a variety of cations [4–9].

Isovalent substitution of Bi³⁺ by Y³⁺ in Bi₂O₃ yields fluorite related compounds over a wide compositional range [7,10,11] and at the 3:1 B:Y ratio a cubic δ -type structure is observed. We have previously reported on details of the defect structure and conductivity of δ -Bi₃YO₆ using reverse Monte Carlo modelling of total neutron scattering data and energy minimization calculations [12]. Changes in oxide ion vacancy distribution were shown to occur and clear evidence for a preferred vacancy pair alignment was presented. Defect trapping effects in this system were studied using ab initio calculations and confirmed the importance of the preferred coordination of the dopant cation (Y³⁺) in defect trapping and its effect on conductivity [13,14].

A major issue that remains with the rare earth substituted bismuth oxides is their tendency to exhibit conductivity decay on prolonged

annealing at temperatures around 600 °C. In the case of δ -Bi₃YO₆, this decay is associated with the appearance of a rhombohedral phase that exhibits significantly lower conductivity [15]. Indeed, it was argued that the cubic δ -type phase in bismuth based oxides is invariably metastable and that intermediate temperature annealing always results in the formation of more stable phases [16]. Subsequently, studies revealed that true stabilization can be achieved by low levels of secondary doping, for example with W⁶⁺ [17]. Conductivity decay has been found to be greatly reduced by low levels of tungsten doping in the closely related systems bismuth erbium oxide [17] and bismuth dysprosium oxide [18,19]. We are currently investigating the influence of tungsten doping on conductivity decay in δ -Bi₃YO₆. Here, we focus on the extent of solid solution formation in tungsten doped δ -Bi₃YO₆ and examine its effect on defect structure and conductivity.

2. Experimental

2.1. Preparations

Samples of composition Bi₃Y_{1-x}W_xO_{6+3x/2} (0.00 ≤ x ≤ 0.40) were prepared using appropriate amounts of Bi₂O₃ (Aldrich, 99.9%), WO₃ (Aldrich, 99.99%) and Y₂O₃ (Aldrich, 99.99%). The starting mixtures were ground in ethanol using a planetary ball mill. The dried mixtures were heated initially at 750 °C for compositions in the range

* Corresponding authors.

E-mail addresses: centkowska@if.pw.edu.pl (A. Borowska-Centkowska), i.abrahams@qmul.ac.uk (I. Abrahams).

$0.00 \leq x \leq 0.30$ or $850\text{ }^\circ\text{C}$ for the $x = 0.40$ composition. After cooling, samples were reground and heated for a further 24 h at $800\text{ }^\circ\text{C}$ for all compositions, apart from $x = 0.40$, which required heating at $900\text{ }^\circ\text{C}$ to give a diffraction pattern which was predominantly that of a fluorite phase. A third 24 h heating step was required for two of the samples; at $850\text{ }^\circ\text{C}$ for $x = 0.20$ and $950\text{ }^\circ\text{C}$ for $x = 0.40$. In all cases, following the heat treatments, samples were slow cooled in the furnace to room temperature over a period of ca. 12 h. Through thermogravimetric measurements on green powders, mass loss due to volatilization of bismuth oxide during synthesis was confirmed to be negligible. For electrical measurements, pellets of 10 mm diameter and 2–3 mm thickness were pressed isostatically from synthesised powder at a pressure of 400 MPa and sintered at temperatures ranging from 800 to $1000\text{ }^\circ\text{C}$ for 10 h.

