Preparation and Characterization of New Oxide Ion Conductors in Bi$_2$O$_3$-As$_2$O$_5$ System

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Abstract: Materials in $x$Bi$_2$O$_3$-As$_2$O$_5$ binary system: $1 \leq x \leq 7$, were prepared by solid state reaction. XRD shows that single phase materials were formed when $x = 5$, $5.5$, $5.667$, $5.75$, $6$ and $7$. The symmetry and space group of the materials were determined. Compositions with $5 \leq x \leq 6.25$ are solid solutions. Electrical properties of the single phase materials were studied using ac impedance spectroscopy at a frequency range of 10 Hz to 13 MHz. These materials are thermally stable and appear to be oxide ion conductors. Highest conductivity was obtained in Bi$_{13}$As$_{12.5}$O$_{44.5}$ with $\sigma$ value of $5.66 \times 10^{-5}$ ohm$^{-1}$ cm$^{-1}$, $E_a = 0.72$ eV at 300°C.

Key words: bismuth arsenate, oxide ion conductor

Introduction

A number of investigations have been undertaken on the crystal structure of materials in the Bi$_2$O$_3$-As$_2$O$_5$ system; however, studies on the physical properties of these materials are limited. A nonstoichiometric sillenite-type phase was found in the Bi-rich portion of the Bi$_2$O$_3$-As$_2$O$_5$ system [1]. The authors reported that this phase, with body-centered cubic symmetry, formed solid solutions over an extremely limited range between 6.23 and 6.74 mol % As$_2$O$_5$ at 650°C.

The crystal structure of BiAs$_2$O$_6$ has been reported [2,3]. In addition, the crystal structure of compositions Bi$_2$O$_3$: As$_2$O$_5$ = 4 : 1, 6 : 1 and 7 : 1 were reported [4]. It was postulated that in the structure, square Bi$_2$O$_4$ layers were connected via layers of isolated tetrahedral As$_4$O$_4$ groups. The discovery of Bi$_2$O$_3$-As$_2$O$_5$ system having structures closely related to that of CaF$_2$ and S-Bi$_2$O$_3$ [4, 5] initiated research on the electrical properties of these materials since bismuth oxide systems are well known for their high oxide ion conductivity [6].

We have undertaken to study $x$Bi$_2$O$_3$-As$_2$O$_5$ binary system with $x$ ranging from 1 to 7. Here we report the results on the formation and characterization of these materials.

Experimental

Bismuth arsenate compounds with $x$Bi$_2$O$_3$: As$_2$O$_5$: $1 \leq x \leq 7$ were prepared using Bi$_2$O$_3$ (99.9%, Aldrich) and As$_2$O$_5$ (99.9%, Alfa Aesar) via solid state reaction. Bi$_2$O$_3$ was dried at 300°C prior to weighing, while As$_2$O$_5$ was dried at 200°C. Stoichiometric mixtures were weighed (ca. 4g total), mixed with acetone in an agate mortar, dried and fired in Au foil boats at 900 - 980°C for 48 – 240 h, depending on compositions.

The samples were air-quenched and examined by X-ray diffraction (XRD) using a Shimadzu diffractometer XRD 6000 and CuK$_\alpha$ radiation ($\lambda = 1.5406$ Å). Scans were conducted at scanning range of 10 to 60° 2θ with a scanning rate of 2°/min and a step size of 0.02°. A lower scanning rate of 0.1°/min with step size of 0.01° was applied to collect data for the refinement of selected materials using “CHEKCELL” program. Angle correction was carried out based on Si standard. Elemental compositions of selected samples were determined using inductively-coupled plasma atomic emission spectrometry (ICP-AES, Perkin Elmer P1000).

Pellets for electrical property measurement were cold pressed and sintered at 900°C overnight; Au paste electrodes were then fired on at 200-600°C. The electrical properties were determined by ac impedance spectroscopy using a Hewlett-Packard Impedance Analyzer HP 4192A in the frequency range of 10 Hz to 13 MHz. Measurements were made between 200°C and 850°C by incremental steps of 50°C with 30 min stabilization time. Most
measurements were made in air, and where necessary in oxygen-free nitrogen (OFN).

For differential thermal analysis (DTA) and thermogravimetric analysis (TGA), Perkin-Elmer instruments (model DTA 7 and TGA 7) with a heating and cooling rate of 10°C min⁻¹ were used.

