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Abstract

The low temperature stable alpha-phase of pure Bi₂O₃ is known to have an oxygen ion diffusivity that is over 7 orders of magnitude lower than the high temperature fluorite-structured delta-phase. Tracer oxygen-18 diffusion studies of polycrystalline alpha-Bi₂O₃ at 600C using an ion microscope with lateral resolutions of 50 nm for the surface distributions of the oxygen isotopes have resolved the secondary fast migration pathways as well as the normal bulk diffusion profile in the grains. A grain boundary pathway for the oxygen migration is distinguished from other extended defects, some of which are also active in the overall oxygen diffusivity. This experimental study highlights the potential manipulation of the micro-structure of this material for enhanced oxygen ion conduction in intermediate temperature solid oxide fuel cells as has been shown for perovskite MIEC electrode materials.

Keywords	Bismuth oxide; alpha-phase; fast oxygen-migration; grain-boundary
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Cover Letter

Dear Editor

All figures are single-column fitting

Please place the Figures on facing pages

Thank you

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Monday, 13 June 2016

Highlights

- Secondary oxygen migration paths in the alpha-phase of pure Bi_2O_3 are visualized.
- Tracer oxygen-18 with SIMS mapping analysis in an ion microscope.
- Grain boundary oxygen-diffusivity in alpha- Bi_2O_3 is similar to bulk YSZ & GDC.
- Microstructure manipulation potential for enhanced oxygen ion conduction.

Title

Fast Grain Boundary Oxygen Ion Diffusion in the α -Phase of Bi_2O_3

Authors

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Abstract

The low temperature stable α -phase of pure Bi_2O_3 is known to have an oxygen ion diffusivity that is over 7 orders of magnitude lower than the high temperature fluorite-structured δ -phase. Tracer oxygen-18 diffusion studies of polycrystalline α - Bi_2O_3 at 600°C using an ion microscope with lateral resolutions of ~50 nm for the surface distributions of the oxygen isotopes have resolved the secondary fast migration pathways as well as the normal bulk diffusion profile in the grains. A grain boundary pathway for the oxygen migration is distinguished from other extended defects, some of which are also active in the overall oxygen diffusivity. This experimental study highlights the potential manipulation of the micro-structure of this material for enhanced oxygen ion conduction in intermediate temperature solid oxide fuel cells as has been shown for perovskite MIEC electrode materials.

Highlights (3 to 5, max 85 characters including spaces)

- Secondary oxygen migration paths in the α -phase of pure Bi_2O_3 are visualized.
- Tracer oxygen-18 with SIMS mapping analysis in an ion microscope.
- Grain boundary oxygen-diffusivity in α - Bi_2O_3 is similar to bulk YSZ & GDC.
- Microstructure manipulation potential for enhanced oxygen ion conduction.

Keywords

Bismuth oxide, α -phase, fast oxygen migration, grain boundary, extended defects

1. Introduction

The highest conductivity reported in any oxygen ion conducting solid electrolyte is the high temperature fluorite-structured δ -phase of Bi_2O_3 that is only stable in a narrow temperature range of 705°C to its melting point, 825°C [1]. The ionic conductivity is associated with the high intrinsic oxygen vacancy concentration of 25%, well above the typical values of vacancy concentrations ~5-10% achieved through aliovalent doping strategies in other fluorite-structured systems such as Gd-doped CeO_2 (GDC) and yttria-stabilized ZrO_2 (YSZ). The low temperature, monoclinic, α -phase of Bi_2O_3 has an oxygen-ion conductivity 7 orders of magnitude lower than the δ -phase, which is as expected in a low symmetry structure, with no inherent vacancies to facilitate ion migration.

The study by Bayliss *et al* [1] using oxygen-18 isotopic tracer and Secondary Ion Mass Spectrometry (SIMS) depth profiling methods to quantify the mass transport properties of the α - and δ -phases of Bi_2O_3 showed that the measured oxygen tracer diffusion profiles in the low temperature α -phase of Bi_2O_3 always deviated from a single bulk diffusion (D_b) process. The origin of these secondary, fast diffusion paths was assigned to fast grain boundary diffusion (D_{gb}) with the proviso that the fast conduction path could possibly be due to materials defects, such as porosity or cracking allowing gas phase permeation, or equipment artifacts present, such as SIMS sputter variations and crater roughening. The results reported in this contribution are an extension of the work presented in Bayliss *et al* [1] in which the secondary oxygen conduction path in the α -phase of bulk Bi_2O_3 is explored using oxygen-18 tracer exchange at 600°C and analysed by SIMS. The SIMS instrument used in this study is an ion microscope with nanoscale resolution and imaging capabilities for

distinguishing extended defects in the bulk Bi_2O_3 material such as pores and cracks. The issues associated with the SIMS sputter-etching technique have also been addressed using optical interferometry techniques.