2.2. X-ray diffraction

Ambient temperature X-ray powder diffraction data were collected on a Philips X'Pert Pro X-ray diffractometer fitted with an X'Celerator detector, using Ni filtered Cu-K α radiation ($\lambda_1 = 1.54056\text{ \AA}$ and $\lambda_2 = 1.54439\text{ \AA}$), in flat plate θ/θ geometry on a spinning sample holder. Data collection was carried out in the range $5\text{--}125^\circ 2\theta$, in steps of 0.0167° , with an effective scan time of 250 s per step. Calibration was carried out with an external LaB $_6$ standard. Variable temperature data were collected with an Anton-Paar HTK 1200 high temperature camera, in flat plate θ/θ geometry, on a Pt coated ceramic sample holder. Diffraction patterns were acquired at selected temperatures from ambient temperature up to $850\text{ }^\circ\text{C}$, over the range $5\text{--}125^\circ 2\theta$, in steps of 0.033° , with an effective scan time of 50 to 60 s per step. Data collections at $800\text{ }^\circ\text{C}$ were carried out with a longer scan time of up to 250 s per step.

2.3. Neutron diffraction

Powder neutron diffraction data were collected on the $x = 0.05$, 0.10 , 0.20 and 0.30 compositions on the Polaris diffractometer at the ISIS Facility, Rutherford Appleton Laboratory, UK. Samples were placed in 11 mm diameter vanadium cans and data collected on back-scattering (average angle 146.72°) and 90° (average angle 92.5°) detector banks were used in subsequent refinements. Data collections of ca. $200\text{ }\mu\text{A h}$ were made for the $x = 0.05$, 0.20 and 0.30 compositions, with a longer collection of $1000\text{ }\mu\text{A h}$ made for the $x = 0.10$ composition. For elevated temperature measurements, samples were placed in an evacuated furnace. Measurements of $30\text{ }\mu\text{A h}$ were made from room temperature to $650\text{ }^\circ\text{C}$, with an extended collection of $200\text{ }\mu\text{A h}$ at $700\text{ }^\circ\text{C}$. For the $x = 0.30$ composition, the sample was sealed in an evacuated silica tube and placed in an 11 mm diameter thin walled vanadium can inside the furnace, while for all other compositions, samples were contained directly in the vanadium can.

2.4. Structure analysis

Structure refinement was carried out by combined Rietveld whole profile fitting of X-ray and neutron data sets using the program GSAS [20]. A fluorite structural model in space group $Fm\text{-}3m$ was used for all refinements, as previously described [21]. Bi, Y and W were located on the ideal $4a$ site (0, 0, 0), with oxide ions distributed over three sites; $8c$ at (0.25, 0.25, 0.25); $32f$ at approximately (0.3, 0.3, 0.3) and $48i$ at around (0.5, 0.2, 0.2). A total oxide ion occupancy constraint was applied. In the final refinements, isotropic thermal parameters were refined, with those of the oxide ions tied to a single variable. Crystal and refinement parameters for the $x = 0.05$, 0.10 and 0.20 compositions at ambient temperature and $700\text{ }^\circ\text{C}$ are given in Tables 1 and 2.

Table 1

Crystal and refinement parameters for $\text{Bi}_3\text{Y}_{1-x}\text{W}_x\text{O}_6 + 3x/2$ at room temperature.

