



The double rare-earth substituted bismuth oxide system $\text{Bi}_3\text{Y}_{1-x}\text{Yb}_x\text{O}_6$



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ABSTRACT

Structure and electrical conductivity in the double rare-earth substituted system $\text{Bi}_3\text{Y}_{1-x}\text{Yb}_x\text{O}_6$ ($0.00 \leq x \leq 1.00$) is discussed. Structural characterization, by X-ray and neutron powder diffraction, confirms a full $\delta\text{-Bi}_2\text{O}_3$ type solid solution. This structure is maintained up to 850 °C, with no visible evidence for phase separation over the timescale of the diffraction experiments. Small compositional changes in oxide ion distribution are observed, with Yb rich compositions favoring a more centralized oxide ion distribution in the tetrahedral cavities. Electrical characterization, by a.c. impedance spectroscopy, reveals the system to be highly conducting, with measurements of transference number indicating this conductivity to be almost purely ionic at temperatures above ca. 600 °C. At lower temperatures, transference number decreases with increasing ytterbium content. Maxima in activation energy and conductivity pre-exponential factor at high temperatures are observed at $x = 0.50$ and are discussed in terms of changes in configurational entropy. This behaviour resembles the “mixed alkali effect” frequently observed in glasses. However, in the present case there is no corresponding minimum in conductivity and the effect is associated with the immobile sublattice.

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1. Introduction

Despite their relative instability under reducing conditions, bismuth oxide based electrolytes have attracted a great deal of attention, due to their exceptionally high oxide ion conductivities at relatively low temperatures. Recently, it has been shown that through careful design of the electrolyte and device construction, these materials can be utilized in intermediate temperature solid oxide fuel cells (IT-SOFCs) [1,2]. The δ -phase of Bi_2O_3 exhibits the highest known oxide ion conductivity of any solid and represents the benchmark for oxide ion conducting solid electrolytes. Unfortunately, this high temperature polymorph is stable only at elevated temperatures (above ca. 730 °C [3]) and readily transforms to more poorly conducting phases (α , β and γ) at lower temperatures, depending on cooling conditions. Stabilization of the δ -phase to room temperature, can be achieved by solid solution formation with other metal oxides, in particular the rare-earth oxides RE_2O_3 [4–9]. It has been argued that many of these so called “stabilized” phases are in fact metastable and that annealing at intermediate temperatures, around 600 °C, invariably leads to the formation of stable phases or phase separation [10,11]. However, double substitution has been acknowledged as a route to truly stable δ -type phases [12–15]. In these

systems, it has been argued that the increased stability arises from increased configurational entropy [16,17].

Both the systems $\text{Bi}_2\text{O}_3\text{-Y}_2\text{O}_3$ [3,10,11,18–21] and $\text{Bi}_2\text{O}_3\text{-Yb}_2\text{O}_3$ [20, 22–27] yield face centred cubic (fcc) fluorite phases over wide compositional ranges. The widely studied $\text{Bi}_2\text{O}_3\text{-Y}_2\text{O}_3$ system shows exceptionally high conductivity and is reviewed elsewhere [7]. At 25% Y_2O_3 substitution, the fcc phase is readily obtained at room temperature and its structure has been confirmed as a fully disordered $\delta\text{-Bi}_2\text{O}_3$ type phase [28,29].

Despite early claims that the fcc phase could not be stabilized in the $\text{Bi}_2\text{O}_3\text{-Yb}_2\text{O}_3$ system [20], it was later found that this phase could indeed be obtained, depending on composition and thermal treatment [22]. In the most recent study of the $\text{Bi}_2\text{O}_3\text{-Yb}_2\text{O}_3$ equilibrium phase diagram [24], the fcc phase is reported to be stable at higher temperatures, in compositions around 25% substitution of Bi by Yb, with phase separation occurring at lower temperatures. Of the rare earth substituted bismuth oxides, the Yb substituted system shows the highest conductivity decay on prolonged annealing at 500 °C [25–27]. This has been associated with a redistribution of the oxide ions as well as vacancy ordering.

