PREPARATION AND CHARACTERISATION OF NEW OXIDE ION CONDUCTORS IN THE Bi2-(W, Mo)-O6 SYSTEM

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PREPARATION AND CHARACTERISATION OF NEW OXIDE ION CONDUCTORS IN THE Bi$_2$-(W, Mo)-O$_6$ SYSTEM

By

SIM LENG TZE

Thesis Submitted in Fulfilment of the Requirements for the Degree of Master of Science in the Faculty of Science and Environmental Studies
Universiti Putra Malaysia

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For my parents, with love
Bi₂WO₆, Bi₂MoO₆ and their related materials were prepared by solid state reactions. The phase purity of the materials was determined by X-ray diffraction (XRD). Further characterisation using Fourier-transform infrared (FT-IR) spectroscopy, differential thermal analysis (DTA) and impedance spectroscopy were carried out on single phase materials. Thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) were also performed on selected samples.

Only Nb and Ta could be introduced as dopant into Bi₂WO₆ with rather limited solid solution formation while introduction of dopants other than W into γ-Bi₂MoO₆ was unsuccessful. From results obtained in IR and DTA studies, it appears that the metal-oxygen bondings in Nb- and Ta-doped materials are weaker as compared to those in the parent material, Bi₂WO₆. The conductivity of these materials was about two orders of magnitude higher than that of Bi₂WO₆. Introduction of lower valency cation results in the creation of oxygen vacancies resulting in higher conductivity.
The IR and XRD patterns of both $\gamma$-$\text{Bi}_2\text{WO}_6$ and $\gamma$-$\text{Bi}_2\text{MoO}_6$ are very similar since the materials are isostructural.

Complete solid solutions in the $\gamma$-$\text{Bi}_2\text{WO}_6$ - $\gamma$-$\text{Bi}_2\text{MoO}_6$ system were obtained when prepared via low temperature route. This was made possible since the Hume-Rothery rules were fully obeyed by these materials. However, some of these materials were metastable and decomposed into mixed phases upon heating at higher temperatures. Generally, the conductivity in the system was comparable.

The conductivity of $\gamma'$-$\text{Bi}_2\text{MoO}_6$ is very dependent on sintering temperature and time. It is possible that loss of oxygen occurs upon sintering at elevated temperatures leading to the formation of non-stoichiometric $\gamma'$-$\text{Bi}_2\text{MoO}_6$. From ac impedance studies, oxide ions appear to be the main charge carriers in this material.

Phase diagram in the $\text{Bi}_2\text{WO}_6$ - $\text{Bi}_2\text{MoO}_6$ system was constructed based on results obtained from different heating experiments, XRD and DTA results.
Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN AND PENCIRIAN KONDUKTOR ION OKSIDA BARU DALAM SISTEM Bi₂-(W, Mo)-O₆

Oleh

SIM LENG TZE

Disember 2000

Pengerusi: Professor Lee Chnoong Kheng, Ph.D.

Fakulti: Sains dan Pengajian Alam Sekitar


Hanya Nb dan Ta dapat diperkenalkan sebagai dopan ke dalam Bi₂WO₆ dengan pembentukan larutan pepejal yang agak terhad manakala dopan selain daripada W gagal diperkenalkan ke dalam γ-Bi₂MoO₆. Keputusan yang diperolehi daripada IR dan DTA menunjukkan bahawa ikatan logam-oksigen adalah lebih lemah dalam bahan-bahan yang didopkan dengan Nb dan Ta berbanding dengan dalam Bi₂WO₆. Kekonduksian bahan tersebut adalah lebih kurang dua tertib magnitud lebih tinggi
Pengenalan kation bervalensi lebih rendah membawa kepada penghasilan kekosongan tapak oksigen yang membawa kepada kekonduksian yang lebih tinggi.

