UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF BI2-O3-M2O5 (M = P,AS, V) OXIDE ION CONDUCTORS

LEE SIEW LING.

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By

LEE SIEW LING

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for Bon and family with love

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PREPARATION AND CHARACTERIZATION OF Bi_2O_3-M_2O_5 (M = P, As, V) OXIDE ION CONDUCTORS

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Chairman: Professor Lee Chnoong Kheng Ph.D.

Faculty: Science and Environmental Studies

Bi_2O_3-M_2O_5, M = P, As, V systems and related materials were prepared by solid state reactions. The phase purity of the materials was determined by X-ray diffraction (XRD). Further characterization using ac impedance spectroscopy and differential thermal analysis (DTA) were carried out on single phase materials. Besides, inductively coupled plasma-atomic emission spectrometry (ICP-AES), density measurement, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), Fourier-transform infrared (FT-IR) spectroscopy and Raman spectroscopy were also performed on selected materials. The crystal system and space group of the single phase materials were determined.

Two narrow solid solution series were formed in $x$$Bi_2O_3$-$P_2O_5$: $5.5 \leq x \leq 6$ and $7 \leq x \leq 7.25$. In DTA study, a phase transition was clearly seen in Bi_7PO_{13} and $Bi_{29}P_4O_{53.5}$ at ~860°C.

XRD shows that single phase materials were formed in xBi$_2$O$_3$-As$_2$O$_5$ binary system when $x = 5, 5.5, 5.667, 5.75, 6$ and 7. Among these, materials in the composition range of $5 \leq x \leq 6.25$ appeared to be solid solutions. Attempts to synthesize materials of composition of xBi$_2$O$_3$-As$_2$O$_5$, $1 \leq x \leq 4$ were unsuccessful.

Single phase materials were formed in xBi$_2$O$_3$-V$_2$O$_5$ binary system, $5 \leq x \leq 6$ and $x = 7$. A phase transition was observed in $Bi_{17}V_3O_{33}$ and $Bi_{23}V_4O_{44.5}$ at ~180°C. However, its origin is unknown.

Materials of composition xBi$_2$O$_3$-M$_2$O$_5$, $5.5 \leq x \leq 6$ (M = P) and $5 \leq x \leq 6$ (M = As, V) are refined in triclinic symmetry with space group of *P-1*. Meanwhile, monoclinic symmetry was found in materials where $x = 7, 7.25$ (M = P) and $x = 7$(M = As, V). The XRD and IR patterns of both series of xBi$_2$O$_3$-As$_2$O$_5$, $5 \leq x \leq 6.25$ and xBi$_2$O$_3$-V$_2$O$_5$, $5.5 \leq x \leq 6$ solid solutions are very similar since these materials are isostructural. Generally, lattice parameters, volumes and densities of the materials in xBi$_2$O$_3$-M$_2$O$_5$ system, M = P, As, V increased with the increase of Bi content.

A complete solid solution series was formed in the $Bi_{22}P_4O_{43}$-$Bi_{22}As_4O_{43}$, $Bi_{22}P_4O_{43}$-$Bi_{22}V_4O_{43}$, $Bi_{22}As_4O_{43}$-$Bi_{22}V_4O_{43}$, $Bi_{23}P_4O_{44.5}$-$Bi_{23}As_4O_{44.5}$, $Bi_{23}P_4O_{44.5}$-$Bi_{23}V_4O_{44.5}$, $Bi_{23}As_4O_{44.5}$-$Bi_{23}V_4O_{44.5}$, $Bi_{12}P_2O_{23}$-$Bi_{12}As_2O_{23}$, $Bi_{12}P_2O_{23}$-$Bi_{12}V_2O_{23}$, $Bi_{12}As_2O_{23}$-$Bi_{12}V_2O_{23}$ and Bi_7AsO_{13}-Bi_7VO_{13} systems. In Bi_7PO_{13}-Bi_7AsO_{13} and Bi_7PO_{13}-Bi_7VO_{13} systems a two-phase region was seen. All the single phase materials studied above appeared to be oxide-ion conductors. Conductivity increased with increasing vanadium

content, followed by arsenic and phosphorus. Among the materials prepared, the highest conductivity is obtained in $Bi_{23}V_4O_{44.5}$ with a σ value of 1.34×10^{-4} ohm^{-1} cm^{-1} at 300°C. In an attempt to optimize oxide ion conductivity, chemical doping using PbO, $Sr(NO_3)_2$, Al_2O_3, Ga_2O_3, La_2O_3, Fe_2O_3 *etc.* was carried out in selected materials, resulting in the formation of limited solid solutions. These materials, however, exhibit conductivity slightly lower than that of the parent materials.

