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Rita Punni, Ian Gameson, Frank Berry, Colin Greaves. The local environment of cations in BiErReO. Journal of Physics and Chemistry of Solids, 2010, 69 (11), pp.2687. 10.1016/j.jpcs.2008.07.003 . hal-00614337

HAL Id: hal-00614337

<https://hal.science/hal-00614337>

Submitted on 11 Aug 2011

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Author's Accepted Manuscript

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PII: S0022-3697(08)00355-7
DOI: doi:10.1016/j.jpcs.2008.07.003
Reference: PCS 5658

To appear in: *Journal of Physics and Chemistry of Solids*

Received date: 7 April 2008
Revised date: 1 July 2008
Accepted date: 4 July 2008

Cite this article as: Rita Punni, Ian Gameson, Frank Berry and Colin Greaves, The local environment of cations in $\text{Bi}_{12.5}\text{Er}_{1.5}\text{ReO}_{24.5}$, *Journal of Physics and Chemistry of Solids* (2008), doi:10.1016/j.jpcs.2008.07.003

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The Local Environment of Cations in $\text{Bi}_{12.5}\text{Er}_{1.5}\text{ReO}_{24.5}$

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Abstract

The local environments of cations in a recently reported $\delta\text{-Bi}_2\text{O}_3$ -related phase stabilised by erbium and rhenium, and which shows exceptionally high oxide ion conductivity at low temperatures, have been examined by Bi L_{III} -, Er L_{III} - and Re L_{III} -edge extended X-ray absorption fine structure (EXAFS) measurements. The Bi L_{III} - and Er L_{III} -edge data recorded from the compound $\text{Bi}_{12.5}\text{Er}_{1.5}\text{ReO}_{24.5}$ revealed a high level of oxygen disorder and the adoption by bismuth and erbium of different local environments than those previously observed in erbium-doped $\delta\text{-Bi}_2\text{O}_3$. The Re L_{III} -edge EXAFS recorded from $\text{Bi}_{12.5}\text{Er}_{1.5}\text{ReO}_{24.5}$ endorsed the highly disordered nature

of the oxygen system and showed rhenium to adopt four fold oxygen coordination and to be significantly different from that of the local environment of rhenium in $\text{Bi}_{28}\text{Re}_2\text{O}_{49}$.

1.Introduction

$\delta\text{-Bi}_2\text{O}_3$ is observed as the high temperature cubic phase of bismuth oxide at temperatures exceeding 730°C . The material adopts a defect fluorite-related structure in which ca. 25% of the anion sites are vacant [1]. The basic structure of $\delta\text{-Bi}_2\text{O}_3$ phases (Figure 1) contains two partially occupied oxygen sites: $8c$ ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) and $32f$ (x , x , x) with $x \approx 0.3$ [2]. The anion vacancies facilitate an oxide ion conductivity [3] which is two- to three- orders of magnitude greater than that observed in calcium- or yttrium- stabilised zirconia [4]. The $\delta\text{-Bi}_2\text{O}_3$ -related structure can be retained at room temperature by doping with ca. 15-42 mol % of iso- or alio-valent cations [3-11] although the dopants appear to induce ordering of the anion vacancies and a consequent reduction in oxide ion conduction. The $\delta\text{-Bi}_2\text{O}_3$ structure has been stabilised by smaller rare earth cations and, for example by substituting with 20% erbium, conductivities at ca. 530°C comparable to those of stabilised zirconia at 830°C have been recorded [12, 13].

Figure 1 about here

We have recently reported [14] on the synthesis of new phases in which Bi_2O_3 is doped with both rare earth- and rhenium-cations. These materials have significantly higher low temperature ($<400^\circ\text{C}$) oxide ion conductivities than those previously reported for $\delta\text{-Bi}_2\text{O}_3$ -related phases and appear to be the best low-temperature isotropic oxide ion conductors currently known. Interestingly, neutron powder diffraction showed significant structural differences between these rare earth- and

rhodium- doped Bi_2O_3 -related phases and the simple rare-earth doped $\delta\text{-Bi}_2\text{O}_3$ materials [2,15] where the cations may undergo displacement and be accompanied by oxygen occupancy of interstitial sites.

