In this study, after doping Lu$_2$O$_3$ to α-Bi$_2$O$_3$ in the range of 11% ≤ n ≤ 20% in a series of different mole ratios, heat treatment was performed by applying a cascade temperature rise in the range of 700-800 °C for 72 hours and new phases were obtained in the (Bi$_2$O$_3$)$_{1-x}$(Lu$_2$O$_3$)$_x$ system. After 72 hours of heat treatment at 800 °C, mixtures containing 14-16% Lu$_2$O$_3$ formed a face-centered cubic phase. Mixtures containing 11–13%, 17%, 18% mole Lu$_2$O$_3$ were subjected to a quenching process at 825 °C and face-centered cubic phases were obtained. With the help of XRD, the crystal systems and lattice parameters of the solid solutions were obtained and their characterization was carried out. Thermal measurements were made using a simultaneous DTA/TG system. The total conductivity ($\sigma_T$) in the δ-Bi$_2$O$_3$ doped with Lu$_2$O$_3$ system was measured using the four-probe DC method. Keywords: Bismuth oxide; lutesium oxide; oxygen ionic conductivity; X-ray techniques; thermal analysis.

**Keywords:** Bismuth oxide; Lutesium oxide; Oxygen ionic conductivity; X-ray techniques; Thermal analysis.

**INTRODUCTION**

Up to now, researchers have reported six polymorphs of bismuth trioxide (Bi$_2$O$_3$). These are the monoclinic (α-Bi$_2$O$_3$), body-centered cubic (bcc) (γ-Bi$_2$O$_3$), face-centered cubic (fcc) (δ-Bi$_2$O$_3$), tetragonal (β-Bi$_2$O$_3$), triclinic (ω-Bi$_2$O$_3$) and orthorhombic (ε-Bi$_2$O$_3$) phases.

The α-phase is stable at room temperature while the other five forms are unstable crystal modifications that are formed at high temperatures. If pure α-Bi$_2$O$_3$, whose melting temperature is 824 °C, is heated up to about 729 °C, it is transformed into the δ-Bi$_2$O$_3$ phase, which is stable at high temperature, and this phase is stable up to melting point. When it is cooled again, it transforms into the β-Bi$_2$O$_3$ phase at ~650 °C and the γ-Bi$_2$O$_3$ phase at ~639 °C. If the β- and γ-phases are cooled to lower temperatures, they are transformed into the α-Bi$_2$O$_3$ phase again at around ~500 °C. Orthorhombic (ε-Bi$_2$O$_3$) and triclinic phases (ω-Bi$_2$O$_3$), of which there is scarce information, can be obtained with notable special synthesis reactions and hydrothermal heat treatment processes at 240 °C and 800 °C respectively.

Solid electrolytes are the most important components of solid-state electrochemical devices and are becoming increasingly important for applications in energy conversion, chemical processing, and sensing and combustion control. Bismuth oxide systems exhibit high oxide ionic conductivity and have been proposed as good electrolyte materials for applications such as solid oxide fuel cell and oxygen sensors. However, due to their instability under low oxygen partial pressure conditions there has been difficulty in developing these materials as alternative electrolyte materials compared to state of the art cubic stabilized zirconia electrolyte. Bismuth oxide and doped bismuth oxide systems exhibit a complex array depending on dopant concentration, temperature and atmosphere.

**EXPERIMENTAL**

The Lu$_2$O$_3$ was added to the α-Bi$_2$O$_3$ in the range of 11% ≤ n ≤ 20% mole in different ratios. The combined substances were milled in an agate mortar and were subjected to 72 hours of heat treatment in a porcelain crucible. The mixtures were heat treated from 700 °C to 800 °C, with a rise of 50 °C per step. After each reaction, the products were cooled gradually until they reached room temperature. After each solid-state reaction, the product was examined to detect whether there was any change in the mass of each powder sample. Powder patterns were recorded using the XRD method and their crystal systems were detected. XRD data were recorded with a Bruker AXS D8 Advance model diffractometer (Bragg-Brentano geometry, graphite monochromator.
with CuKα radiation, 0.002° pitch angle, 2θ = 10°-90°). Thermal measurements were made by using a simultaneous DTA/TG system (Shimadzu FC-60 type). The δ-Bi2O3 samples doped with Lu2O3 were heated at a rate of 10 °C min⁻¹ from room temperature to 830 °C. Measurements were made in a 60 mL min⁻¹ nitrogen atmosphere using a platinum sample holder and an α-Al2O3 inert reference substance. The total electrical conductivity (σT) measurements were made on pelletized samples (diameter 10 mm, thickness ~1 mm) using a four-probe DC method in the temperature range 100 °C – 750 °C. To reduce contact resistance, fine platinum wires were attached directly to the surface of the samples. All data were made by a Keithley 2400 source meter and a Keithley 2700 electrometer, which are controlled by computer.

RESULTS AND DISCUSSION

The minimum temperature needed to obtain a crystal system that is stable in its simple phase under reaction circumstances is 800 °C. Solid solutions were obtained in δ-Bi2O3 crystallized in a face-centered cubic crystal system and in (Bi2O3)1-x(Lu2O3)x in the range of 0.11 ≤ x ≤ 0.18 mole fractions. Stable δ-phases were obtained by applying a quenching process at 825 °C from the powder samples which could not preserve their phase stability while being cooled to room temperature after 72-hour heat treatment. Mixtures containing 11, 12, 13, 17% and 18% mole Lu2O3 were subjected to a quenching process at 825 °C tetragonal phases were obtained. When x = 0.19 and 0.20, reaction conditions and doping ratio are inadequate to achieve crystallization in a stable system. The powder patterns of 17% mole Lu2O3 doped solid solution are given in Fig. 1 as a sample.

