

Anomalous lattice expansion of Y^{3+} and Sc^{3+} co-doped δ - Bi_2O_3 solid electrolytes

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1. Introduction

The most commonly used electrolyte in solid oxide fuel cells (SOFCs) is yttria stabilized zirconia (YSZ), but it requires a high operating temperature of > 1000 °C which increases the cost of the components of the SOFCs.^[1,2] As a result much research has been undertaken to develop solid oxide electrolytes that are fast ion conductors at lower temperatures. Of interest in this work are δ - Bi_2O_3 -based electrolytes as these materials have the highest ionic conductivity amongst the most commonly used solid electrolytes.^[3] The δ -phase of Bi_2O_3 is only stable in the narrow temperature range between 730 °C and 825 °C, above which it melts and below which it transforms to other polymorphs (the identity of which depends on the cooling rate).^[4] However, it has been shown that by doping or co-doping Bi_2O_3 with a range of trivalent cations the δ -phase can be stabilized to room temperature, but doping also lowers the oxide ion conductivity relative to pure δ - Bi_2O_3 , due to contraction of the host lattice.^[4,5] When co-doping, generally if the proportion of the larger dopant cation is increased (at the expense of the smaller dopant cation), there is a slight expansion of the lattice, resulting in an improved oxide ion conductivity. Unfortunately this also results in the material being less stable.^[4] Almost all co-doped Bi_2O_3 materials involve the use of at least one lanthanide metal cation. In this work we studied the Y^{3+} and Sc^{3+} co-doped system and found that as the proportion of Sc^{3+} (the smaller dopant cation) is increased at the expense of Y^{3+} (the larger dopant cation) a slight (anomalous) lattice expansion is triggered. This confirmed results found by Wang *et al.*^[6] They proposed that the lattice expansion was due to the reduction of Sc^{3+} to Sc^{2+} , but this is highly unlikely since Sc^{2+} is not stable (this oxidation state has not been identified before) and the synthetic route does not involve reducing conditions. As such this work embarks on a more comprehensive structural characterization of the Bi_2O_3 - Y_2O_3 - Sc_2O_3 system at various compositions using Rietveld refinement on powder X-ray diffraction (PXRD) data. Both *in-situ* (temperature dependent) and *ex-situ* laboratory data – as well as *ex-situ* synchrotron data – were analysed. This was also related to data obtained for simultaneous differential thermal and thermogravimetric analyses (STA).

2. Results

Bi_2O_3 was co-doped with Y^{3+} and Sc^{3+} at a fixed total dopant concentration of 20 mol%. The concentration of Sc^{3+} was increased at the expense of Y^{3+} . Rietveld refinement of both *ex-situ* laboratory and synchrotron PXRD data showed that co-doping Bi_2O_3 with Y^{3+} and Sc^{3+} does stabilize the δ -phase. Also apparent was that both the lattice parameter and the magnitude of microstrain increased with Sc^{3+} dopant concentration (see Figures 1 and 2), which may suggest that the lattice expansion could be related to the increased microstrain within the materials. Refinement of the *in-situ* PXRD data revealed that the δ -phase structure remained stable throughout heating and cooling between 30°C and 780 °C. Analysis of aged materials (at ambient conditions for 7 months) revealed the growth of a bismuth carbonate impurity to a small extent, suggesting that the materials react with CO_2 in air. This impurity is not persistent as STA showed that CO_2 can be driven off by heating to ~ 450 °C. Additionally, STA indicated a reversible order-disorder transition of the oxide ion sublattice.

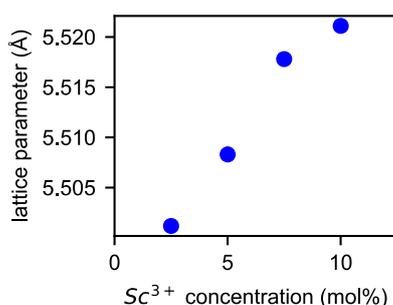


Fig. 1: Variation of the cubic lattice parameter with Sc^{3+} dopant concentration

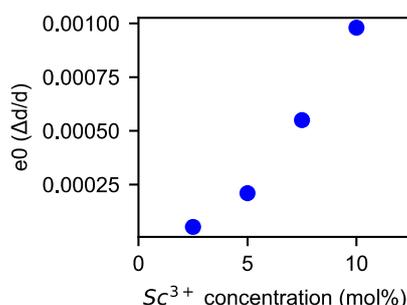


Fig. 2: Variation of microstrain with Sc^{3+} dopant concentration

3. References

- [1] P. R. Chandran, T. V Arjunan, *Int. J. ChemTech Res. CODEN* **2014**, 7, 488.
- [2] D. J. L. Brett, A. Atkinson, N. P. Brandon, S. J. Skinner, *Chem. Soc. Rev.* **2008**, 37, 1568.
- [3] K. C. Wincewicz, J. S. Cooper, *J. Power Sources* **2005**, 140, 280.
- [4] P. Shuk, H.-D. Wiemhöfer, U. Guth, W. Göpel, M. Greenblatt, *Solid State Ionics* **1996**, 89, 179.
- [5] M. J. Verkerk, A. J. Burggraaf, *J. Electrochem. Soc.* **1981**, 128, 75.
- [6] S. F. Wang, Y. F. Hsu, W. C. Tsai, H. C. Lu, *J. Power Sources* **2012**, 218, 106.