2. Experimental

The details of the preparation of the solid Bi_2O_3 pellet from high purity powder (99.999% Sigma-Aldrich) is given by Bayliss [1]. It is important to note that the sample was sintered at a low temperature, 670°C to avoid the formation of the δ -phase and the other meta-stable polymorphs of Bi_2O_3 . The structure was verified by XRD after slow cooling to room temperature. The final density was ~90% of the theoretical value for α - Bi_2O_3 . The oxygen-18 tracer anneal of the solid pellet was at a temperature of 590.6°C for 17.3 minutes and an oxygen partial pressure of 200 mbar, Bayliss [1]. The normal oxygen pre-anneal was carried out for ~6 hours at the same temperature.

Microstructural examination of the original surface of the pellet was carried using an ion microscope (FIB200 SIMS Workstation, FEI, USA). A micro-focus beam of 30keV gallium ions is raster scanned over the surface of the sample to generate either the total positive sputtered secondary ion emission or the ion-induced secondary electron (SE) emission collected with a biased single-channel detector (channeltron) to form an image. Minimal sputter erosion of the surface for site selection occurs using a low current gallium ion current of <50 pA. No conducting coating was applied to the surface of the Bi_2O_3 pellet although the material has low electronic conductivity at room temperature. Surface charge compensation is achieved using an earthed 1 micron diameter tungsten needle probe located on the pellet surface in close proximity to the selected site. All the results from the selected area used the same beam current (346 pA) for acquiring the dynamic SIMS oxygen-16 and oxygen-18 negative secondary ion intensity maps, I^{O16} & I^{O18} and the images. The oxygen-18 isotopic fraction map, $I^{O18}/(I^{O18} + I^{O16})$, is derived directly without any image pixel shifts, Poisson corrections to the intensities or background subtraction. Finally the crater topography and depth is measured with a microscope-based white light interferometer (NewView 200, Zygo Corp., USA).

3. Results and discussion

3.1 Ion induced secondary ion micrographs

The ion-induced image shown in Figure 1 is formed from positive ions originating at the outmost atomic surface of the solid. There is no indication of surface charging for any of the surface features. The grains are visualised as smooth areas of approximately constant light contrast with a range of shapes and their boundaries slightly darker contrast changes but are approximately linear. These features enable the grain size distribution to be estimated for the histogram shown in Figure 2 for comparison with the diffusion length. The measured bulk oxygen self-diffusion at 600°C, D_b , is $1.5 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ [1], thus for the oxygen-18 anneal the corresponding diffusion length, $2\sqrt{D_b t}$ is ~0.8 microns. The grain size is significantly greater than the diffusion length so the conditions for Harrison type B kinetics [2] are valid. Cracks are visible in the image, Figure 1, and are highlighted with white arrows. The contrast profile measured across the lower right crack in Figure 1 indicates a beam spot size of <50 nm for the 346 pA current setting used for this image, slightly less than the image pixel resolution of 59 nm. Most of the cracks observed in Figure 1 are trans-granular but there is also an indication that some follow grain boundaries. Surface cracks were imaged on samples that were pre-annealed in normal oxygen only (not shown here). It is assumed the cracks in Figure 1 occurred during the 'roll-on' or 'roll-off' phase of either of the normal or tracer oxygen anneals.

Figure 1 Total positive secondary ion image of the pellet surface acquired by scanning a 346 pA beam of 30keV gallium positive ions. Several cracks are highlighted with white arrows.

Figure 2 Grain size histogram of 57 grains showing both the minimum and maximum dimensions of the grains.

3.2 Oxygen-18 isotopic fraction map

The oxygen-18 fraction map, Figure 3, is derived from depths between 1.5 microns and 3.0 microns, well below the depth of the bulk diffusion profile for the surface grains. Pixels with values of the isotopic fraction over 0.4 represent 3.78% of the total and are associated with

voids and a particularly noticeable horizontal line structure of re-deposited material at the top of the isotopic fraction map, an artefact of the sputtering with the gallium ion beam line-by-line raster [3]. The trans-granular cracks located in Figure 1, shown by the lower pair of white arrows are not visible on this image, and do not appear to have been active during the oxygen-18 anneal and so are most likely to have occurred during the 'roll-off' period at the completion of the oxygen-18 exchange anneal.