Pola spektrum IR dan XRD bagi kedua-dua $\gamma$-Bi$_2$WO$_6$ dan $\gamma$-Bi$_2$MoO$_6$ adalah serupa kerana kedua-duanya memiliki struktur yang serupa.

Larutan pepejal yang lengkap diperolehi dalam sistem $\gamma$-Bi$_2$WO$_6$ - $\gamma$-Bi$_2$MoO$_6$ apabila disediakan pada suhu rendah. Ini adalah mungkin memandangkan kesemua petua Hume-Rothery dipatuhi oleh bahan tersebut. Akan tetapi, sesetengah bahan tersebut adalah metastabil dan terurai kepada fasa tercampur apabila dipanaskan pada suhu yang lebih tinggi. Secara amnya, kekonduksian bahan dalam sistem tersebut adalah lebih kurang sama.

Kekonduksian $\gamma'$-Bi$_2$MoO$_6$ adalah sangat bergantung kepada suhu dan jangka masa pemanasan. Ada kemungkinan bahawa kehilangan oksigen berlaku semasa pemanasan pada suhu yang tinggi dan membawa kepada bahan tidak stoikiometri, $\gamma$-Bi$_2$MoO$_{6.8}$. Daripada ujikaji dengan impedans ac, ion oksida merupakan pembawa cas yang utama bagi bahan tersebut.

Gambarajah fasa dalam sistem Bi$_2$WO$_6$ - Bi$_2$MoO$_6$ telah dibina berdasarkan kepada keputusan yang diperolehi daripada ujikaji pemanasan yang berbeza, XRD dan DTA.
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I certify that an Examination Committee met on 19th December 2000 to conduct the final examination of Sim Leng Tze on her Master of Science thesis entitled “Preparation and Characterisation of New Oxide Ion Conductors in the Bi₂-(W, Mo)-O₆ System” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

SIM LENG TZEN

Date: 21 December 2000
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4.65 IR spectra of $\gamma$-Bi$_2$W$_{1-x}$Mo$_x$O$_6$ solid solutions prepared at 530 - 
710°C: (a) x=0, (b) x=0.1, (c) x=0.3, (d) x=0.5, (e) x=0.7, 
(f) x=0.9 and (g) x=1

4.66 IR spectra of Bi$_2$W$_{1-x}$Mo$_x$O$_6$ solid solutions prepared at 800°C: 
(a) x=0, (b) x=0.10, (c) x=0.20, (d) x=0.35, (e) x=0.50 and 
(f) $\gamma$-Bi$_2$Mo$_6$

4.67 IR spectra of $\gamma'$-Bi$_2$Mo$_x$W$_{1-x}$O$_6$ solid solutions prepared at 800°C: 
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4.79 Arrhenius plots of $\gamma\text{-Bi}_2\text{W}_{0.30}\text{Mo}_{0.70}\text{O}_6$

4.80 Arrhenius plots of $\gamma\text{-Bi}_2\text{W}_{0.20}\text{Mo}_{0.80}\text{O}_6$

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4.85 Arrhenius plots of $\gamma'$-Bi$_2$Mo$_x$W$_{1-x}$O$_6$ solid solutions
LIST OF ABBREVIATIONS

ac  alternating current
BIMEVOX  bismuth metal vanadium oxide
dc  direct current
DTA  differential thermal analysis
EMF  electromotive force
EPMA  electron probe microanalysis
FT-IR  Fourier-transform infrared
JCPDS  Joint Committee on Powder Diffraction Standards
μPDSM  micro Powder Diffraction Search/Match
OFN  oxygen free nitrogen
SEM  scanning electron microscope
SOFC  solid oxide fuel cell
TGA  thermogravimetric analysis
XRD  X-ray diffraction
YSZ  yttria stabilised zirconia
A  area
a, b, c  cell parameters
β  angle between a and c
C  capacitance
C_b  bulk capacitance
C_{gb}  grain boundary capacitance
D  diffusion coefficient
e  elementary charge
\( \varepsilon_0 \) \hspace{1cm} \text{permittivity of free space}

