

# The structural and conductivity evolution of fluorite-type $\text{Bi}_2\text{O}_3\text{--Er}_2\text{O}_3\text{--PbO}$ solid electrolytes during long-term annealing

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## Abstract

Quenched-in *fcc* fluorite-type materials in the  $\text{Bi}_2\text{O}_3\text{--Er}_2\text{O}_3\text{--PbO}$  system were annealed in air at 500 and 600 °C for up to 2000 h. Each material experienced a conductivity-lowering structural transformation, thus making them unsuitable for use in SOFCs. For example, the materials  $(\text{BiO}_{1.5})_{0.80}(\text{ErO}_{1.5})_{0.20-x}(\text{PbO})_x$ ,  $x = 0.03, 0.06$  and  $0.09$ , underwent a fluorite-type to tetragonal transformation during annealing at 500 °C due to  $\langle 100 \rangle$  oxide-ion vacancy ordering, and the rate of conductivity decay at 500 °C increased with increasing  $\text{Pb}^{2+}/\text{Er}^{3+}$  ratio.

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## 1. Introduction

$\text{Bi}_2\text{O}_3$ -based solid electrolytes with the *fcc* fluorite-type structure (space group  $Fm\bar{3}m$ ) are of interest for use in solid oxide fuel cells (SOFCs) due to their high oxide-ion conductivity. The need to develop oxide-ion conductive materials with high conductivity and excellent structural stability at lower temperatures underpins most of the research directed at solid electrolyte materials [1]. For pure  $\text{Bi}_2\text{O}_3$ , the fluorite-type phase ( $\delta\text{-Bi}_2\text{O}_3$ ) has a conductivity of  $\sim 1 \text{ S cm}^{-1}$  at 750 °C [2], and is the most highly conductive oxide-ion conductor known [3]. However,  $\delta\text{-Bi}_2\text{O}_3$  is stable only between 730 °C and the melting point, 825 °C, and cannot be quenched to room temperature [4]. By doping with some rare earth (Sm to Lu, including Y) [5–12] and transition metal (V, Nb, Ta and W) [13,14] oxides, the fluorite-type phase can be quenched-in. It is also possible to use a combination of metal oxides, so-called double doping, to quench-in the  $\text{Bi}_2\text{O}_3$ -based fluorite-type

phase. Examples include the ternary oxide systems Bi–Dy–W [15,16], Bi–Er–W [17], Bi–*Ln*–Te (*Ln* = La, Sm, Gd, Er) [18], Bi–Y–Nb [19], Bi–*Ln*–V (*Ln* = La–Yb) [20,21], Bi–La–U [22], Bi–Ca–Pb [23,24], Bi–Y–Pb [25] and Bi–*Ln*–Pb (*Ln* = La, Nd, Dy and Eu) [26]. We have recently reported a partial air-quenchable domain of the fluorite-type phase in the  $\text{Bi}_2\text{O}_3\text{--Er}_2\text{O}_3\text{--PbO}$  system [27], and several of these fluorite-type materials displayed very high oxide-ion conductivity at 750 °C. The high conductivity of  $\text{Bi}_2\text{O}_3$ -based materials is attributed to the  $\text{Bi}^{3+}$  cation, with its  $6s^2$  lone pair electrons, being highly polarisable [28], and the highly disordered nature of the oxide-ion sublattice (occupancy and positional disorder) [27,29–36].

The behaviour of a solid electrolyte material during prolonged exposure to intermediate temperatures (between  $\sim 500$  and 650 °C), in terms of its structural and conductivity evolution, determines its suitability for practical use as a solid electrolyte within this temperature range. If a solid electrolyte was highly conductive over a long period of time at intermediate temperatures, to allow for the efficient operation of a SOFC at these temperatures, it would lower the thermal energy requirement for operation of the SOFC. Watanabe [37] originally suggested that the fluorite-type form of  $\text{Bi}_2\text{O}_3$  cannot be stabilised by an oxide addition, and that all of the reported