The Scanning Electron Microscopy (SEM) experiments were run on selected materials using SEM JEOL JSM-6400 operated at 15 kV, with working distance of 15 mm. Infrared (IR) spectra of selected materials were recorded using a FT-IR Spectrophotometer (Perkin-Elmer Model 1725x).

Figure 1: XRD patterns of Bi₂O₃-As₂O₅ binary system:
(a) x = 1, (b) x = 2, (c) x = 3, (d) x = 4, (e) x = 5, (f) x = 5.5, (g) x = 5.667, (h) x = 6, (i) x = 6.25, (k) x = 6, (l) x = 6.5, and (l) x = 7.

- $\text{BiAsO}_4$ (monoclinic)
- $\text{BiAsO}_4$ (ICDD card no. 7-387)
- unindexed peaks

Intensity (arbitrary units)

Degree (2θ)

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)

(j)

(k)

(l)
Results and Discussion

Phase purity and stability

Materials with Bi$_2$O$_3$:As$_2$O$_5$ ratios of 1:1 to 7:1 in Bi$_2$O$_3$-As$_2$O$_5$ system have been prepared (Fig. 1). Among these materials, BiAsO$_4$, Bi$_4$As$_2$O$_{11}$ [4], Bi$_3$As$_2$O$_7$ (ICDD card no: 46-191), Bi$_4$As$_2$O$_{17}$ [4], Bi$_{12}$As$_2$O$_{23}$ (ICDD card no: 44-175), and Bi$_3$As$_2$O$_{11}$ [4] have been reported as single phase materials. Our XRD results show that under the experimental conditions adopted single phase materials exist only at Bi$_2$O$_3$:As$_2$O$_5$ ratios of 5:1 and above. At lower Bi:As ratios mixed phase materials were obtained despite prolonged heating or heating at temperatures close to melting. Three different crystal modifications of BiAsO$_4$ have been reported: tetragonal (ICDD card no: 5-573, 47-1850, 85-906), monoclinic (ICDD card no: 25-89, 74-1412) and a phase with unknown crystal symmetry (ICDD card no: 7-387). The XRD pattern of BiAsO$_4$ prepared in this work indicates the coexistence of the monoclinic phase and the phase with unknown crystal symmetry. Refinement of the XRD data of the material of composition 2Bi$_2$O$_3$-As$_2$O$_5$ using the lattice constants reported by Jie and Eysel [4] as starting parameters left the major peaks at $2\theta = 26.8^\circ$, 27.2$^\circ$, 30.9$^\circ$, 31.3$^\circ$ and 44.5$^\circ$ unindexed. The XRD pattern of 3Bi$_2$O$_3$-As$_2$O$_5$ was similar to that in ICDD card no: 46-191. However some additional peaks were observed at around $2\theta = 31.7^\circ$, 33.6$^\circ$, and 45.7$^\circ$. These peaks could be attributed to the presence of BiAsO$_4$ (ICDD card no: 7-387) as a secondary phase. 4Bi$_2$O$_3$-As$_2$O$_5$ was reported to be orthorhombic with cell parameters of a = 5.718 Å, b = 9.985 Å, c = 3.304 Å. Refinement of the XRD data of 4Bi$_2$O$_3$-As$_2$O$_5$ prepared based on lattice values reported left five unindexed peaks at $2\theta = 27.9^\circ$, 33.4$^\circ$, 44.6$^\circ$, 46.5$^\circ$ and 47.3$^\circ$, indicating the presence of Bi$_{12}$As$_2$O$_{23}$ in the sample.

The compositions of phase pure compounds in $x$Bi$_2$O$_3$-As$_2$O$_5$ binary system, 5 $\leq x \leq 7$ were determined by ICP-AES (Table 1).

