Conductivity in lead substituted bismuth yttrate fluorites

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ABSTRACT

The di-substituted bismuth oxide based oxide ion conducting electrolyte system $Bi_{2.5+x}Pb_{0.5}YO_{5.75+3x/2-\delta}$ ($x = 0$, 1 and 2) has been investigated by X-ray powder diffraction, a.c. impedance spectroscopy, thermal analysis and X-ray photoelectron spectroscopy. δ-Bi_2O_3 type phases are observed for all compositions studied and showed no obvious changes in structure up to 850 °C. XPS results show an increasing trend in binding energy with increasing x-value. Results from thermal analysis and the thermal variation of the lattice parameter indicate a small degree of reduction occurs at high temperature, which is preserved on quenching. This reduction is reversed on heating at intermediate temperatures. The redox reactions appear to be correlated to a degree of curvature in the Arrhenius plot of conductivity. Measurement of transference numbers indicates that these materials are predominantly ionic conductors, with conductivity values at high temperature comparable with mono-substituted analogues.

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1. Introduction

Oxide ion conducting solid electrolytes continue to be of interest as materials for solid oxide fuel cells (SOFCs), gas separation membranes and oxygen pumps. The highest known oxide ion conductivity in a solid is observed above 730 °C for the high temperature δ-polymorph of bismuth oxide [1]. The structure of δ-Bi_2O_3 may be described as that of a defect fluorite, i.e. ccp Bi^{3+} cations with O^{2-} in 3/4 of the tetrahedral sites. δ-Bi_2O_3 therefore has a very high vacancy concentration of 0.5 vacancies per metal atom. This feature, combined with the high polarizability of bismuth [2] and three dimensional conduction pathways, lead to the very high oxide ion conductivity of this phase. On cooling, δ-Bi_2O_3 undergoes phase transitions to more poorly conducting phases [3]. However, the highly disordered fluorite structure can be preserved to lower temperatures through solid solution formation with other metal oxides [4–9]. The size and valency of the substituting cation is known to play a key role in δ-phase stabilisation, with high conductivity and wide solid solution limits observed for materials substituted by those rare earth metals, which have an ionic radius comparable to that of Bi^{3+} [10]. Substituted bismuth oxide based fluorites often show instabilities at moderate temperatures, which depend on the ionic radius of the metal dopant and its

polarizability [11–13]. These thermal instabilities, along with instability at reduced oxygen partial pressures, have limited the direct application of these materials in fuel cells. However, it has recently been shown that with suitable device construction these materials can indeed be used in SOFCs and offer suitable performance at intermediate temperatures [14].

Extensive research has been carried out on binary systems of the type Bi_2O_3–MO_x [e.g. 4–13]. It has been shown that di-substitution of bismuth in ternary systems can result in: (i) preservation of the δ-phase to low temperatures, where similar levels of a single substituent do not; and (ii) enhanced stability of the δ-phase at intermediate temperatures [15–18]. The former has been explained in terms of an increase in configurational entropy [19]. We have previously studied a number of ternary systems of the type Bi_2O_3–RE_2O_3–Nb_2O_5 (where RE = Y, Yb, Er) [20–22]. In these systems, involving isovalent and supervalent substituents, the vacancy concentration per metal atom is less than or equal to that in δ-Bi_2O_3. Subvalent substitution of bismuth by Pb^{2+} represents an attractive option, since it offers the possibility of increasing the nominal vacancy concentration per metal atom beyond that in pure δ-Bi_2O_3. Pb^{2+} ions show many similarities to Bi^{3+}, with similar stereochemical activity of the $6s^2$ electron pairs, comparable polarizabilities ($\alpha_D = 46$ and 50 a.u., respectively, for the neutral atoms of Pb and Bi [23]) and adoption of similar distorted coordination environments in oxide systems. Despite these apparent similarities, the cubic δ-phase in the Bi_2O_3–PbO binary system is only observed at elevated temperatures [24]. However, in ternary systems of the type

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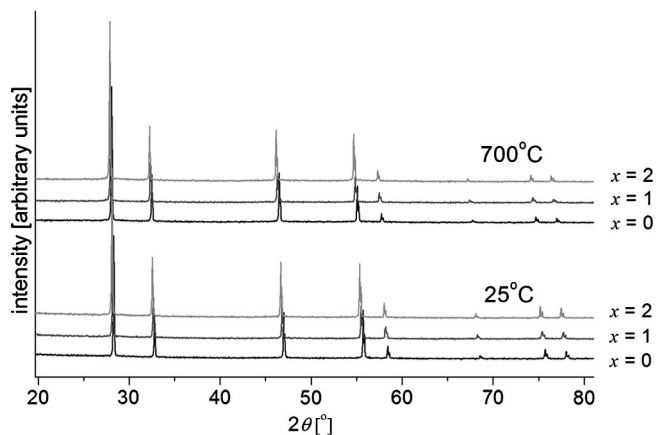(I. Abrahams).

Fig. 1. X-ray powder diffraction patterns for $Bi_{2.5 + x}Pb_{0.5}YO_{5.75 + 3x/2 - \delta}$ at room temperature and 700 °C.

Bi_2O_3–MO_x–PbO (M = Ca, Y, Er and La) it has been shown that δ-type phases can be preserved to room temperature [25–30].

In the present study, the thermal dependence of structure and conductivity in the di-substituted system $Bi_{2.5 + x}Pb_{0.5}YO_{5.75 + 3x/2}$ has been investigated. In the only previous study of the Bi_2O_3–Y_2O_3–PbO system, that we are aware of, δ-type phases were quenchable over a large compositional range, with compositions exhibiting very high conductivities [27].

