PREPARATION AND CHARACTERIZATION OF BISMUTH-NIOBIUM OXIDE ION CONDUCTORS

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ABSTRACT

Oxide ion conductors have been attracting considerable attention for many years due to their application in technological devices such as solid oxide fuel cells, oxygen sensors and many more. In this study, material with desirable electrical properties in the Bi$_2$O$_3$-Nb$_2$O$_5$ binary system was studied. Bismuth-niobium oxide has been prepared by solid state reaction. Powder X-ray diffraction (XRD) analysis showed that single-phase materials were formed with a general formula of Bi$_x$NbO$_{6.5}$: $2.5 \leq x \leq 6$. Electrical properties of the single-phase materials in these solid solution series were studied by a.c. impedance spectroscopy. Conductivity measurements were also carried out in dry oxygen free nitrogen (OFN) in order to confirm the conduction species of the materials. Results showed that these materials appeared to be oxide ion conductors. Further characterizations of the materials using thermal analysis (DTA), thermogravimetric analysis (TGA) and the results showed that there were no thermal changes and phase transitions were observed and all the materials were thermally stable. Scanning electron microscopy (SEM) has been carried out to study the morphology of the materials and all the grain size of the samples were in micrometers.

INTRODUCTION

Oxide ion conductor is a very interesting group of solid electrolytes, where the oxide ions are the charge carriers. Oxide ion conductors have been presenting great interest for numerous technological applications such as solid oxide fuel cells (SOFCs), oxygen sensors, dense ceramic membranes for high-purity oxygen separation, and partial oxidation of hydrocarbons [1-4].

Bismuth oxide based solid electrolytes show extremely high oxide ion conducting property and are promising material used in electrochemical devices [5]. Bismuth (III) oxide (Bi$_2$O$_3$) exists in four polymorphs, which are α, β, γ, and δ. The high-temperature form of bismuth oxide δ- Bi$_2$O$_3$, which has an oxygen-deficient fluorite type structure, has been recognized as one of the best oxide ion conductors due to the high concentration of intrinsic oxygen vacancies [6]. However, δ- Bi$_2$O$_3$ is only stable in a narrow temperature range, from 730 °C to its melting point at 824 °C. Below 730 °C, the monoclinic α- Bi$_2$O$_3$ is the stable phase. In order to enhance the stability of high-temperature and good conducting δ-phase, it can be doped with transition metal oxides such as Nb$_2$O$_5$, Ta$_2$O$_5$, WO$_3$ or rare-earth oxides [7-11]. Among the many choices of substituting cations in δ- Bi$_2$O$_3$, Nb$^{5+}$ is probably the most frequently used due to its...
high efficiency to stabilize the cubic phase to room temperature [12].

Bismuth niobate (Bi₃NbO₇) exist under two crystallographic modifications, a tetragonal (type III) phase and pseudocubic (type II) phase. The tetragonal phase shows a higher electrical conductivity than the pseudocubic phase. It was suggested to be associated with the redistribution of oxygen sublattice (or oxygen vacancies) induced by superstructure ordering in the tetragonal Bi₃NbO₇, which appears to increase the mobility of free charge carriers and therefore improves the electrical conductivity [12-13]. In this paper, we examine the properties of the solid solutions in Bi₃NbO₇ (type III), which include the phase purity, thermal stability, surface morphology and the electrical properties.