Composition	$x = 0.05$	$x = 0.10$	$x = 0.20$
Chemical formula	$\text{Bi}_3\text{Y}_{0.95}\text{W}_{0.05}\text{O}_{6.075}$	$\text{Bi}_3\text{Y}_{0.90}\text{W}_{0.10}\text{O}_{6.15}$	$\text{Bi}_3\text{Y}_{0.80}\text{W}_{0.20}\text{O}_{6.30}$
Formula weight	817.79 g mol^{-1}	823.74 g mol^{-1}	835.63 g mol^{-1}
Crystal system	Cubic	Cubic	Cubic
Space group	$Fm\text{-}3m$	$Fm\text{-}3m$	$Fm\text{-}3m$
Unit cell dimension	$a = 5.49920(4)\text{ \AA}$	$a = 5.50432(36)\text{ \AA}$	$a = 5.51022(14)\text{ \AA}$
Volume	$166.302(4)\text{ \AA}^3$	$166.767(32)\text{ \AA}^3$	$167.304(13)\text{ \AA}^3$
Z	1	1	1
Density (calculated)	8.169 Mg m^{-3}	8.205 Mg m^{-3}	8.297 Mg m^{-3}
μ (Cu-K α X-ray)	165.41 mm^{-1}	165.96 mm^{-1}	167.44 mm^{-1}
F(000)	338.35	340.70	345.40
Sample description	Yellow powder	Yellow powder	Yellow powder
R-factors ^a	Neutron (back-scattering) $R_{\text{wp}} = 0.0195$ $R_p = 0.0237$ $R_{\text{ex}} = 0.0078$ $R_{\text{f}2} = 0.0482$ Neutron (90°) $R_{\text{wp}} = 0.0189$ $R_p = 0.0339$ $R_{\text{ex}} = 0.0086$ $R_{\text{f}2} = 0.0632$ X-ray $R_{\text{wp}} = 0.0508$ $R_p = 0.0330$ $R_{\text{ex}} = 0.0222$ $R_{\text{f}2} = 0.0590$ Totals $R_{\text{wp}} = 0.0249$ $R_p = 0.0329$ $\chi^2 = 5.454$	Neutron (back-scattering) $R_{\text{wp}} = 0.0185$ $R_p = 0.0216$ $R_{\text{ex}} = 0.0033$ $R_{\text{f}2} = 0.0719$ Neutron (90°) $R_{\text{wp}} = 0.0161$ $R_p = 0.0504$ $R_{\text{ex}} = 0.0037$ $R_{\text{f}2} = 0.0579$ X-ray $R_{\text{wp}} = 0.0531$ $R_p = 0.0410$ $R_{\text{ex}} = 0.0402$ $R_{\text{f}2} = 0.0572$ Totals $R_{\text{wp}} = 0.0178$ $R_p = 0.0406$ $\chi^2 = 13.97$	Neutron (back-scattering) $R_{\text{wp}} = 0.0162$ $R_p = 0.0197$ $R_{\text{ex}} = 0.0071$ $R_{\text{f}2} = 0.0671$ Neutron (90°) $R_{\text{wp}} = 0.0151$ $R_p = 0.0303$ $R_{\text{ex}} = 0.0077$ $R_{\text{f}2} = 0.0463$ X-ray $R_{\text{wp}} = 0.0608$ $R_p = 0.0452$ $R_{\text{ex}} = 0.0417$ $R_{\text{f}2} = 0.0589$ Totals $R_{\text{wp}} = 0.0185$ $R_p = 0.0446$ $\chi^2 = 3.403$
No. of variables	119	119	119
No of profile points used	1420 (Neutron, back-scattering) 1899 (Neutron, 90°) 3140 (X-ray)	1458 (Neutron, back-scattering) 1929 (Neutron, 90°) 3140 (X-ray)	1511 (Neutron, back-scattering) 1929 (Neutron, 90°) 3140 (X-ray)
No of reflections	33 (Neutron, back-scattering) 38 (Neutron, 90°) 32 (X-ray)	37 (Neutron, back-scattering) 40 (Neutron, 90°) 32 (X-ray)	44 (Neutron, back-scattering) 40 (Neutron, 90°) 32 (X-ray)

^a For definition of R-factors see reference [20].

2.5. Electrical measurements

Electrical parameters were determined by a.c. impedance spectroscopy in $20\text{ }^\circ\text{C}$ steps from ca. $300\text{ }^\circ\text{C}$ up to ca. $850\text{ }^\circ\text{C}$, using a Solartron 1255/1286 system, over the frequency range 1 Hz to 5×10^5 Hz. Samples were prepared as rectangular blocks (ca. $6 \times 3 \times 3\text{ mm}^3$) cut from slow cooled sintered pellets using a diamond saw. Platinum electrodes were sputtered by cathodic discharge on the two smallest faces. Impedance spectra were recorded over two cycles of heating and cooling at stabilised temperatures. Impedance at each frequency was measured repeatedly until consistency (2% tolerance in drift) was achieved or a maximum number of 25 repeats had been reached.

3. Results and discussion

3.1. Solid solution formation

Fig. 1 shows X-ray diffraction patterns for the studied compositions.

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