2. Experimental

2.1. Sample preparations

Samples of general composition $Bi_{2.5 + x}Pb_{0.5}YO_{5.75 + 3x/2 - \delta}$ ($x = 0$, 1 and 2) were prepared using stoichiometric amounts of Bi_2O_3 (Sigma Aldrich, 99.9%), PbO (Sigma Aldrich, 99.99%) and Y_2O_3 (Sigma Aldrich, 99.99%). The starting mixtures were ground in ethanol using a planetary ball mill and the dried mixtures were heated in air at 650 °C for 20 h, then cooled and reground in an agate mortar. The samples were then heated at 800 °C for 24 h and quenched to room temperature. For electrical measurements, samples were subsequently reground in the ball mill, dried and pelletised. Pellets were pressed iso-statically at a pressure of 400 MPa and heated to 850 °C for 15 h before quenching in air to room temperature.
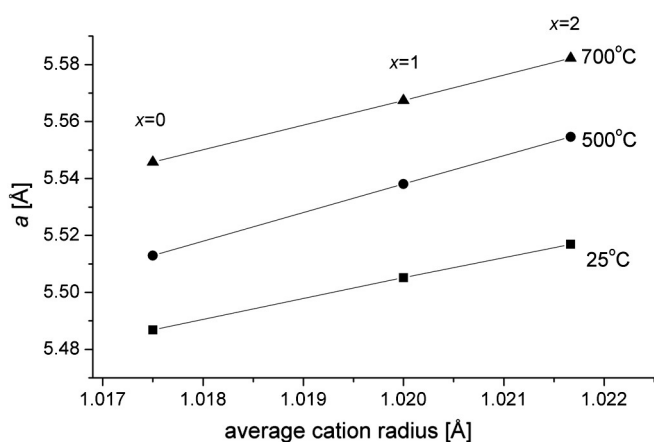

Fig. 2. Variation of cubic lattice parameter, a, at selected temperatures as a function of average cation radius (values based on weighted average of ionic radii for six coordination [35]).
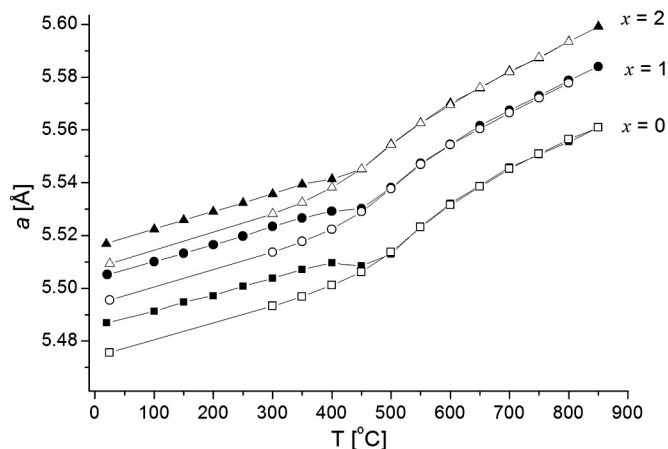

Fig. 3. Thermal variation of cubic lattice parameter, a, from Rietveld analysis of X-ray powder diffraction for $Bi_{2.5 + x}Pb_{0.5}YO_{5.75 + 3x/2 - \delta}$ on heating (filled symbols) and cooling (open symbols).

2.2. Electrical measurements

Electrical parameters were determined by a.c. impedance spectros-copy up to ca. 840 °C using a fully automated Solartron 1255/1286 system, in the frequency range of 1 Hz to 5×10^5 Hz. Samples for impedance measurements were prepared as rectangular blocks (ca. $6 \times 3 \times 3$ mm^3) cut from quenched 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 stabilised temperatures. Impedance at each frequency was measured repeatedly until consisten-cy (2% tolerance in drift) was achieved or a maximum number of 25 repeats had been reached, using an algorithm described earlier [31].

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 ($pO_2 = 1.01 \times 10^5$ Pa): Pt | oxide | Pt: O_2 ($pO_2 = 0.2095 \times 10^5$ Pa) as described in detail elsewhere [32]. Measurements were performed on cooling between 800 °C and 500 °C at stabilised temperatures.

2.3. Diffraction

X-ray powder diffraction data were obtained on a PANalytical X'Pert Pro diffractometer fitted with an X'Celerator detector, using Ni filtered Cu-Kα 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
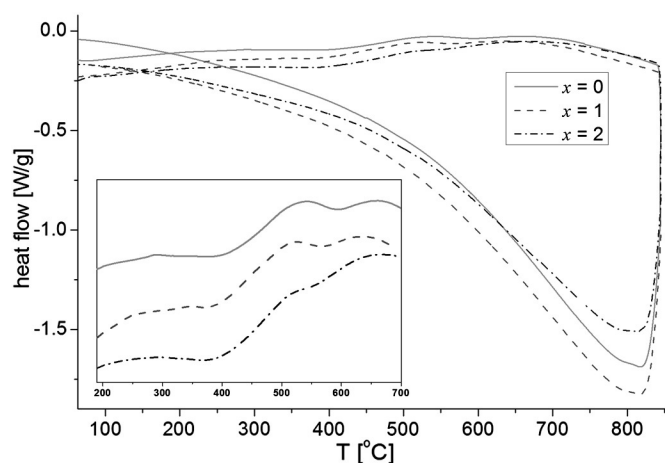

Fig. 4. DTA thermograms for $Bi_{2.5 + x}Pb_{0.5}YO_{5.75 + 3x/2 - \delta}$, with detail of the heating profiles inset.