Ball milling process has been carried out in the preparation of $Bi_{23}V_4O_{44.5}$ and $Bi_{14}PO_\delta$ in addition to manual grinding prior to firing of the samples. In ball milling process, high-density, fine-grained powders with uniform grain-size distribution were obtained, resulting in an increase in conductivity and dielectric constants.

Sillenite compounds in the Bi_2O_3-P_2O_5 binary system with Bi:P ratios of 13:1 to 16:1 have been synthesized and found to be solid solutions. Substitution of P by V and As in the material where Bi:P = 14:1 results in partial and complete solid solutions, respectively. Enhancement in conductivity was observed in these solid solutions with V-doped materials exhibiting the highest conductivity. Substitution of P by elements such as Pb^{2+}, Sr^{2+}, Al^{3+}, Ga^{3+}, Fe^{3+}, Si^{4+}, Ge^{4+}, and Ti^{4+} leads to formation of limited solid solutions. Most of these materials have conductivity similar to or slightly higher than that of the parent compound. These materials appeared to be predominantly oxide ion conductors especially at temperatures above 800°C where $\gamma \rightarrow \delta'$ polymorphic transformation occurred.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENYEDIAAN DAN PENCIRIAN KONDUKTUR ION OKSIDA Bi_2O_3-M_2O_5 (M = P, As, V)

Oleh

LEE SIEW LING

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Fakulti: Sains dan Pengajian Alam Sekitar

Sistem-sistem Bi_2O_3-M_2O_5, M = P, As, V dan bahan-bahan berkaitan telah disediakan melalui tindak balas keadaan pepejal. Ketulenan fasa bahan tersebut dikenalpastikan dengan penggunaan pembelauan sinar-X (XRD). Pencirian lanjutan telah dijalankan ke atas sampel yang berfasa tunggal dengan menggunakan spektroskopi impedans arus ulang-alik dan penganalisa pembezaan terma (DTA). Di samping itu, analisis-analisis termasuk analisis plasma induktif pasangan-pemancaran pengatoman (ICP-AES), penyukatan ketumpatan, analisis termogravimetri (TGA), kalorimetri pembezaan imbasan (DSC), mikroskopi imbasan elektron (SEM), spektroskopi infra merah transformasi Fourier (FT-IR) dan spektroskopi Raman telah dijalankan ke atas sampel-sampel terpilih. Sistem hablur dan kumpulan ruangan bagi sample-sampel yang berfasa tunggal juga dikenalpastikan.

Larutan pepejal telah terbentuk dalam sistem $x\mathrm{Bi_2O_3}$-$\mathrm{P_2O_5}$: $5.5 \leq x \leq 6$ dan $7 \leq x \leq 7.25$. Dalam kajian DTA, suatu peralihan fasa didapati dalam $\mathrm{Bi_7PO_{13}}$ dan $\mathrm{Bi_{29}P_4O_{53.5}}$ pada ~860°C.

XRD menunjukkan bahan berfasa tunggal telah terbentuk dalam sistem $\mathrm{Bi_2O_3}$-$\mathrm{As_2O_5}$ apabila $x = 5, 5.5, 5.667, 5.75, 6$ and 7. Bahan-bahan dengan komposisi $5 \leq x \leq 6.25$ wujud sebagai pepejal larutan. Percubaan untuk menyintesiskan komposisi $x\mathrm{Bi_2O_3}$-$\mathrm{As_2O_5}$, $1 \leq x \leq 4$ telah mengalami kegagalan.

Bahan berfasa tunggal terbentuk dalam sistem $x\mathrm{Bi_2O_3} : \mathrm{V_2O_5}$, $5 \leq x \leq 6$ dan $x = 7$. Suatu peralihan fasa telah didapati dalam $\mathrm{Bi_{17}V_3O_{33}}$ dan $\mathrm{Bi_{23}V_4O_{44.5}}$ pada ~180°C. Tetapi, sifat asalnya tidak diketahui.