We report here on an examination of the material of composition $\text{Bi}_{12.5}\text{Er}_{1.5}\text{ReO}_{24.5}$ by extended X-ray absorption spectroscopy (EXAFS) to investigate the local environment of the cation sites in these types of materials.

2.Experimental

The material of composition $\text{Bi}_{12.5}\text{Er}_{1.5}\text{ReO}_{24.5}$ was prepared from stoichiometric amounts of high purity metal powders which were intimately ground and heated in an alumina boat at 1073K for 12 hours. The product was reground and heated for a further two 12 hour periods at 1073K.

EXAFS measurements were performed at Station 9.3 (Bi L_{III} -, Er L_{III} - and Re L_{III} - edges) at the Synchrotron Radiation Source at Daresbury Laboratory operating at an energy of 2.0 GeV, an average current of 200 mA, and a Si (220) double crystal monochromator. The samples were mixed with boron nitride, pressed into 13mm discs and placed between adhesive tape. Data were collected at 80K in transmission mode using ion chambers filled with noble gases. The EXAFS oscillations were isolated after background subtraction of the raw data using the Daresbury program EXSPLINE [16] and converted into k space. The data were weighted by k^3 , where k is the photoelectron wave vector, to compensate for the diminishing amplitude of EXAFS at high k . The data were fitted using the Daresbury programme EXCURV98 [17].

3.Results and discussion

The Bi L_{III} edge EXAFS recorded from Bi_{12.5}Er_{1.5}ReO_{24.5} and their Fourier transforms are shown in Figure 2. The best fit parameters to the data are contained in Table 1.

Figure 2 about here

Table 1 about here

The Bi L_{III} EXAFS were not amenable to fitting beyond a first shell coordination of 1.84 oxygen atoms at a distance of 2.12 Å indicative of a high level of anion disorder in Bi_{12.5}Er_{1.5}ReO_{24.5}. The neutron powder diffraction data recorded [14] at 10K from Bi_{12.5}Er_{1.5}ReO_{24.5} were refined using a starting model based on δ -Bi₂O₃, space group Fm $\bar{3}$ m. The results indicated a shorter distance (2.293 Å) between bismuth and oxygen atoms located on the 32*f* (x,x,x) site than that between bismuth and oxygen atoms located on the 8*c* (¼,¼,¼) site (2.405 Å). The refinement of the data also showed that ca. 25% of the oxygen atoms were located on the 32*f* (x,x,x) site which equates to approximately 1.57 oxygen atoms. Hence we associate the first shell coordination of bismuth in Bi_{12.5}Er_{1.5}ReO_{24.5} as determined by EXAFS to reflect the dominating effect of the occupancy by oxygen of the 32*f* (x, x, x) site with a consequent shorter average bismuth-oxygen distance.

It is also interesting to note that whilst EXAFS investigations [18] of erbium-doped δ -Bi₂O₃ showed the first bismuth-oxygen shell to be highly disordered, our Bi L_{III} edge EXAFS data were not amenable to fitting to models used [18] for Er₂O₃/Bi₂O₃ solid solutions and, consistent with the neutron powder diffraction results [14], are indicative of differences between the local environment of bismuth in Bi_{12.5}Er_{1.5}ReO_{24.5} and of bismuth in erbium-doped δ -Bi₂O₃.

The Er L_{III} EXAFS recorded from Bi_{12.5}Er_{1.5}ReO_{24.5} and their Fourier transforms are shown in Figure 3 and the best fit parameters are collected in Table 1.