**EXPERIMENTAL**

Polycrystalline Bi₃NbO₇ and theirs solid solutions were prepared via solid state reaction technique using Nb₂O₅ (99.9% Alfa Aesar) and Bi₂O₃ (99.9% Aldrich). Bi₂O₃ and Nb₂O₅ were dried overnight to remove moisture and kept in vacuum desiccators prior to experimentation. A stoichiometric mixture of the required reagents was weighed and mixed together manually using an agate mortar. Sufficient amount of acetone was added to ensure the homogeneity of the mixture. After mixing, the samples were heated in gold foil boats at 800 °C with intermediate regrinding. The samples were characterized by XRD (Shimadzu diffractometer XRD 6000, CuKα radiation) in 2θ range of 10-60° at 2°/min. Chekcell refinement program was used to obtain cell parameters. Calibration was carried out with an external Si standard. The thermal events of samples were studied from room temperature to 800 °C on heat and cool cycles with a heating rate of 10 °C/min by differential thermal analysis (DTA, Perkin-Elmer instrument with model DTA 7). TGA was carried out using Mettler Toledo instrument (model TGA/SDTA 851), in a temperature range of 50 °C to 850 °C with a heating rate of 10 °C min⁻¹ in nitrogen atmosphere (50 mL min⁻¹). The change in the weight of the sample as a function of temperature was measured in order to check for its thermal stability. Scanning electron microscopy (SEM) was used to investigate the morphology and surface structure of single-phase materials. The SEM analyses were carried out using SEM JEOL JSM-6400 operated at 15 kV, with a working distance of 15 mm. The samples were palletized and sintered at 850 °C for 24 hours prior to electrical measurements. Gold electrodes were attached on both faces of the sample and then fired at 200-600 °C. The electrical properties were determined by ac impedance spectroscopy using a Hewlett Packard Impedance Analyzer, HP4192A in the frequency range of 5 Hz to 13 MHz. Measurements were made from 200 °C to 850 °C by incremental steps of 50 °C on a heating cycle with 30 min equilibration time. The samples were left overnight at around 850 °C and a cooling cycle performed the next day.

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RESULTS AND DISCUSSION

XRD Analysis
Materials with a general formula of Bi\textsubscript{x}NbO\textsubscript{δ} (2 ≤ x ≤ 7) were prepared via solid state reaction. The formation of single-phase materials was confirmed by the absence of the characteristic XRD lines of the constituent oxides and other phases in the XRD diffraction patterns.

Figure 1: XRD patterns of Bi\textsubscript{x}NbO\textsubscript{δ} (2 ≤ x ≤ 7) prepared via solid state method.

Figure 1 shows the XRD patterns of Bi\textsubscript{x}NbO\textsubscript{δ} (2 ≤ x ≤ 7). Solid solutions with single-phase were formed at the range of 2.5 ≤ x ≤ 6. There is a small shift in 2θ at ~28.200° as expected due to the increasing Bi content that could change the atomic arrangement in the structure resulting in a shift in d-spacing [14]. Refinements were performed using checkcell program with lattice parameters of Bi\textsubscript{3}NbO\textsubscript{7} (x=3) reported by Ling and Johnson as starting values [13]. The results showed that these materials were successfully refined in tetragonal system with space group I4m2.

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Bi2NbO5.5 (x=2) a mixed-phase that consists of Bi3NbO7 and Bi5Nb3O15 was obtained. The presence of Bi5Nb3O15 phase was indicated by unindexed peaks at 2θ = 12.683 and 48.106°.

For x values higher than 6, the peak around 27.944° was obtained as Bi concentration increased (Figure 1, x=6.5). This peak corresponds to BiNbO4 and indicates the presence of a mixed-phase. The XRPD pattern of Bi7NbO13 was compared to the BiNbO reported in ICDD card number: 00-016-0486. The intensity of this peak was not change even after heat treatment increased to 850 °C and time prolonged to 72 hours.

**Thermal Analyses**

DTA measurements were carried out on the single-phase parent compound, Bi3NbO7 and all the solid solutions to investigate the thermal events. Figure 2 shows the DTA thermograms of materials in Bi xNbO δ (2.5 ≤ x ≤ 6) solid solutions at a heating and cooling rate of 10 °C min⁻¹. From the results, no thermal changes and phase transitions were observed.

Figure 3 shows the TGA thermogram of Bi3NbO7 and all solid solutions; a straight line observed in the thermogram (starting at 100 %) of each sample shows that there was no weight loss when the samples were heated to 800 °C. This indicates that these materials were thermally stable.

![DTA thermograms](image)

**Figure 2:** DTA thermograms: (a) Bi2.5NbO6.25; (b) Bi3NbO7; (c) Bi4NbO8.5; (d) Bi5NbO10; (e) Bi6NbO11.5.

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Figure 3: TGA thermograms: (a) Bi$_{2.5}$NbO$_{6.25}$; (b) Bi$_3$NbO$_7$; (c) Bi$_4$NbO$_{8.5}$; (d) Bi$_5$NbO$_{10}$; (e) Bi$_6$NbO$_{11.5}$.