<table>
<thead>
<tr>
<th>$x$</th>
<th>Element</th>
<th>Calculated</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Bi</td>
<td>31.25</td>
<td>31.52 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>6.25</td>
<td>6.06 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>62.50</td>
<td>62.42 ± 0.02</td>
</tr>
<tr>
<td>5.5</td>
<td>Bi</td>
<td>31.88</td>
<td>32.17 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>5.80</td>
<td>5.59 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>62.32</td>
<td>62.24 ± 0.01</td>
</tr>
<tr>
<td>5.667</td>
<td>Bi</td>
<td>32.08</td>
<td>32.31 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>5.66</td>
<td>5.49 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>62.26</td>
<td>62.20 ± 0.01</td>
</tr>
<tr>
<td>5.75</td>
<td>Bi</td>
<td>32.17</td>
<td>32.51 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>5.59</td>
<td>5.35 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>62.24</td>
<td>62.14 ± 0.03</td>
</tr>
<tr>
<td>6</td>
<td>Bi</td>
<td>32.43</td>
<td>32.63 ± 0.13</td>
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<tr>
<td></td>
<td>As</td>
<td>5.41</td>
<td>5.26 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>62.16</td>
<td>62.10 ± 0.04</td>
</tr>
<tr>
<td>6.25</td>
<td>Bi</td>
<td>32.68</td>
<td>32.94 ± 0.02</td>
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<tr>
<td></td>
<td>As</td>
<td>5.23</td>
<td>5.04 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>62.09</td>
<td>62.02 ± 0.01</td>
</tr>
<tr>
<td>7</td>
<td>Bi</td>
<td>33.33</td>
<td>33.79 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>4.76</td>
<td>4.44 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>61.90</td>
<td>61.77 ± 0.03</td>
</tr>
</tbody>
</table>
The atomic percent of oxygen present in the materials was calculated by difference. In general, the experimental values agreed (within errors) with calculated values, thus confirming the compositions of these phases.

Thus, \( \text{Bi}_{12}\text{As}_{2}\text{O}_{23} \), \( \text{Bi}_{22}\text{As}_{4}\text{O}_{43} \), \( \text{Bi}_{17}\text{As}_{3}\text{O}_{33} \), and \( \text{Bi}_{23}\text{As}_{4}\text{O}_{44.5} \) appear to be new compounds in \( \text{Bi}_2\text{O}_3 \)-\( \text{As}_2\text{O}_5 \) binary system. The XRD pattern of \( \text{Bi}_{23}\text{As}_{4}\text{O}_{44.5} \) is similar to that of \( \text{Bi}_{12}\text{P}_{2}\text{O}_{44.5} \)[10, 13]. This implies that \( \text{Bi}_{23}\text{As}_{4}\text{O}_{44.5} \) and \( \text{Bi}_{12}\text{P}_{2}\text{O}_{44.5} \) could be isostructural. XRD analysis with scan rate of 0.1°/min, was run on \( x\text{Bi}_2\text{O}_3 \)-\( \text{As}_2\text{O}_5 \); 5 ≤ \( x \) ≤ 6.25 over 2\( \theta \) range of 10 to 60°. Indexing of their XRD patterns showed that these materials exhibited very similar crystal chemistry (Table 2). These materials were successfully refined in triclinic symmetry with space group of \( P-1 \). Compositions with \( \text{Bi}_2\text{O}_3 \)-\( \text{As}_2\text{O}_5 \) ratios of 5:1 to 6.25:1 appeared to be solid solutions. They have similar XRD patterns with a shift in 2\( \theta \) at ~26.8° and 46.4° (Figure 1). It was expected that the increasing Bi content could change atomic arrangement in the structure which would result in a shift in d-spacing. Generally, lattice parameters and volumes of these materials increased with increasing Bi content, thus obeying Vegard’s law (Figure 2). The ionic radius of \( \text{Bi}^{3+} \) (0.96 Å) is larger than that of \( \text{As}^{5+} \) (0.335 Å) [7]; Bi – O bond length is thus expected to be longer than As – O bond which may lead to an increase in cell parameters of the materials with increase of Bi content.

The material \( \text{Bi}_{12}\text{As}_{2}\text{O}_{23} \) has been reported previously to crystallize in monoclinic symmetry with space group of \( P2_1 \) (ICDD card no: 44-175; Jie and Eysel [4]). The XRD pattern of \( \text{Bi}_{12}\text{As}_{2}\text{O}_{23} \) is similar to that reported in ICDD card number 44-175. However, peaks at 2\( \theta = 18.6^\circ \) and 26.0° in \( \text{Bi}_{12}\text{As}_{2}\text{O}_{23} \) could not be indexed in the space group \( P2_1 \) when the refinement was performed based on cell parameters reported in ICDD. On the other hand, peaks at 2\( \theta = 14.0^\circ \) and 18.6° could not be indexed when the refinement was performed based on cell parameters reported by Jie and Eysel [4]. It is, however possible to index all the peaks in \( \text{Bi}_{12}\text{As}_{2}\text{O}_{23} \) in the triclinic symmetry with space group of \( P-1 \) using Chekcell refinement program.