Figure 3 Oxygen-18 isotopic fraction map with a false colour scale. This map is of the same area as Figure 1. The parallel sides between the pairs of 'T' marks define the area for a profile plot across the grain boundaries, GB1 and GB2. Cracks located in Figure 1 are highlighted with the same white arrows.

To investigate the effect of diffusion into the grains from the grain boundary a block of data from Figure 3 defined by the 'T' marks is used for the isotopic fraction profile across the grain boundary (GB1). This block of data or selected matrix of isotopic fraction data was rotated through 20° anti-clockwise using the Matlab[4] software as if the data was a black and white image. This transformation allows the matrix dimensions to expand in size to accommodate the whole image after rotation. Pixel values are interpolated where necessary on a nearest neighbour basis. Finally pixel values are averaged column by column for the profile result that is plotted in Figure 4. The pixel interval reduces to 56 nm by this transformation. Note that the final image of the crater, Figure 5, shows that sputtering in

the region for the GB1 profile has left little indication of the contrast change interpreted as the grain boundary seen in Figure 1, in contrast to the cracks. The semi-infinite solution profile (SI Fit) from the diffusion equation [5] using the measured bulk oxygen self-diffusion at 600°C, D_b , from Bayliss [1] for these anneal conditions has been added to Figure 4 as expected for diffusion into both crystal grains from a bi-crystal boundary. The SI Fit is used for the left hand side of the peak at the grain boundary. As the profile on the right hand side (RHS) of the boundary is associated with a small grain, the sheet solution profile of the diffusion equation (Sheet Fit) [5] using the same diffusivity and a sheet thickness of 3 microns was chosen for the profile points on the RHS of the peak at the grain boundary. Note that the grain boundary width is expected to be negligible, ~1nm as suggested in Bayliss [1]. The lateral position of the diffusion equation solution profile in the plot, Figure 4, is judged by eye and is sensitive to position increments of approximately 10 nm along the distance axis. The surface exchange coefficient, k , used for both the SI Fit and Sheet Fit is the same and the value obtained by Bayliss [1], $5 \times 10^{-9} \text{ cm s}^{-1}$, even though the tracer bulk diffusion into the grains is occurring from the grain boundary at depths between 1.5 microns and 3 microns below the surface of the bulk Bi_2O_3 solid pellet. The measured isotopic fraction corresponding to the grain boundary position in Figure 4 is (0.124 ± 0.030) whilst the isotopic fraction was (0.159 ± 0.031) for the same grain boundary at a shallower depth range between 0.5 microns and 1.5 microns corresponding to a low concentration gradient of the tracer oxygen-18 in the grain boundary. In using the diffusion equation fits it is also assumed that the oxygen-18 isotopic fraction in the grain boundary rises to an approximately constant value for the whole duration of the exchange anneal. This is a reasonable assumption as it is shown by modelling and is in contrast to the grain free surface where the isotopic fraction is increasing throughout the anneal. The vertical scaling of the SI Fit and Sheet Fit were very similar, approximately a factor of 1.05 and fitted by eye.

A second grain boundary (GB2) indicated in Figure 3 was also analysed and gave a result (not shown here) that was indistinguishable with the profile for GB1, Figure 4. The angle between GB1 and GB2 is ~50°. The analysis by Bayliss [1] for the secondary, fast oxygen migration pathway as the grain boundary network assumed a grain boundary width of 1 nm for an oxygen diffusivity, D_{gb} , at 600°C of $3 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, a value that is very similar to the bulk diffusivity for GDC [6]. Even if the width of the grain boundary is expanded to

~10 nm as estimated from the fit in Figure 4 then the grain boundary diffusivity, D_{gb} , from Bayliss has to be reduced by an order of magnitude but remains comparable to the bulk diffusivity for YSZ [7].

Figure 4 Oxygen-18 isotopic fraction profile across the grain boundary labelled GB1 in Figure 3. Fraction values are plotted with a single standard deviation error bar. See section 3.1 for SI Fit and Sheet Fit profile details.

Figure 5 Total positive secondary ion image of the pellet surface after sputtering for the isotopic fraction map. The depth of this area is approximately 3 microns. Arrows highlighting cracks are in the same locations as Figure 1. The parallel sides between the pair of 'T' marks define the area for a profile plot across the grain boundary, GB1, as positioned in Figure 3.