In the present study, structure and conductivity in the double rare-earth substituted pseudo-binary system $\text{Bi}_3\text{YO}_6\text{-Bi}_3\text{YbO}_6$ are investigated. Y^{3+} and Yb^{3+} have similar ionic radii (0.900 Å and 0.868 Å, for six-coordinate geometry with oxide ions [30]) and being isovalent with Bi^{3+} , this system allows for a study of the effects of double substitution in isolation from changes in nominal vacancy concentration and long-range ordering.

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2. Experimental

2.1. Preparations

Samples of general composition $\text{Bi}_3\text{Y}_{1-x}\text{Yb}_x\text{O}_6$ ($0.00 \leq x \leq 1.00$) were prepared using stoichiometric amounts of Bi_2O_3 (Sigma Aldrich, 99.9%), Y_2O_3 (Sigma Aldrich, 99.99%) and Yb_2O_3 (Sigma Aldrich, 99.9%). The starting mixtures were ground in ethanol using a planetary ball mill with agate balls in an agate cup for 24 h at 400 rpm. The dried mixtures were heated at 750 °C for 24 h, then cooled and reground. The samples were then reheated at 950 °C for a further 24 h, before cooling in air to room temperature, over a period of approximately 5 h. For electrical measurements, synthesized powders were pelletized, pressed isostatically at a pressure of 400 MPa and sintered at 950 °C for 10 h, before cooling in air to room temperature over a period of ca. 5 h.

2.2. Electrical measurements

Electrical parameters were determined by a.c. impedance spectroscopy up to ca. 840 °C, using a fully automated Solartron 1255/1286 system, in the frequency range 1 Hz to 5×10^5 Hz, with a signal strength of 50 mV. Samples for impedance measurements were prepared as rectangular blocks (ca. $6 \times 3 \times 3$ mm³) cut from sintered pellets, using a diamond saw. Platinum electrodes were sputtered by cathodic discharge on the two smallest faces. Impedance spectra were acquired over two cycles of heating and cooling at stabilized 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, using an algorithm described earlier [31]. We have previously reported electrical parameters for the $x = 0.00$ composition [29]. These have been re-measured in the present study over a greater temperature range.

For the $x = 0.00, 0.50$ and 1.00 compositions, the ionic and electronic contributions to the total conductivity were measured using a modified EMF method, with an external adjustable voltage source in the

concentration cell O_2 ($p\text{O}_2 = 1.01 \times 10^5$ Pa): Pt | oxide | Pt: O_2 ($p\text{O}_2 = 0.2095 \times 10^5$ Pa), as described in detail elsewhere [32]. Measurements were performed on cooling between ca. 820 °C and ca. 450 °C at stabilized temperatures.

2.3. Diffraction

X-ray powder diffraction data were obtained on a Philips X'Pert Pro diffractometer fitted with an X'Celerator detector, using Ni filtered $\text{Cu-K}\alpha$ radiation ($\lambda_1 = 1.54056$ Å and $\lambda_2 = 1.54439$ Å). Data were collected in flat plate θ/θ geometry and calibrated against an external Si standard. Room temperature data, suitable for detailed Rietveld refinement, were collected in the 2θ range 5–125°, in steps of 0.0167°, with an effective scan time of 250 s per step. Elevated temperature measurements were made using an Anton Paar HTK-1200 camera. Samples were mounted on a Pt coated ceramic sample holder and data collected in steps of 50 °C from 100 °C to 850 °C, in the 2θ range 5–125°, with a step width of 0.033° and an effective scan time of 50 s per step.

Neutron powder diffraction data were obtained on the Polaris diffractometer at the ISIS Facility, Rutherford Appleton Laboratory at room temperature. Data collected on the back-scattering (130–160°), and low-angle (28–42°) detectors were used in subsequent refinements. Samples were contained in cylindrical vanadium cans of 11 mm diameter, located in front of the back-scattering detectors. Data were collected for ca. 200 μA h for each sample.