The sample where Bi/As = 6.5 appeared to be a mixture of 6.25:1 and 7:1 phase. The XRD data of \( \text{Bi}_7\text{AsO}_{13} \) were indexed on a monoclinic cell as reported [4].

All the materials studied in \( x\text{Bi}_2\text{O}_3 \)-\( \text{As}_2\text{O}_5 \) binary system, 5 ≤ \( x \) ≤ 7 were thermally stable up to 900°C as no weight loss was observed in TGA. No phase transition was observed for these materials in their DTA thermograms.

**Table 2**: Lattice parameters of \( x\text{Bi}_2\text{O}_3 \)-\( \text{As}_2\text{O}_5 \) binary system from X-ray diffraction data

<table>
<thead>
<tr>
<th>( x )</th>
<th>Crystal system</th>
<th>Lattice parameters (Å)</th>
<th>Unit-cell volume (Å(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Triclinic</td>
<td>( a = 11.4821 ) (8)</td>
<td>( b = 11.5188 ) (7)</td>
</tr>
<tr>
<td>5.5</td>
<td>Triclinic</td>
<td>( a = 11.4979 ) (11)</td>
<td>( b = 11.5177 ) (15)</td>
</tr>
<tr>
<td>5.667</td>
<td>Triclinic</td>
<td>( a = 11.5036 ) (11)</td>
<td>( b = 11.5177 ) (12)</td>
</tr>
<tr>
<td>5.75</td>
<td>Triclinic</td>
<td>( a = 11.5179 ) (5)</td>
<td>( b = 11.5226 ) (6)</td>
</tr>
<tr>
<td>6</td>
<td>Triclinic</td>
<td>( a = 11.5312 ) (8)</td>
<td>( b = 11.5357 ) (9)</td>
</tr>
<tr>
<td>6.25</td>
<td>Triclinic</td>
<td>( a = 11.5362 ) (12)</td>
<td>( b = 11.5401 ) (14)</td>
</tr>
<tr>
<td>7</td>
<td>Monoclinic</td>
<td>( a = 4.0669 ) (3)</td>
<td>( b = 3.8879 ) (4)</td>
</tr>
</tbody>
</table>
Conductivity studies

The conductivity of materials with compositions \( x\text{Bi}_2\text{O}_3\text{-As}_2\text{O}_5 \), \( 1 \leq x \leq 7 \), has not been reported. Conductivity values were extracted from ac impedance data. In general, a broadened semicircle with a low-frequency spike was obtained for temperatures below 400\(^\circ\)C; the spike became more pronounced at higher temperatures. Typical impedance data are shown in Figure 3 for \( \text{Bi}_{23}\text{As}_{4}\text{O}_{44.5} \); at 300\(^\circ\)C the associated capacitance of...
the semicircle (Figure 3a) has a value of \(9.1 \times 10^{-12}\) F cm\(^{-1}\), which is typical of bulk component [8]. At higher temperatures, the predominant feature is a low-frequency spike inclined at \(\approx 70^\circ\) to the horizontal axis (Figure 3b). Its associated capacitance of \(\approx 10^{-6}\) F cm\(^{-1}\) is characteristic of ionic polarization phenomena at the blocking electrodes, and a diffusion-limited Warburg impedance, thus supporting the idea the conduction was predominantly ionic.

**Figure 3**: Impedance data of Bi\(_{23}\)As\(_8\)O\(_{44.5}\) at (a) 300°C; (b) 500°C. \(Z'\) and \(Z''\) are the real and imaginary part of the complex impedance \(Z^*\), respectively.
In order to confirm the conduction species of the material conductivity measurements were carried out in dry oxygen free nitrogen (OFN). Figure 4 shows such a plot for Bi$_{23}$As$_4$O$_{44.5}$. No change in conductivity was seen on changing the atmosphere, indicating that contribution in conductivity by electrons if present is negligible. Similar results were obtained for the other materials studied in $x$Bi$_2$O$_3$-As$_2$O$_5$ binary system, $5 \leq x \leq 7$. It thus appears that these materials are oxide ion conductors, as have been reported for the phosphate analogues [9, 10].

EMF measurements of an oxygen concentration cell containing these materials as the membrane are needed in order to confirm this.

