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Variable temperature neutron diffraction study of crystal structure and transport pathways in oxide ion conductors Bi$_{12.5}$Ln$_{1.5}$ReO$_{24.5}$ (Ln = Lu, Er)

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Abstract

Samples of highly conducting Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$ and Bi$_{12.5}$Er$_{1.5}$ReO$_{24.5}$ have been studied by neutron powder diffraction at room temperature for both phases and at 25 °C ≤ T ≤ 500 °C in the case of Bi$_{12.5}$Er$_{1.5}$ReO$_{24.5}$. Both materials crystallize in the cubic δ-Bi$_2$O$_3$ related system, space group Fm-3m. Changes in the oxygen sublattice at 25 °C ≤ T ≤ 500 °C have been investigated by the Rietveld and maximum entropy methods.

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1. Introduction

The high ionic conductor δ-Bi$_2$O$_3$ crystallises in a defect fluorite related structure, space group Fm-3m [1]. Its crystal structure is typically described with cations occupying the 4$a$ (0 0 0) position and oxygens in 8$c$ ($\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$) with some interstitial oxygens shifted towards ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) [2], however slightly different systems to model the disordered distribution of the oxide ions have been proposed [3,4]. Its high ionic conduction is linked to the presence of ~25% oxygen ion vacancies in the structure [1,5]. The phases exist only above 730 °C, and attempts to stabilise the high oxide ion conductor δ-phase at lower temperature have been the subject of numerous studies [6,7]. Amongst them, the stabilised δ-phase family of compounds with composition Bi$_{12.5}$Ln$_{1.5}$ReO$_{24.5}$ presents very high ionic conductivity at low temperature [8] and their detailed crystal structure characteristics appear to differ from those of Bi$_2$O$_3$ doped with rare-earth only. In these materials, rhenium is apparently tetrahedrally coordinated at the local scale [9], while in the related ordered phase both tetrahedral ReO$_4$ and octahedral ReO$_6$ species are present [10,11]. To date NPD data have been obtained only for T ≤ 25 °C, and indicate significant differences in the O positions compared with conventional lanthane stabilised phases: the interstitial oxygen position is significantly displaced and is thought to be related to the enhanced conductivity [8]. In the present study we investigate the crystal structure of the Bi$_{12.5}$Ln$_{1.5}$ReO$_{24.5}$ (Ln = Lu, Er) system and the change in oxygen sublattice for 25 °C ≤ T ≤ 500 °C in Bi$_{12.5}$Er$_{1.5}$ReO$_{24.5}$.

2. Experimental

Polycrystalline samples of Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$ and Bi$_{12.5}$Er$_{1.5}$ReO$_{24.5}$ have been prepared by traditional solid state synthesis from stoichiometric quantities of Bi$_2$O$_3$, Lu$_2$O$_3$/Er$_2$O$_3$, and NH$_4$ReO$_4$. The powders were thoroughly mixed and ground, and subsequently heated in air at 800 °C for 24 h with one intermediate grinding and allowed to cool slowly in the furnace.

X-ray powder diffraction (XRD) data were obtained at room temperature on a Siemens D5000 diffractometer operating in transmission mode (Ge primary beam monochromator giving Cu-Kα$_1$ radiation, wavelength 1.5406 Å). Neutron powder diffraction (NPD) data of the samples were collected on the D2B diffractometer (wavelength 1.5943 Å) at the Institut Laue Langevin, Grenoble, France. Approximately 8 g of each material was loaded in a cylindrical vanadium can of 8 mm diameter for data collection at temperatures of 25 °C, 200 °C, 300 °C, 400 °C, and 500 °C.

Rietveld refinements were carried out using GSAS [12] with EXPGUI graphical user interface [13]. The nuclear density distribution was obtained by the maximum entropy method (MEM)/MEM-based pattern fitting (MPF) method using the program PRIMA [14] with 128 × 128 × 128 pixels in conjunction with Rietan-FP software [15].
Crystal structures and nuclear density distribution representations were drawn with VESTA [16].

For electrical measurements, dense sintered pellets of approximately 8 mm diameter and 2 mm thickness were prepared and silver electrodes painted on both surfaces. Conductivity was measured over the temperature range 200–600 °C by a.c. impedance spectroscopy with a Solartron SI 1260 impedance analyzer in the frequency range 1 Hz to 10⁶ Hz.

3. Results and discussion

XRD data confirmed the phase purity of the samples. As with other lanthanide doped bismuth rhenium oxides, they both adopt the cubic Fm-3m space group, lattice parameter $a = 5.5592(1)$ Å and 5.5687(1) Å for Bi₁₂₅Lu₁.₅ReO₂₄.₅ and Bi₁₂₅Er₁.₅ReO₂₄.₅ respectively at 25 °C.

Conductivity measurement (Fig. 1) demonstrated the high conductivity of the materials with values close to the ones previously reported [8]. Both materials have conductivity higher than conductivity of the materials with values close to the ones doped Bi₂O₃ by Boyapati et al. [17] and Y-doped Bi₂O₃ by Abrahams et al. [18]; while in the Bi₃Ta₁.₅O₇ crystal structure as a starting model. The direct oxide-ion diffusion pathway along the $b$-axis is observed for Y₀.₇₈₅Ta₀.₂₁₅O₁.₇₁₅ [23], as opposed from straight pathway is explained by the repulsion of anion to maintain a reasonable distance. However, a straight pathway is observed for Y₀.₇₈₅Ta₀.₂₁₅O₁.₇₁₅ [23], as is the case for the present material. This suggests that Ta and Re cations might play a similar role in these systems.