Structure refinement was carried out by Rietveld analysis using the GSAS suite of programs [33]. For the room temperature structures, combined refinements using X-ray and neutron data were carried out. A cubic model in space group $Fm-3m$ was used for all refinements, with Bi, Y and Yb located on the ideal $4a$ site (0,0,0) [34]. O atoms were refined on three crystallographically distinct sites 8c, 32f and 48i. Isotropic thermal parameters for the oxygen atoms were tied to a single value and a total oxide occupancy constraint applied. Crystal and refinement parameters for the room temperature analyses are summarised in Table 1, with the fitted diffraction profiles given in Fig. 1. For elevated

Table 1
Crystal and refinement parameters for $\text{Bi}_3\text{Y}_{1-x}\text{Yb}_x\text{O}_6$ at room temperature.^a

Composition	$x = 0.25$	$x = 0.50$	$x = 0.75$
Chemical formula	$\text{Bi}_3\text{Y}_{0.75}\text{Yb}_{0.25}\text{O}_6$	$\text{Bi}_3\text{Y}_{0.5}\text{Yb}_{0.5}\text{O}_6$	$\text{Bi}_3\text{Y}_{0.25}\text{Yb}_{0.75}\text{O}_6$
Formula weight	832.873	853.908	874.940
Crystal system	Cubic	Cubic	Cubic
Space group	$Fm-3m$	$Fm-3m$	$Fm-3m$
Unit cell dimension	$a = 5.48207(3)$ Å	$a = 5.47634(8)$ Å	$a = 5.47060(9)$ Å
Volume	$164.753(3)$ Å ³	$164.237(7)$ Å ³	$163.722(9)$ Å ³
Z	1	1	1
Density (calculated)	8.395 Mg m ⁻³	8.634 Mg m ⁻³	8.874 Mg m ⁻³
μ (CuK α X-ray)	169.40 mm ⁻¹	173.40 mm ⁻¹	177.43 mm ⁻¹
F(000)	343.75	351.50	359.25
Sample description	Yellow powder	Yellow powder	Yellow powder
R-factors ^a	Neutron (back-scattering) $R_{\text{wp}} = 0.0278, R_p = 0.0401$ $R_{\text{ex}} = 0.0097, R_{\text{f}2} = 0.0576$ Neutron (low angle) $R_{\text{wp}} = 0.0245, R_p = 0.0197,$ $R_{\text{ex}} = 0.0271, R_{\text{f}2} = 0.0547$ X-ray $R_{\text{wp}} = 0.0437, R_p = 0.0290,$ $R_{\text{ex}} = 0.0231, R_{\text{f}2} = 0.0752$ Totals $R_{\text{wp}} = 0.0316, R_p = 0.0289$ $\chi^2 = 4.004$	Neutron (back-scattering) $R_{\text{wp}} = 0.0129, R_p = 0.0186$ $R_{\text{ex}} = 0.0083, R_{\text{f}2} = 0.0564$ Neutron (low angle) $R_{\text{wp}} = 0.0213, R_p = 0.0170,$ $R_{\text{ex}} = 0.0229, R_{\text{f}2} = 0.0614$ X-ray $R_{\text{wp}} = 0.0645, R_p = 0.0500,$ $R_{\text{ex}} = 0.0507, R_{\text{f}2} = 0.1229$ Totals $R_{\text{wp}} = 0.0171, R_p = 0.0463$ $\chi^2 = 1.628$	Neutron (back-scattering) $R_{\text{wp}} = 0.0158, R_p = 0.0239$ $R_{\text{ex}} = 0.0073, R_{\text{f}2} = 0.0706$ Neutron (low angle) $R_{\text{wp}} = 0.0206, R_p = 0.0165,$ $R_{\text{ex}} = 0.0200, R_{\text{f}2} = 0.0571$ X-ray $R_{\text{wp}} = 0.0651, R_p = 0.0510,$ $R_{\text{ex}} = 0.0533, R_{\text{f}2} = 0.0796$ Totals $R_{\text{wp}} = 0.0183, R_p = 0.0467$ $\chi^2 = 2.408$
No. of variables	124	124	124
No. of profile points used	3247 (neutron, back-scattering) 3521 (neutron, low-angle) 6282 (X-ray)	3248 (neutron, back-scattering) 3572 (neutron, low-angle) 3141 (X-ray)	3248 (neutron, back-scattering) 3521 (neutron, low-angle) 3141 (X-ray)
No of reflections	41 (neutron, back-scattering) 46 (neutron, low-angle) 31 (X-ray)	39 (neutron, back-scattering) 48 (neutron, low-angle) 31 (X-ray)	38 (neutron, back-scattering) 41 (neutron, low-angle) 30 (X-ray)

^a For definition of R-factors see Ref. [33].

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