\( \varepsilon \) \hspace{1cm} \text{permittivity}

\( \varepsilon' \) \hspace{1cm} \text{relative permittivity}

\( E \) \hspace{1cm} \text{electric field}

\( E_a \) \hspace{1cm} \text{activation energy}

\( f \) \hspace{1cm} \text{frequency}

\( I \) \hspace{1cm} \text{current}

\( k \) \hspace{1cm} \text{force constant}

\( l \) \hspace{1cm} \text{length}

\( \mu \) \hspace{1cm} \text{reduced mass}

\( \mu_{\text{ion}} \) \hspace{1cm} \text{mobility of ions}

\( M^* \) \hspace{1cm} \text{dopant introduced}

\( M^* \) \hspace{1cm} \text{complex electric modulus}

\( M' \) \hspace{1cm} \text{real part of electric modulus}

\( M'' \) \hspace{1cm} \text{imaginary part of electric modulus}

\( N_{\text{ion}} \) \hspace{1cm} \text{number of ions}

\( \omega \) \hspace{1cm} \text{angular frequency}

\( P'_{\text{O}_2} \) \hspace{1cm} \text{partial pressure of O}_2 \text{ of sample}

\( P''_{\text{O}_2} \) \hspace{1cm} \text{partial pressure of O}_2 \text{ of reference material}

\( R \) \hspace{1cm} \text{resistance}

\( \rho \) \hspace{1cm} \text{resistivity}

\( \sigma \) \hspace{1cm} \text{conductivity}
\( \tau \)  
relaxation time

\( T \)  
temperature

\( \bar{\nu} \)  
wavenumber

\( X \)  
reactance

\( Z^* \)  
impedance

\( Z' \)  
real part of impedance

\( Z'' \)  
imaginary part of impedance
CHAPTER 1
INTRODUCTION

1.1 Solid Electrolytes and Oxide Ion Conductors

Electrical conduction occurs by the long-range diffusion of either electrons or ions. Usually, conduction by one or the other type of charge carrier predominates but in some inorganic materials both ionic and electronic conduction are significant.

Migration of ions at normal temperatures does not occur to any appreciable extent in most ionic and covalent bonded solids such as oxides and halides. For example, NaCl is an insulator at room temperature with a conductivity of only $\sim 10^{-15}$ S cm$^{-1}$.

The idea that ions can diffuse as rapidly in a solid as in an aqueous solution or in a molten salt may seem astonishing. However, since the 1960s, a variety of solids that include crystalline compounds, glasses, polymers and composite materials with exceptionally high ionic conductivities have been discovered. Many of these materials have been synthesised and studied. These include materials where the conduction species are anions (e.g. $F^-$ and $O^{2-}$) or cations (e.g. $H^+$, $Li^+$, $Na^+$, $Cu^+$, $Ag^+$). A variety of names have been given for these materials including solid electrolytes, superionic conductors, and fast-ion conductors. ‘Solid electrolytes’ arguably provides the least misleading and broadest description for this class of materials. Such materials often have rather special crystal structures in that there are open tunnels or layers through which the mobile ions may move.
In Figure 1.1, the electrical conductivities of several common substances and representative solid electrolytes are shown at the temperatures where the materials have potential application. The solid electrolytes have conductivities that fall between those of a typical semiconductor, silicon and a typical aqueous electrolyte, sodium chloride.

There has been active research in the area of fast-ion transport in solids in recent years, partly because of the many potential technological applications of solid electrolytes. These applications include high-energy-density batteries, fuel cells, sensors, electrochromic materials for both optical display and ‘smart window’ devices, low-cost electrolysis of water and selective atomic filters. Devices using solid electrolytes are already available commercially: oxygen detectors for automotive pollution-control systems employ solid $\text{O}^2$- conductors and solid-state batteries using $\text{Li}^+$ conducting solid electrolytes are employed in heart pacemakers.