The direct oxide-ion diffusion pathway along the $<100>$ direction is visible at 400 and 500 °C, with coherent scattering length of 0.21 f. Å⁻³ at the 24d (0.5, 0.25, 0.25) site (distances cation – 24d site = 1.99 Å). Some density “bulges” from the tetrahedral volume covering the 8c and 32f sites pointing toward the $<111>$ direction and the 24e (0.33 0 0) site, are also present. This suggests a possible supplementary curved conduction path along the $<110>$ direction going through the 8c/32f 24e 8c/32f sites around the cation (distances cation – 24e site = 1.86 Å). Reducing the coherent scattering length to 0.11 f. Å⁻³ allows visualising the pathway (Fig. 6).

Fig. 1. Arrhenius plot of total conductivity for Bi₁₂₅Lu₁.₅ReO₂₄.₅ and Bi₁₂₅Er₁.₅ReO₂₄.₅.

Fig. 2. Evolution of lattice parameter with temperature for Bi₁₂₅Lu₁.₅ReO₂₄.₅ and Bi₁₂₅Er₁.₅ReO₂₄.₅.

It is interesting to note that the different nuclear densities associated to anion distribution at (i) 200–300 °C and (ii) 400–500 °C appear to reflect the non linear behaviour of atomic parameter variation with temperature. Non linear evolution of lattice parameter.
with temperature in Bi$_{3}$Ta$_{0.50}$Nb$_{0.50}$O$_{7}$, resulting in slightly higher than expected cell volume at higher temperature, has been explained by the increased occupancy at the 24d position – which is interstitial to the cubic closed packed (ccp) fluorite lattice – at elevated temperatures [19]. Since in the present materials nuclear densities are observed at the 24d site at 400 and 500 °C only, this explanation can also be applied to the present case.

### 4. Conclusions

Both Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$ and Bi$_{12.5}$Er$_{1.5}$ReO$_{24.5}$ crystallise in the cubic 6-$\beta$-Bi$_2$O$_3$ type system. New information on the evolution with temperature in the oxygen sublattices of the highly disordered Bi–Ln–Re–O system has been collected. At 500 °C, an oxide ion diffusion pathway along $<100>$ is clearly observed. Contrarily to most Bi$_2$O$_3$-

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**Table 1**

Final atomic positions for Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$ (BiLu) and Bi$_{12.5}$Er$_{1.5}$ReO$_{24.5}$ (BiEr) from Rietveld refinement. Space group Fm-3m (225); all cations in 4a $(0,0,0)$, O(1) in 8c $(1/4,1/4,1/4)$, O(2) in 32f $(x,x,x)$. Cations occupancies Bi/Ln/Re = 0.8333/0.1/0.0667.

<table>
<thead>
<tr>
<th></th>
<th>BiLu-25°C</th>
<th>BiEr-25°C</th>
<th>BiEr-200°C</th>
<th>BiEr-300°C</th>
<th>BiEr-400°C</th>
<th>BiEr-500°C</th>
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<td>$a$ (Å)</td>
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<td>5.569(1)</td>
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<td>5.594(2)</td>
<td>5.612(2)</td>
<td>5.631(3)</td>
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<tr>
<td>$x$ 3f</td>
<td>0.364(1)</td>
<td>0.368(1)</td>
<td>0.359(1)</td>
<td>0.356(1)</td>
<td>0.354(1)</td>
<td>0.354(1)</td>
</tr>
<tr>
<td>Occ O(1)</td>
<td>0.592(5)</td>
<td>0.586(5)</td>
<td>0.578(5)</td>
<td>0.568(5)</td>
<td>0.554(5)</td>
<td>0.554(6)</td>
</tr>
<tr>
<td>Occ O(2)</td>
<td>0.060(1)</td>
<td>0.053(1)</td>
<td>0.053(1)</td>
<td>0.053(1)</td>
<td>0.061(1)</td>
<td>0.066(1)</td>
</tr>
<tr>
<td>Usio cations</td>
<td>4.55(4)</td>
<td>3.92(4)</td>
<td>3.33(2)</td>
<td>5.63(3)</td>
<td>6.21(4)</td>
<td>7.01(4)</td>
</tr>
<tr>
<td>Usio oxygens</td>
<td>11.5(1)</td>
<td>10.2(1)</td>
<td>11.7(1)</td>
<td>11.8(1)</td>
<td>11.9(1)</td>
<td>12.6(1)</td>
</tr>
<tr>
<td>$\chi^2$ (47 var.)</td>
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<td>2.780</td>
<td>3.478</td>
<td>3.304</td>
<td>2.887</td>
<td>2.696</td>
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<tr>
<td>Rwp</td>
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<td>0.0237</td>
<td>0.0274</td>
<td>0.0268</td>
<td>0.0251</td>
<td>0.0243</td>
</tr>
</tbody>
</table>

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Fig. 3. Final Rietveld plot of a) Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$ and b) Bi$_{12.5}$Er$_{1.5}$ReO$_{24.5}$ at room temperature.
fluorite related systems, the pathway in the \( <100> \) direction is not curved but straight. An additional pathway in the \( <110> \) direction passing through the \( 24e \) \((0.33 0 0)\) site is also suggested. These features would explain the enhanced oxide ion conductivity observed in these materials.

Acknowledgments

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References

Fig. 5. 3D nuclear-density distribution of Bi$_{12.5}$Er$_{1.5}$ReO$_{24.5}$ at a) 25 °C, b) 300 °C, c) 500 °C.

Fig. 6. Nuclear-density distribution on the (110) plane of Bi$_{12.5}$Er$_{1.5}$ReO$_{24.5}$ at 500 °C. Saturation level 0 – 5%, with contours lines in the range 0.1 to 2 f Å$^{-3}$ (0.2 f Å$^{-3}$ step). Arrows indicate apparent oxide ion diffusion paths along the 100 and 110 directions.