UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERISATION OF NEW OXIDE ION CONDUCTORS IN THE Bi2-(W, Mo)-O_6 SYSTEM

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For my parents, with love

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chairperson: Professor Lee Chnoong Kheng, Ph.D.

Faculty: Science and Environmental Studies

Bi_2WO_6, Bi_2MoO_6 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 Bi_2WO_6 with rather limited solid solution formation while introduction of dopants other than W into γ-Bi_2MoO_6 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, Bi_2WO_6. The conductivity of these materials was about two orders of magnitude higher than that of Bi_2WO_6. Introduction of lower valency cation results in the creation of oxygen vacancies resulting in higher conductivity.

The IR and XRD patterns of both γ-Bi_2WO_6 and γ-Bi_2MoO_6 are very similar since the materials are isostructural.

Complete solid solutions in the γ-Bi_2WO_6 - γ-Bi_2MoO_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 γ'-Bi_2MoO_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 γ'-$Bi_2MoO_{6-\delta}$. From ac impedance studies, oxide ions appear to be the main charge carriers in this material.

Phase diagram in the Bi_2WO_6 - Bi_2MoO_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 Bi_2-(W, Mo)-O_6

Oleh

SIM LENG TZE

Disember 2000

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Fakulti: Sains dan Pengajian Alam Sekitar

Bi_2WO_6, Bi_2MoO_6 dan bahan yang berkaitan telah disediakan melalui tindak balas keadaan pepejal. Ketulenan fasa bahan tersebut ditentukan dengan menggunakan pembelauan serbuk sinar-X (XRD). Teknik pencirian lanjutan menggunakan spektrometer inframerah transformasi Fourier (FT-IR), analisis pembezaan terma (DTA) dan spektroskopi impedans telah dijalankan ke atas sampel yang berfasa tunggal. Analisis termogravimetri (TGA) dan mikroskopi imbasan elektron (SEM) juga dijalankan ke atas sampel-sampel terpilih.

Hanya Nb dan Ta dapat diperkenalkan sebagai dopan ke dalam Bi_2WO_6 dengan pembentukan larutan pepejal yang agak terhad manakala dopan selain daripada W gagal diperkenalkan ke dalam γ-Bi_2MoO_6. 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 Bi_2WO_6. Kekonduksian bahan tersebut adalah lebih kurang dua tertib magnitud lebih tinggi

daripada Bi_2WO_6. 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 γ-Bi_2WO_6 dan γ-Bi_2MoO_6 adalah serupa kerana kedua-duanya memiliki struktur yang serupa.

Larutan pepejal yang lengkap diperolehi dalam sistem γ-Bi_2WO_6 - γ-Bi_2MoO_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 γ'-Bi_2MoO_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, γ-$Bi_2MoO_{6-\delta}$. Daripada ujikaji dengan impedans ac, ion oksida merupakan pembawa cas yang utama bagi bahan tersebut.

Gambarajah fasa dalam sistem Bi_2WO_6 - Bi_2MoO_6 telah dibina berdasarkan kepada keputusan yang diperolehi daripada ujikaji pemanasan yang berbeza, XRD dan DTA.

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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

e_o	permittivity of free space
ε	permittivity
ε'	relative permittivity
E	electric field
E_a	activation energy
f	frequency
I	current
k	force constant
l	length
μ	reduced mass
μ_{ion}	mobility of ions
M*	dopant introduced
M*	complex electric modulus
M'	real part of electric modulus
M"	imaginary part of electric modulus
N_{ion}	number of ions
ω	angular frequency
$P"_{O_2}$	partial pressure of O_2 of reference material
P'_{O_2}	partial pressure of O_2 of sample
R	resistance
ρ	resistivity
σ	conductivity

τ	relaxation time
T	temperature
$\tilde{\nu}$	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 ~ 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 (eg. 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.

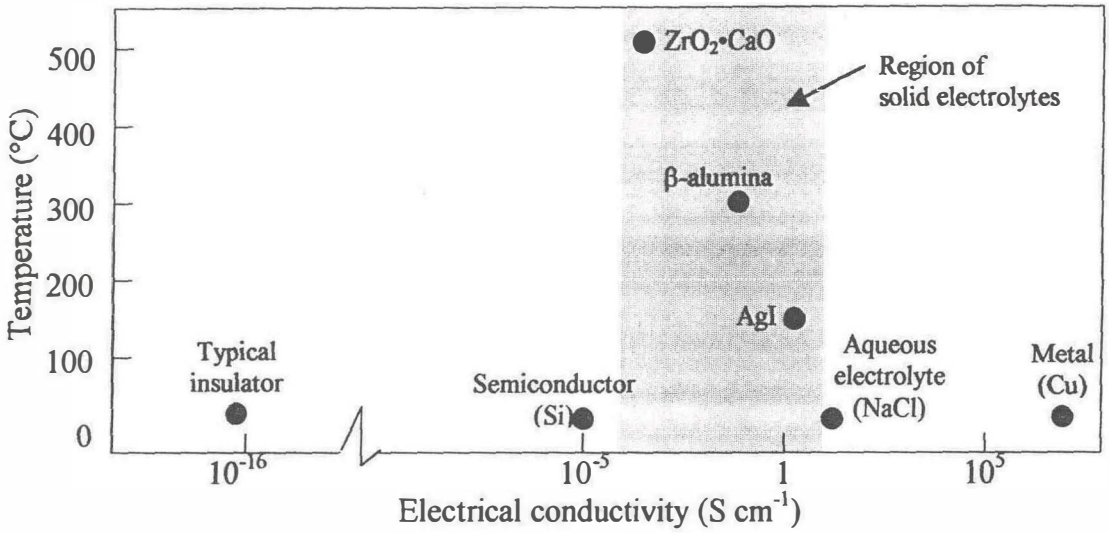

Figure 1.1: Electrical conductivities of selected common substances and representative solid electrolytes (Greenblatt, 1994)

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 O^{2-} conductors and solid-state batteries using Li^{+} conducting solid electrolytes are employed in heart pacemakers.