All the patterns of the samples indexed in the face-centered cubic crystal system show a similarity with the designs in Fig. 1. The unit cell parameters of the δ-phases are given in Table 1.

Producing a phase in the (Bi2O3)1-x(Lu2O3)x system requires a long duration (72 h) of heat application. In solid-state reactions that take place at high temperature, lutesium(III) ions are diffused gradually into the Bi2O3 lattice. If the doping process is successful, diffused lutesium (III) cations prefer to change place with bismuth(III) cations in the lattice. This situation is thought to cause non-stoichiometry and transformation to a defect structure in the lattice as well as causing O²⁻ ion conductivity.

In Fig. 2, the electrical conductivity plots of δ-Bi2O3 doped with 17% mole Lu2O3 content are presented, and the σT plots for the other δ-Bi2O3 phases are quite similar.

<table>
<thead>
<tr>
<th>mole% Lu2O3</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (pm)</td>
<td>551</td>
<td>551</td>
<td>551</td>
<td>550</td>
<td>550</td>
<td>550</td>
<td>550</td>
<td>550</td>
</tr>
<tr>
<td>V x 10⁶ (pm³)</td>
<td>167</td>
<td>167</td>
<td>167</td>
<td>166</td>
<td>166</td>
<td>166</td>
<td>166</td>
<td>166</td>
</tr>
</tbody>
</table>

These data were obtained during a repeated heating run at a constant heating rate in atmosphere. The electrical conductivity of δ-Bi2O3 doped with 11-18% mole percentage Lu2O3 increased with increasing temperature up to ~750 °C and a sharp increase in conductivity was not observed up to 750 °C.

The DTA/TG measurements also suggested that the phase transition was not observed on the DTA curve at about the same temperature range (Fig. 3).

The experimental results showed that in our samples the oxygen lattice points of the δ-Bi2O3 doped with Lu2O3.

![Fig. 1. XRD patterns of δ-Bi2O3 doped with 17% mol Lu2O3, (a) at 700 °C, (b) at 750 °C, (c) at 800 °C, (d) at 825 °C, water quench.](image1)

![Fig. 2. Electrical conductivity plot of δ-Bi2O3 doped with 17% mol Lu2O3.](image2)
were not completely occupied with oxygen ions. If the oxygen sub-lattices were fully occupied by $O^{2-}$ ions, the Lu$_2$O$_3$ doped $\delta$-Bi$_2$O$_3$ phases would not show such a high degree of electrical conductivity. Some of the oxygen lattice points located around the tetrahedral sites may have been vacant, forming an oxygen vacancy. These oxygen vacancies were filled randomly with neighboring oxygen ions at an increasing rate as the temperature increased. Jumping oxygen ions left their former sites vacant, thus another vacancy was formed, since this process was random, the total oxygen flow was zero in any direction without an applied electric field.

The ionic conductivity of $\delta$-Bi$_2$O$_3$ phases doped with Lu$_2$O$_3$ increased with increasing temperature. It was proposed that this was related to ionic mobility, which rises with increasing temperature. At elevated temperatures, the thermal vibrational energy of the ions increased causing a higher oxygen ion-jumping rate. Although oxygen vacancies were present in the crystal structure at low temperatures (below 200 °C), the thermal energy of the anions was not high enough for them to jump out of their lowest energy positions. Thermal vibrations may also have assisted the jumping process for a short time by either shortening the jumping distance or by widening the jumping channels through the crystal.

CONCLUSIONS

As a result of this research the $\delta$-phases of Bi$_2$O$_3$ substances which are unstable at room temperature were obtained by doping a Lu$_2$O$_3$ substance to $\alpha$-Bi$_2$O$_3$ substance with solid-state reactions. The effective factors in the synthesis of these polymorphs are high temperature application, reaction duration and the amount of Lu$_2$O$_3$ doped. It was observed that increasing the Lu$_2$O$_3$ amount influenced phase stability and those solid solutions that had a greater doping amount were more resistant to high temperature.

It can be concluded from the change of Lu$^{3+}$ with crystal structured Bi$^{3+}$ cations that non-stoichiometric phases are synthesized. Since the synthesis process was performed using a high temperature application that lasted for a long period, we can say that lutetium cations diffuse in the crystal structure very slowly. Face-centered cubic $\delta$-phase (Bi$_2$O$_3$)$_{1-x}$(Lu$_2$O$_3$)$_x$ ($x = 0.11 - 0.19$) binary oxide compounds possessing oxygen ionic conductivity were synthesized. The non-stoichiometry of the $\delta$-Bi$_2$O$_3$ phase was thought to lead to interesting electrical properties.

The ionic conductivity in the $\delta$-Bi$_2$O$_3$ phases supports the view that there is an average occupation of oxide ions in the oxygen lattice sites, which can move from site to site through the bismuth sub-lattice. The sample with the highest conductivity of $-1.555 \Omega^{-1}\text{cm}^{-1}$ at 750 °C was the $\delta$-phase of the (Bi$_2$O$_3$)$_{0.83}$(Lu$_2$O$_3$)$_{0.17}$ system.

ACKNOWLEDGEMENTS

This work was supported by Erciyes University (EUBAP).

REFERENCES