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“stabilised” fluorite-type phases are quenched-in, metastable phases. Indeed, quenched-in fluorite-type materials based on  $\text{Bi}_2\text{O}_3\text{--Ln}_2\text{O}_3$  typically undergo a slow transformation from the *fcc* fluorite-type form to stable  $\beta_2$  rhombohedral layered phases (space group  $R\bar{3}n$ , hexagonal setting) during long-term annealing below  $\sim 700$  °C [37–43], with the kinetics most rapid between  $\sim 600$  and  $650$  °C [44]. The rhombohedral phases have lower conductivity than the quenched-in fluorite-type materials [44]. Drache et al. [45] reported that the fluorite-type material  $(\text{BiO}_{1.5})_{0.778}(\text{YbO}_{1.5})_{0.222}$ , after annealing at  $600$  °C for  $\sim 45$  days, had completely transformed into a mixture of  $\alpha\text{-Bi}_2\text{O}_3$  and an orthorhombic compound  $\text{Bi}_{17}\text{Yb}_7\text{O}_{36}$  (space group *Pmmm*), which is a  $3a \times 2a \times 1a$  supercell of the *fcc* fluorite-type structure caused by ordering of  $\text{Bi}^{3+}$  into the face-centre positions and  $\text{Yb}^{3+}$  into the corner positions [46]. The behaviour of fluorite-type  $\text{Bi}_{1.76}\text{U}_{0.12}\text{La}_{0.12}\text{O}_{3.18}$  during long-term annealing at  $600$  °C was investigated by Lazarraga et al. [22]. The fluorite-type phase transformed to a mixture of hexagonal and monoclinic  $\text{Bi-U-La-O}$  phases, and  $\alpha\text{-Bi}_2\text{O}_3$ . Recently, Watanabe and Sekita [17] reported a compositional domain in the  $\text{Bi}_2\text{O}_3\text{--Er}_2\text{O}_3\text{--WO}_3$  system of what were claimed to be the first fully stabilised  $\text{Bi}_2\text{O}_3$ -based fluorite-type materials. After annealing at  $600$  °C for  $1000$  h, the conductivity of the material  $(\text{Bi}_2\text{O}_3)_{0.705}(\text{Er}_2\text{O}_3)_{0.245}(\text{WO}_3)_{0.050}$  had not decayed, whilst the conductivity of the material  $(\text{Bi}_2\text{O}_3)_{0.720}(\text{Er}_2\text{O}_3)_{0.220}(\text{WO}_3)_{0.060}$  had decayed by only  $\sim 1\%$  after annealing for  $\sim 800$  h.

In addition to the phase transformations described above, conductivity decay can also occur in quenched-in fluorite-type  $\text{Bi}_2\text{O}_3\text{--Ln}_2\text{O}_3$  materials during annealing below  $\sim 600$  °C, without a change in symmetry as established by powder X-ray diffraction (XRD) [34,47–49]. Jiang and Wachsman describe the phenomenon as being distinct from a conventional crystallographic phase transformation [48]. The rate of conductivity decay is dependent on annealing temperature, and for  $(\text{BiO}_{1.5})_{0.80}(\text{ErO}_{1.5})_{0.20}$ , the conductivity decay is most rapid at  $500$  °C [50]. Jiang and Wachsman observed that for  $\text{Bi}_2\text{O}_3\text{--Er}_2\text{O}_3$  materials, the rate of decay decreased as the amount of  $\text{Er}^{3+}$  increased [48]. The conductivity decay can be attributed to long-range ordering of the oxide-ion sublattice, where the oxide-ion vacancies order along the  $\langle 111 \rangle$  directions [33,34,48–51]. This ordering is evidenced by the presence of superlattice reflections corresponding to a  $2a \times 2a \times 2a$  *bcc* superlattice in selected area electron diffraction (SAED) patterns of annealed materials [39,47,49]. Differential thermal analysis (DTA) can be used to detect an endotherm, at  $\sim 630$  °C for  $(\text{BiO}_{1.5})_{0.80}(\text{ErO}_{1.5})_{0.20}$  annealed at  $500$  °C for  $100$  h, which corresponds to an order/disorder transition on heating [50].