3.3 Fast oxygen migration and cracks

The secondary electron (SE) image of the pellet surface after sputtering for the oxygen fraction map, Figure 6, is complementary to the positive ion image, Figure 5, but includes sub-surface information due to the mean free path of emitted electrons in the solid Bi_2O_3 and their sub-surface generation by the 30 keV gallium ions. The surface trans-granular crack in the lower RHS of the surface, Figure 6, is readily visible as a thin bright feature highlighted with the white arrow. The contrast profile across the crack is plotted in Figure 7. This crack is not seen in the isotopic fraction map, Figure 3, as it is assumed to have formed after the oxygen-18 exchange anneal. The 'T' marks in Figure 6 define a region that in Figure 3 appears to be an active grain boundary, GB3. The oxygen-18 data for this region has been extracted as an isotopic fraction profile in exactly the same procedure as for GB1 and GB2. The result is very similar and so isotopic fraction profile is represented in Figure 7 by the SI Fit profile used in Figure 4 but on this occasion for both sides of the boundary as the grains of the bi-crystal couple are large. The contrast profile for GB3 is additionally plotted in Figure 7 and is broad compared with the crack profile but not as broad as the SI Fit profile that indicates a bulk diffusion profile into the adjacent grains. Note that the contrast profiles for GB1 and GB2 are at background levels for the SE image, Figure 6, so neither grain boundary was resolved in this image. This implies that the grain boundary GB3 was active during the oxygen-18 exchanged but subsequently fractured obliquely within the first few nm of the surface.

Figure 6 Secondary electron image of the pellet surface after sputtering for the isotopic fraction map. Arrows highlighting cracks are in the same location as Figure 1. 'T' marks highlight the positions for the GB1 and GB3 grain boundary profiles.

Figure 7 Contrast profiles across the grain boundary labelled GB3 and the crack in Figure 6. See section 3.1 for SI Fit profile details. All three profiles have been arbitrarily centred with a common peak position.

4. Summary

This experimental study of oxygen-18 tracer diffusion at 600°C in poly-crystalline α -Bi₂O₃ has distinguished between bulk oxygen diffusion in the grains and the secondary fast migration pathways for oxygen. The artefacts of sputtering, extended defects such as voids and cracks are distinguished to show that grain boundaries are the fast migration paths. The methods used here are adequate to confirm the result in Bayliss [1] that the grain boundary diffusivity in pure α -Bi₂O₃ is similar to the bulk oxygen diffusivity of GDC and YSZ.

Microstructural engineering of nanostructures with a high density of aligned grain boundary and a high concentration of strain-induced defects has been reported for the perovskite oxide La_{0.8}Sr_{0.2}MnO_{3- δ} (LSM) by Saranya et al [8] and Navickas et al [9]. LSM was transformed from a “bulk” electronic conductor into a “bulk” mixed ionic and electronic conductor through the concept of grain boundary utilization. This experimental study has shown that pure poly-crystalline solid α -Bi₂O₃ exhibits the same potential for an intermediate-temperature electrolyte with enhanced ionic conduction without the strain-induced defects that will self-heal.

Acknowledgements

The authors would like to thank the EMRS-2016, Symposium D organizers for the invitation to present this study both orally and as a publication.

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Revision requested for SSI_2016_344

From: John Kilner (Solid State Ionics) [mailto:EviseSupport@elsevier.com]
Sent: 17 July 2016 07:27
To: Chater, Richard
Subject: Revision requested for SSI_2016_344

Ref: SSI_2016_344

Title: Fast Grain Boundary Oxygen Ion Diffusion in the Alpha-Phase of Bi₂O₃

Journal: Solid State Ionics

Dear Dr. Chater,

Thank you for submitting your manuscript to Solid State Ionics. I have received comments from reviewers on your manuscript. Your paper should become acceptable for publication pending suitable minor revision and modification of the article in light of the appended reviewer comments.

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Kind regards,

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Comments from the editors and reviewers:

-Reviewer 1

- The study by Chater et al. is a very welcome contribution to the research of conductivity enhancement/modification of ceramics for SOFC applications. It nicely illustrates the high grain boundary contribution to the oxygen conductivity in alpha-Bi₂O₃. This makes further investigations on nano/micro-structured material very interesting. There is just one minor point I would like to address.

p.6 line 25: The block of data is first rotated through an angle of 20° anti-clockwise before being averaged with the result for plotted in Figure 4.

