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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 ($\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$) 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 phase 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 lanthanide 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-K$_\alpha$ 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 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].

The direct oxide-ion diffusion pathway along the \( 100 \) direction is found, indicative of oxide-ion diffusion along this direction. In the literature, curved pathways along the \( 100 \) direction passing through the \( 48i \) site are generally observed in 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, 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).

![Fig. 1. Arrhenius plot of total conductivity for Bi₁₂₅Lu₁₅ReO₂₄₅ and Bi₁₂₅Er₁₅ReO₂₄₅.](image-url)

![Fig. 2. Evolution of lattice parameter with temperature for Bi₁₂₅Lu₁₅ReO₂₄₅ and Bi₁₂₅Er₁₅ReO₂₄₅.](image-url)
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
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 (000), 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>BiLu-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>5.5948(2)</td>
<td>5.6118(2)</td>
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<td>0.368(1)</td>
<td>0.359(1)</td>
<td>0.356(1)</td>
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<td>Occ O(2)</td>
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<td>Uiso cations</td>
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<td>3.92(4)</td>
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<td>6.21(4)</td>
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<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>
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<td>2.780</td>
<td>3.478</td>
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<td>2.887</td>
<td>2.696</td>
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<tr>
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<td>0.0237</td>
<td>0.0274</td>
<td>0.0268</td>
<td>0.0251</td>
<td>0.0243</td>
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</tbody>
</table>

#### 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.

### 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 \(\delta\)-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$_3$-
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. 4. Nuclear-density distribution on the (110) plane of a) Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$ at 25 °C and Bi$_{12.5}$Er$_{1.5}$ReO$_{24.5}$ at b) 25 °C, c) 200 °C, d) 300 °C, e) 400 °C, f) 500 °C. Saturation level 0–5% with contours lines in the range 0.2 to 2 f. Å$^{-3}$ (0.2 f. Å$^{-3}$ step). The maximum densities corresponding to 100% are: for Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$: 53.91 f. Å$^{-3}$ at 25°C; for Bi$_{12.5}$Er$_{1.5}$ReO$_{24.5}$: 51.04 f. Å$^{-3}$ at 25°C; 38.31 f. Å$^{-3}$ at 200°C, 44.52 f. Å$^{-3}$ at 300°C, 53.20 f. Å$^{-3}$ at 400°C, 43.32 f. Å$^{-3}$ at 500°C. The black crosses indicate Wyckoff position 24d (0.5, 0.25, 0.25).
Fig. 5. 3D nuclear-density distribution of Bi₁₂.₅Er₁.₅ReO₂₄.₅ at a) 25 °C, b) 300 °C, c) 500 °C.

Fig. 6. Nuclear-density distribution on the (110) plane of Bi₁₂.₅Er₁.₅ReO₂₄.₅ 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.