Scanning Electron Microscopy (SEM)
Figure 4 shows the SEM micrographs of the parent compound Bi$_3$NbO$_7$, as well as Bi$_6$NbO$_{11.5}$ and Bi$_{2.5}$NbO$_{6.25}$ pellets. Each pellet was sintered at 850 °C for 24 hours prior to the SEM experiment to increase the mechanical strength of the pellets. From the SEM results, there were no significant changes in the grain size of the parent and other solid solutions. However, Bi$_{2.5}$NbO$_{6.25}$ was found in slightly smaller grain size (1.8-2.2 μm) with higher porosity compared to the pellets of Bi$_3$NbO$_7$ and Bi$_6$NbO$_{11.5}$ (2.4-6 μm).
(a) Bi$_3$NbO$_7$, synthesized at 800 °C; 24 hours sintered at 850 °C; 24 hours

(b) Bi$_6$NbO$_{11.5}$, synthesized at 800°C; 24 hours sintered at 850 °C; 24 hours
Figure 4: SEM micrographs of single-phase Bi$_3$NbO$_7$, Bi$_6$NbO$_{11.5}$ and Bi$_{2.5}$NbO$_{6.25}$.

Conductivity Measurements

Conductivity measurements were carried out on single-phase materials. Conductivity values were extracted from ac impedance data. These materials show reproducible conductivity in heating and cooling cycles. In Table 1 the conductivity values at 300°C and 600°C, and the activation energy ($E_a$) values for all the samples in of Bi$_x$NbO$_{\delta}$ ($2.5 \leq x \leq 6$) are listed. The Arrhenius plot of YSZ is included for the comparison [14]. At 300°C, in general, conductivity decreased in order of:

Bi$_6$NbO$_{11.5}$ > Bi$_5$NbO$_{10}$ > Bi$_4$NbO$_{8.5}$ > Bi$_3$NbO$_7$ > Bi$_{2.5}$NbO$_{6.25}$

Table 1: Conductivities ($\sigma_{300}$ and $\sigma_{600}$) and activation energies ($E_a$) of Bi$_x$NbO$_{\delta}$, $2.5 \leq x \leq 6$

<table>
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<th>x</th>
<th>$\sigma_{300} \times 10^{-6}$ ohm$^{-1}$cm$^{-1}$</th>
<th>$\sigma_{600} \times 10^{-3}$ ohm$^{-1}$cm$^{-1}$</th>
<th>$E_a$ (eV)</th>
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</table>

(c) Bi$_{2.5}$NbO$_{6.25}$, synthesized at 800°C; 24 hours; sintered at 850°C; 24 hour
Figure 5 shows Arrhenius plots of $\text{Bi}_x\text{NbO}_y$, $(2.5 \leq x \leq 6)$ during first cooling cycle. The conductivity values range from $10^{-7}$ to $10^{-3}$ ohm$^{-1}$cm$^{-1}$ between 250 and 800$^\circ$C. Among the materials prepared, $\text{Bi}_6\text{NbO}_{11.5}$ has the highest conductivity: $2.50 \times 10^{-5}$ ohm$^{-1}$cm$^{-1}$ at 300 $^\circ$C.

Conductivity measurements were also carried out in dry oxygen free nitrogen (OFN) in order to confirm the conduction species of the material. If the charge carriers were electrons or holes and not just oxide ions, conductivity would vary with oxygen partial pressure. Since no significant change in conductivity was seen on different atmosphere (Figure 6), hence contribution in conductivity by electrons if present is negligible. An isothermal conductivity plot of the material in different environments is shown in Figure 7. From the result, the material was not atmosphere-sensitive since no significant change in conductivity was observed.
CONCLUSIONS

Materials in Bi$_2$O$_3$-Nb$_2$O$_5$ binary system have been successfully synthesized by solid state reaction. Solid solution series, Bi$_x$NbO$_{3+2x}$ was obtained at $2.5 \leq x \leq 6$ and their
electrical properties studied by impedance spectroscopy study. From the analysis, all of them are oxide ion conductors and the Bi$_6$NbO$_{11.5}$ has the highest conductivity (2.50 x 10$^{-3}$ ohm$^{-1}$cm$^{-1}$) with $E_a = 0.94$ eV at 300 oC. Besides, all the materials were thermally stable and no phase transitions were observed in the thermal analyses.

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REFERENCES