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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 4a (0 0 0) position and oxygens in 8c (¼ ¼ ¼) with some interstitial oxygens shifted towards (½, ½, ½) [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 is stable 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$_6^{5-}$ 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-Kα1 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 pellet 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 5.5697(1) Å for Bi₁₂.₅Lu₁.₅ReO₂₄.₅ and Bi₁₂.₅Er₁.₅ReO₂₄.₅ respectively at 25°C.

Conductivity measurement (Fig. 1) demonstrated the high conductivity of the materials with values close to the ones doped Bi₂O₃ by Boyapati et al.[17] and Y-doped Bi₂O₃ by Abrahams positions (\(\sigma = 5.5592(1)\) Å and 5.5697(1) Å for Bi₁₂.₅Lu₁.₅ReO₂₄.₅ and Bi₁₂.₅La₁.₅ReO₂₄.₅). This follows the general trend of stabilized lanthanide doped \(\delta\)-Bi₂O₃, which generally present higher conductivity with increased dopant ionic radius.

NPD data Rietveld refinements were performed using data from reference [8] based on \(\delta\)-Bi₂O₃ crystal structure as a starting model. Lattice parameter variation with temperature deviates from linearity (Fig. 2), which might indicate of a redistribution of oxide ions.

In their study of pure and Y-doped \(\delta\)-Bi₂O₃, Battle et al. [2] observed the presence of interstitial oxygens on 32f (xxx) site in both cases, with another interstitial oxygen in 48i (\(\frac{1}{2}x\frac{1}{2}x\)) site and displacement of cations to the 24e (x 0 0) site in the case of the Y-doped sample. Three oxygen positions (8c, 32f, 48i) were also reported with several lanthanide-doped Bi₂O₃ by Boyapati et al. [17] and Y-doped Bi₂O₃ by Abrahams et al. [18]; while in the Bi₁₂.₅Ta₁₋ₓNbₓO₁.₇₁₅ system some oxygens are located in 24d (0.5, 0.25, 0.25) rather than the 48i site [19].

Our Rietveld refinements of Bi₁₂.₅Ln₁.₅ReO₂₄.₅ (Ln = Lu, Er) indicate that the cations occupy the 4a (0 0 0) site and that anion positions can be modelled by partial occupancy of 8c and 32f sites (Table 1) while possible occupancy of the 48i position is less clear (Fig. 3).

Due to the complicated distribution of anions in these systems, we chose to represent it with nuclear densities obtained by the MEM/MPF methods instead of the classical split-atom system. The methods can provide precise nuclear/electron distribution, is less prone to termination ripples than Fourier methods, and can also indicate to anion distribution from the tetrahedral volume covering the \(8c\) and \(32f\) sites (Table 1) while possible occupancy of the \(48i\) position is less clear (Fig. 3).

After completion of the iterative MEM/MPF procedure, the reliability factors \(R_B\) (R-Bragg factor; also denoted by \(R_b\)) and \(R_F\) (R-structure factor) improved to final values of (%): \(R_B = 4.091, R_F = 1.461\) (Bi₁₂.₅–

\[\text{Lu₁.₅ReO₂₄.₅}, 25^\circ C\]); \(R_B = 3.844, R_F = 1.024\) (Bi₁₂.₅Er₁.₅ReO₂₄.₅, 25°C); \(R_B = 3.095, R_F = 1.342\) (200°C); \(R_B = 2.789, R_F = 1.373\) (300°C); \(R_B = 2.988, R_F = 1.404\) (400°C); \(R_B = 2.487, R_F = 1.508\) (500°C). MEM nuclear density distribution maps on the (110) plane of Bi₁₂.₅Lu₁.₅ReO₂₄.₅ at 25°C and Bi₁₂.₅Er₁.₅ReO₂₄.₅ at various temperatures are displayed in Fig. 4. Examination of nuclear density distribution suggests some cation disorder with slight displacements from their ideal 4e position, but the most obvious feature concerns the disorder in oxide ions positions. As expected, the nuclear densities associated to oxide ions spread over a wide area, forming a continuous tetrahedral volume roughly covering the \(8c\) and \(32f\) positions, which is observed in other fluorite structured materials both experimentally [20,21] and theoretically [22]. This is observed at all studied temperatures and the extent of this volume increases with temperature, which is consistent with higher atomic displacement parameters at higher temperatures. Some differences can however be observed at different temperatures (Figs. 4 and 5).

At 200 – 300°C nuclear densities are localised in the tetrahedral volume roughly covering the \(8c\) and \(32f\) positions with “bulges” of nuclear densities pointing toward the 48i position, while at 400 and 500°C continuous nuclear densities forming a straight line along the \(<100>\) direction are found, indicative of oxide-ion diffusion pathway along that direction. In the literature, curved pathways along the \(<100>\) direction passing through the 48i site are generally observed in fluorite materials [20], the prevalence of curve pathway as opposed from straight pathway is explained by the repulsion between cation and anions, the curved pathway allowing the cation–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 ~ 1.98Å). Some density “bulges” from the tetrahedral volume covering the \(8c\) and \(32f\) sites pointing toward the \(<111>\) direction, and at 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 ~ 1.86Å). Reducing the coherent scattering length to 0.11 f. Å⁻³ allows visualising the pathway (Fig. 6).

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.

### Table 1

<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>
<td>5.5591(1)</td>
<td>5.5698(1)</td>
<td>5.5860(2)</td>
<td>5.5948(2)</td>
<td>5.6118(2)</td>
<td>5.6318(3)</td>
</tr>
<tr>
<td>x 32f</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>0.060(1)</td>
<td>0.062(1)</td>
<td>0.066(1)</td>
<td>0.066(1)</td>
</tr>
<tr>
<td>Usio cations</td>
<td>4.55(4)</td>
<td>3.92(4)</td>
<td>5.33(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>χ² (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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<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>

### 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-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$_3$-

![Fig. 3](image-url)
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.