**Figure 4**: Arrhenius plots of Bi$_{23}$As$_4$O$_{44.5}$ in air (○) and nitrogen (Δ).
These materials show reversible conductivity behavior in heating and cooling cycles. Curvature was observed in the Arrhenius plots. Figure 5 shows Arrhenius plots of $x$Bi$_2$O$_3$-As$_2$O$_5$, $5 \leq x \leq 7$ during the first cooling cycle. The conductivity values range from $10^{-7}$ to $10^{-2}$ ohm$^{-1}$cm$^{-1}$ between 200 and 850°C with an activation energy of 0.75 eV. The Arrhenius plot of YSZ is included for comparison. Generally, at temperatures $\leq 300$°C, the materials studied show decreasing conductivity in the order:

$$5.75:1 \approx 5.667:1 > 6:1 \approx 5.5:1 > 7:1 > 5:1$$

Above 600°C, the material of composition 7Bi$_2$O$_3$-As$_2$O$_5$ has comparable conductivity to that of the others. The change in slope could be associated with the different mechanism taking place in conduction at higher temperature. Similar activation energies were obtained in compositions of 5:1, 5.667:1, 5.75:1 and 6:1 indicating that the charge carriers in these materials which have similar crystal structure could be identical.

![Arrhenius plots of $x$Bi$_2$O$_3$-As$_2$O$_5$ binary system, $5 \leq x \leq 7$.](image)

**Figure 5**: Arrhenius plots of $x$Bi$_2$O$_3$-As$_2$O$_5$ binary system, $5 \leq x \leq 7$.

$\Delta$ $x = 5$; $\bullet$ $x = 5.5$; $\circ$ $x = 5.667$; $\square$ $x = 5.75$; $\odot$ $x = 6$; $\blacktriangle$ $x = 7$; $\blackblacksquare$ YSZ
Among the materials studied in Bi$_2$O$_3$-As$_2$O$_5$ binary system, Bi$_{23}$As$_4$O$_{44.5}$ has the highest conductivity: 5.66 x 10$^{-5}$ ohm$^{-1}$ cm$^{-1}$ at 300$^\circ$C. The conductivity values obtained for the materials studied, except for Bi$_5$AsO$_{10}$, are comparable to that of YSZ, which is used as the electrolyte material in solid oxide fuel cell at present. The activation energies in the system where Bi/As = 5.5, 5.75 and 6 are also comparable to that of YSZ, 0.8 eV (Figure 5).

**IR and SEM studies**

The IR absorption spectra of xBi$_2$O$_3$-As$_2$O$_5$ binary system, 5 ≤ x ≤ 7 are shown in Figure 6. The strong broad absorption at ~3440 cm$^{-1}$ and a medium absorption band at ~1635 cm$^{-1}$ correspond to the O-H stretching and bending mode, respectively. This is due to moisture picked up during the process of KBr disc preparation.

**Figure 6**: IR spectra of xBi$_2$O$_3$-As$_2$O$_5$ binary system, 5 ≤ x ≤ 7.
(a) x = 5, (b) x = 5.5, (c) x = 5.667, (d) x = 5.75, (e) x = 6, (f) x = 7
The IR spectra of \( x\text{Bi}_2\text{O}_3\text{-As}_2\text{O}_5 \) binary system, 5 \( \leq x \leq 7 \) show intense bands at \( \sim 780 \text{ cm}^{-1} \) and \( \sim 500 \text{ cm}^{-1} \), which are assigned to v(As-O) type of vibration [11]. The different Bi content in these materials did not result in noticeable variations in their IR spectra. At 5 \( \leq x \leq 6 \), a weak shoulder at \( \sim 736 \text{ cm}^{-1} \) was observed, which is absent when \( x = 7 \). This implies that the crystal structure of Bi\textsubscript{7}As\textsubscript{5}O\textsubscript{13} is different from the other materials studied in Bi\textsubscript{2}O\textsubscript{3}-As\textsubscript{2}O\textsubscript{5} binary system.

From the results obtained in scanning electron microscopy (SEM) on single phase materials, it appears that there was no significant change in particle size and morphology with the increase of Bi content in these materials.

**Conclusions**

Solid solutions were obtained in \( x\text{Bi}_2\text{O}_3\text{-As}_2\text{O}_5 \); 5 \( \leq x \leq 6.25 \). These materials crystallize in triclinic symmetry. They appear to be thermally stable and behave as oxide ion conductors, with conductivity and activation energies comparable to that of YSZ.

**Acknowledgement**

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**References**