Sistem hablur bagi bahan-bahan berkomposisi $x\mathrm{Bi_2O_3}$-$\mathrm{M_2O_5}$, $5.5 \leq x \leq 6$ (M = P) dan $5 \leq x \leq 6$ (M = As, V) adalah bersimetri triklinik dengan kumpulan ruangan *P-1*. Sementara, sistem hablur bersimetri monoklinik didapati apabila $x = 7, 7.25$ (M = P) dan $x = 7$ (M = As, V). Pola XRD dan IR bagi kedua-dua siri pepejal larutan $x\mathrm{Bi_2O_3}$-$\mathrm{As_2O_5}$, $5 \leq x \leq 6.25$ dan $x\mathrm{Bi_2O_3}$-$\mathrm{V_2O_5}$, $5.5 \leq x \leq 6$ adalah mirip kerana mereka memiliki struktur yang serupa. Secara amnya, parameter kekisi, isipadu dan ketumpatan bahan-bahan dalam sistem $x\mathrm{Bi_2O_3}$-$\mathrm{M_2O_5}$, M = P, As, V meningkat dengan penambahan kandungan Bi.

Siri larutan pepejal yang lengkap terbentuk dalam sistem-sistem $Bi_{22}P_4O_{43}$-$Bi_{22}As_4O_{43}$, $Bi_{22}P_4O_{43}$-$Bi_{22}V_4O_{43}$, $Bi_{22}As_4O_{43}$-$Bi_{22}V_4O_{43}$, $Bi_{23}P_4O_{44.5}$-$Bi_{23}As_4O_{44.5}$, $Bi_{23}P_4O_{44.5}$-$Bi_{23}V_4O_{44.5}$, $Bi_{23}As_4O_{44.5}$-$Bi_{23}V_4O_{44.5}$, $Bi_{12}P_2O_{23}$-$Bi_{12}As_2O_{23}$, $Bi_{12}P_2O_{23}$-$Bi_{12}V_2O_{23}$, $Bi_{12}As_2O_{23}$-$Bi_{12}V_2O_{23}$ dan Bi_7AsO_{13}-Bi_7VO_{13}. Dalam sistem-sistem Bi_7PO_{13}-Bi_7AsO_{13} dan Bi_7PO_{13}-Bi_7VO_{13}, dua fasa yang berlainan telah dikesan. Bahan-bahan berfasa tunggal yang dikaji merupakan konduktor ion oksida. Kekonduksian meningkat dengan penambahan kandungan vanadium, diikuti oleh arsenik dan fosforus. Di antara bahan-bahan yang disediakan, $Bi_{23}V_4O_{44.5}$ telah menunjukkan kekonduksian yang paling tinggi dengan $\sigma = 1.34 \times 10^{-4}$ ohm^{-1} cm^{-1} pada 300°C. Dalam usaha untuk meningkatkan kekonduksian, pendopan kimia dengan menggunakan PbO, $Sr(NO_3)_2$, Al_2O_3, Ga_2O_3, La_2O_3, Fe_2O_3 dan sebagainya telah dilakukan pada bahan-bahan terpilih. Pepejal larutan yang terhad telah terhasil. Walau bagaimanapun, kekonduksian bahan-bahan terdop tersebut adalah kurang daripada bahan-bahan induk.

Selain daripada tindak balas keadaan pepejal, proses pengisaran bebola juga dijalankan dalam penyediaan $Bi_{23}V_4O_{44.5}$ dan $Bi_{14}PO_8$. Dalam proses pengisaran bebola, bahan yang berketumpatan tinggi, berserbuk halus dan bertaburan seragam telah dihasilkan, dan seterusnya membawa kepada peningkatan dalam kekonduksian dan pemalar dielektrik.

Kompoun sillenit dalam sistem Bi_2O_3-P_2O_5 dengan nisbah Bi:P berjulat antara 13:1 dan 16:1 telah disintesiskan dan larutan pepejal telah diperolehi dalam bahan-bahan tersebut. Penggantian P oleh V dalam $Bi_{14}PO_8$ menghasilkan larutan pepejal yang terhad, sementara larutan pepejal yang lengap telah diperolehi apabila P dalam $Bi_{14}PO_{\delta}$ digantikan oleh As. Peningkatan dalam kekonduksian telah diperhatikan dalam larutan pepejal yang didop dengan V. Pembentukan larutan pepejal yang terhad telah diperolehi apabila P digantikan oleh Pb^{2+}, Sr^{2+}, Al^{3+}, Ga^{3+}, Fe^{3+}, Si^{4+}, Ge^{4+}, dan Ti^{4+}. Kekonduksian bahan-bahan tersebut adalah lebih kurang sama dengan kompoun induk. Bahan-bahan tersebut merupakan konduktur ion oksida terutamanya pada suhu lebih daripada 800°C, di mana peralihan fasa $\gamma \rightarrow \delta'$ berlaku.

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