Figure 3 about here

The best fit to the data gave a first shell coordination of six oxygen atoms at a distance of 2.32Å. Shells at longer distances resisted detection and, as in the interpretation of the Bi L_{III} edge EXAFS, the result is consistent with a highly disordered anion system. The erbium-oxygen distance is slightly larger than that found [19] in Er₂O₃ where the average erbium-oxygen distance is 2.27Å. The erbium-oxygen distance in Bi_{12.5}Er_{1.5}O_{24.5} determined from Er L_{III} EXAFS of 2.32Å is consistent with the weighted average of the erbium to oxygen distances in the 8c site (2.30Å) and in the 32f site (2.41Å) as determined by neutron powder diffraction [14] at 10K. The result endorses the interpretation of the Bi L_{III} edge EXAFS in terms of different local environments of cations in Bi_{12.5}Er_{1.5}ReO_{24.5} as compared to those in erbium-doped δ -Bi₂O₃. The erbium-oxygen distance determined by EXAFS in Bi_{12.5}Er_{1.5}ReO_{24.5} is also larger than that of 2.27Å which was determined [18] by EXAFS in the (Bi₂O₃)_{0.6}(Er₂O₃)_{0.4} system and which was interpreted in terms of erbium enjoying similar environments in the solid solution as in pure Er₂O₃. The results from our examination by EXAFS of Bi_{12.5}Er_{1.5}ReO_{24.5} would suggest that the erbium and bismuth environments in Bi_{12.5}Er_{1.5}ReO_{24.5} are different from those in erbium-doped Bi₂O₃ and, in the case of erbium, may approach that of bismuth in δ -Bi₂O₃.

The Re L_{III} edge EXAFS recorded from Bi_{12.5}Er_{1.5}ReO_{24.5} and their Fourier transforms are shown in Figure 4 and the best fit parameters are collected in Table 1.

Figure 4 about here

The data were best fitted to four fold first shell oxygen coordination at 1.76 Å similar to our Re L_{III} edge EXAFS recorded from KReO₄, where [20] rhenium is tetrahedrally coordinated by oxygen at 1.7688 Å, and showed rhenium to be surrounded by four oxygen atoms at 1.74 Å. The smaller Debye–Waller factor for the rhenium coordination probably reflects the presence of the rhenium in discrete ReO₄ groups whereas the higher values for the bismuth– and erbium- coordination reflect the disordered nature of the framework. As with the refinement of the Bi L_{III}- and Er L_{III} – edge EXAFS, the highly disordered nature of the oxygen system precluded detection of more distant shells in the Re L_{III} edge data. Attempts to refine the first shell of the Re L_{III}-edge EXAFS to six oxygen atoms gave highly unsatisfactory fits to the data. The results therefore suggest that rhenium in Bi_{12.5}Er_{1.5}ReO_{24.5} is tetrahedrally coordinated and demonstrates a difference in local environment from that of rhenium in Bi₂₈Re₂O₄₉ which contains both tetrahedral- and octahedral-coordinated rhenium [21].

The influence of the cation displacement and local coordination on the exceptionally high oxygen ion conductivities of these materials is the subject of further investigation.

4. Conclusion

The low temperature oxide ion conductor of composition Bi_{12.5}Er_{1.5}ReO_{24.5} has been shown by EXAFS to contain a high level of oxygen disorder. The local environments of bismuth and erbium are different from those in erbium-doped δ -Bi₂O₃ and rhenium adopts a four-fold coordination which is very different from that in Bi₂₈Re₂O₄₉.

Acknowledgement

We thank EPSRC for financial support.

Accepted manuscript

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Table 1 Best fit parameters to the Bi L_{III}-, Er L_{III}- and Re L_{III}-edge EXAFS recorded from Bi_{12.5} Er_{1.5} Re O₂₄

Edge	Atom type	Coordination number	R [±] 0.03 (Å)	2sigma ² (Å ²)
Bi L _{III}	O	1.84	2.12	0.012
Er L _{III}	O	6	2.32	0.014
Re L _{III}	O	4	1.76	0.004

Legends to Figures

- Figure 1 Part of the δ -Bi₂O₃ unit cell showing the oxygen positions.
- Figure 2 Bi L_{III} edge EXAFS recorded at 80K from Bi_{12.5} Er_{1.5} ReO_{24.5} and corresponding Fourier transform. The experimental data are indicated by the solid line.
- Figure 3 Er L_{III} edge EXAFS recorded at 80K from Bi_{12.5} Er_{1.5} ReO_{24.5} and corresponding Fourier transform. The Experimental data are indicated by the solid line.
- Figure 4 Re L_{III} edge EXAFS recorded at 80K from Bi_{12.5}Er_{1.5}ReO_{24.5} and corresponding Fourier transform. The experimental data are indicated by the solid line.