Herein we describe the evolution of structure and conductivity for several quenched-in, fluorite-type materials recently reported in the  $\text{Bi}_2\text{O}_3\text{--Er}_2\text{O}_3\text{--PbO}$  system [27], during long-term annealing at  $500$  and  $600$  °C, using a combination of techniques including powder XRD, neutron powder diffraction (NPD), SAED and DTA. We also describe the results of variable temperature conductivity experiments performed on quenched-in fluorite-type materials in the  $(\text{BiO}_{1.5})_{0.70}(\text{ErO}_{1.5})_{0.30-x}(\text{PbO})_x$  series.

## 2. Experimental

Powders of  $\text{Bi}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$  and  $\text{PbO}$  (99.9%, Aldrich) were accurately weighed in the desired proportions, and milled with zirconia balls in polypropylene vials for  $4$  h. The milled powders were heated in air in alumina crucibles at  $675\text{--}800$  °C (depending on the amount of  $\text{PbO}$ ) for  $24$  h, air quenched by removing the sample from the furnace, ground using an agate mortar and pestle, reheated for a further  $24$  h, air quenched, and then ground again to produce the final product. The partial air-quenchable compositional domain of the fluorite-type phase is shown in [27]. Each quenched-in fluorite-type material was annealed in air in an alumina crucible at  $500$  and  $600$  °C for up to  $2000$  h, followed by air quenching and grinding.

Powder XRD patterns, collected at room temperature on a Siemens D5000 diffractometer with  $\text{Cu K}\alpha$  radiation, were used to determine the phase(s) present after annealing. A scan rate of  $2^\circ 2\theta$  per minute with a step size of  $0.02^\circ 2\theta$  over an angular range of  $20\text{--}80^\circ 2\theta$  was satisfactory for phase characterisation of the materials. Phase identification was performed using the JCPDS search/match functionality within the resident EVA software.

The thermal behaviour of the annealed materials was investigated by DTA, using a model SDT-2960 thermobalance from TA Instruments. Samples were heated at  $20$  °C  $\text{min}^{-1}$  in an alumina crucible, and then typically cooled quickly to room temperature under a stream of air. Sample masses were  $20\text{--}50$  mg.

Electrical conductivity,  $\sigma$ , was measured in air by two-probe impedance spectroscopy. Pellets,  $5.5$  mm diameter  $\times \sim 2$  mm thick, were fabricated for conductivity measurements by uniaxial pressing using a  $1$  tonne load, and subsequent sintering at  $700\text{--}800$  °C, depending on the composition. Gold was sputter coated onto both faces of the pellets, with care taken not to coat the side. Pellets were placed into a purpose built holder with platinum sheet electrodes spot welded to gold wire, with the gold-coated faces of the electrolyte in intimate contact with the platinum sheets of the holder. The wires were connected to a Hewlett Packard 4192ALF Impedance Analyser, which was used for the impedance measurements. *In situ* annealing/conductivity experiments were performed on some quenched-in fluorite-type materials at  $500$  °C. The holder was inserted into a tube furnace and the temperature was ramped quickly to  $500$  °C. Impedance measurements, in the frequency range  $1\text{--}10^6$  Hz, were taken at regular intervals, especially in the early stages of the experiment when the sample temperature was equilibrating at  $500$  °C and when any conductivity decay was likely to be most rapid, where measurements were taken every  $2\text{--}3$  min. The conductivity of each material after each impedance measurement was calculated from the value of the bulk resistance, measured as the appropriate intercept of the impedance plot with the  $Z'$  axis [52]. Variable temperature conductivity experiments were also performed on the quenched-in fluorite-type materials  $(\text{BiO}_{1.5})_{0.70}(\text{ErO}_{1.5})_{0.30-x}(\text{PbO})_x$ ,  $x = 0, 0.03, 0.10, 0.15, 0.20$  and  $0.22$ , in  $50$  °C intervals between  $400$  and  $750$  °C. Pellets were heated at  $10$  °C per minute to each desired set-point, and  $15$  min stabilisation time was allowed before the measurement was taken. Because the sample resistance

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