I guess a word is missing in this sentence. Additionally, it would be nice for the interested but less informed reader if you could further illustrate what you mean by rotating block data.

-Reviewer 2

- The manuscript describes the continuation of earlier work published by the same group (s. ref. 1). It is another demonstration of instrumental capacity and experimental skill. The authors successfully attempt to differentiate the various potential paths for rapid oxygen transport in alpha-Bi₂O₃. The text is well written. On page 7, however, surface exchange and interface exchange should be distinguished. Extrapolating the present results into a route towards grain boundary engineering of a promising oxygen ion conductor, i. e. alpha-Bi₂O₃, seems, however, at least precocious.

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Manuscript Revision by authors of issues raised by Reviewers

Reviewer 1

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I guess a word is missing in this sentence. Additionally, it would be nice for the interested but less informed reader if you could further illustrate what you mean by rotating block data.

The authors thank Reviewer 1 for these comments and observations. The sentence revision and request for further information have been combined.

The original sentence

The block of data is first rotated through an angle of 20° anti-clockwise before being averaged with the result for plotted in Figure 4.

Has been replaced with,

This block of data or selected matrix of isotopic fraction data was rotated through 20° anti-clockwise using the MATLAB software as if the data was a black and white image. This transformation allows the matrix dimensions to expand in size to accommodate the whole image after rotation. Pixel values are interpolated where necessary on a nearest neighbour basis. Finally pixel values are averaged column by column for the profile result that is plotted in Figure 4.

-Reviewer 2

- The manuscript describes the continuation of earlier work published by the same group (s. ref. 1). It is another demonstration of instrumental capacity and experimental skill. The authors successfully attempt to differentiate the various potential paths for rapid oxygen transport in α - Bi_2O_3 . The text is well written. On page 7, however, surface exchange and interface exchange should be distinguished. Extrapolating the present results into a route towards grain boundary engineering of a promising oxygen ion conductor, i. e. α - Bi_2O_3 , seems, however, at least precocious.

The authors thank Reviewer 2 for their kind comments and observations. These are itemised below together with the revision details

1) Distinguishing ‘surface exchange and interface exchange’ on page 7
On page 7 of the manuscript, the following sentence acknowledges this distinction.
‘The surface exchange coefficient, k , used for both the SI Fit and Sheet Fit is the same and the value obtained by Bayliss [1], $5 \times 10^{-9} \text{ cm s}^{-1}$, even though the tracer bulk diffusion into the grains is occurring from the grain boundary at depths between 1.5 microns and 3 microns below the surface of the bulk Bi_2O_3 solid pellet.’

This sentence has been revised to clarify this point by being more explicit in pointing out the distinction.

‘The surface exchange coefficient, k , used for both the SI Fit and Sheet Fit is the same and the value obtained by Bayliss [1], $5 \times 10^{-9} \text{ cm s}^{-1}$, even though the tracer bulk diffusion into the grains is occurring from the grain boundary at depths between 1.5 microns and 3 microns below the surface of the bulk Bi_2O_3 solid pellet. Below the sample surface, oxygen exchange is ‘interface exchange’ and occurs between the grain boundary region and the bulk material of the grain but at the shallow depths of this measurement, Figure 3, the short and fast migration path from the surface in the grain boundary allows the surface exchange solution to give a good approximation to the diffusion profile in the grains plotted in Figure 4.’

2) Extrapolating the present results into a route towards grain boundary engineering of a promising oxygen ion conductor, i. e. α - Bi_2O_3 , seems, however, at least precocious.

This remark refers to an observation in the ‘Summary’ section

‘Microstructural engineering of nanostructures with a high density of aligned grain boundary and a high concentration of strain-induced defects has been reported for the perovskite oxide $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (LSM) by Saranya et al [8] and Navickas et al [9]. LSM was transformed from a “bulk” electronic conductor into a “bulk” mixed ionic and electronic conductor through the concept of grain boundary utilization. This experimental study has shown that pure poly-crystalline solid α - Bi_2O_3 exhibits the same potential for an intermediate-temperature electrolyte with enhanced ionic conduction without the strain-induced defects that will self-heal.’

The chemical stability of the α - Bi_2O_3 compound, its structure and phase were felt to be sufficiently demonstrated in this manuscript and Bayliss (1) for this predictive, perhaps precocious, comment on its merits once prepared as a nano-structured material.