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PREPARATION AND CHARACTERIAZATION OF BISMUTH NIOBIUM OXIDE ION CONDUCTORS

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PREPARATION AND CHARACTERIAZATION OF BISMUTH NIOBIUM OXIDE ION CONDUCTORS

By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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

PREPARATION AND CHARACTERIAZATION OF BISMUTH NIOBIUM OXIDE ION CONDUCTORS

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Chairman : Tan Yen Ping, Ph.D.

Faculty : Science

Materials in Bi_2O_3-Nb_2O_5 binary system have been successfully synthesized by conventional solid-state method and also mechanochemical method. Solid solution series, Bi_xNbO_δ was obtained at $2.5 \leq x \leq 6$ for both conventional solid-state method and mechanochemical method. Bi_3NbO_7 was successfully obtained by mechanochemical method at lower synthesis temperature (milled at 1000 rpm for 1 hour followed by heating at 700 ^oC for 24 hours) than conventional solid-state method. All the peaks in the XRD patterns can be fully indexed in a tetragonal system with space group *I*4m2.

Electrical measurements indicated that, although both the Bi_3NbO_7 synthesized by two different methods exhibited almost the same conductivities. However the sample prepared by mechanochemical method showed lower activation energy. Among the solid solutions prepared by two different methods, Bi_5NbO_{10} and

$Bi_6NbO_{11.5}$ exhibit the highest conductivity. Conductivity measurements were also carried out in dry oxygen free nitrogen (OFN) and different applied voltage in order to confirm the conduction species of the materials.

Doping was carried on the Nb site with the selected dopants, i.e. Ta, W, V, Zr, Ti, Si, Co and Mo in order to enhance the electrical properties of the material. All dopants can be introduced into Bi_5NbO_{10} with rather limited solid solutions. Among the doped materials, $Bi_5Nb_{0.95}Cu_{0.05}O_{9.925}$ exhibited the highest conductivity, which is one order higher than YSZ, which is used as the electrode material in solid oxide fuel cell currently. The activation energy is also comparable to that of YSZ, 0.8 eV. Conductivity of $Bi_5Nb_{0.91}Zr_{0.09}O_{9.955}$ was slightly higher than that of the parent material. No significant difference in conductivity was observed for other doped materials compared to the parent material Bi_5NbO_{10}.

DTA thermograms of the materials in Bi_xNbO_δ ($2.5 \leq x \leq 6$) solid solutions showed that there are no thermal changes and phase transitions were observed. Whereas TGA result indicates that these materials were thermally stable for the temperature range studied. Elemental analysis was carried by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The analysis confirmed the composition of the stoichiometric for single phase material.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Sarjana Sains

PENYEDIAAN DAN PENCIRIAN KONDUKTOR ION OKSIDA NIOBIUM BISMUTH

Oleh

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Konduktor ion oksida dalam sistem Bi_2O_3-Nb_2O_5 telah berjaya disediakan melalui cara tindak balas keadaan pepejal dan juga mekanokimia. Bagi kedua-dua kaedah ini, siri larutan pepejal bagi Bi_xNbO_δ telah diperolehi dalam julat $2.5 \le x \le 6$. Melalui kaedah mekanokimia, Bi_3NbO_7 telah berjaya disediakan dengan suhu sintesis yang lebih rendah (penginciran pada 1000 rpm selama 1 jam diikuti dengan pemanasan pada 700°C selama 24 jam) berbanding dengan cara tindak balas keadaan pepejal. Semua puncak dalam data XRD dapat diindeks sepenuhnya dalam simetri tetragonal dengan kumpalan ruang *I4*m2.

Ukuran elektrik menunjukkan nilai kekonduksian yang hampir sama bagi Bi_3NbO_7 walaupun disediakan melalui dua cara yang berbeza. Namun demikian, bahan yang disediakan melalui cara mekanokimia menunjukkan tenaga pengaktifan yang lebih rendah. Di antara larutan pepejal yang disediakan melalui dua cara yang berlainan ini, Bi_5NbO_{10} dan $Bi_6NbO_{11.5}$ menunjukkan kekonduksian yang paling tinggi.

Ukuran kekonduksian juga dijalankan dalam keadaan oksigen bebas nitrogen dan dikenakan voltan yang berlainan demi mengenal pasti jenis kekonduksian bahan.

Pendopan dijalankan di kekisi Nb dengan dopan yang terpilih seperti Ta, W, V, Zr, Ti, Si, Co dan Mo bagi meningkatkan kekonduksian bahan. Semua dopan dapat diperkenalkan ke dalam Bi_5NbO_{10} dengan larutan pepejal yang agak terhad. Di antara semua bahan ini, didapati $Bi_5Nb_{0.95}Cu_{0.05}O_{9.925}$ menunjukkan kekonduksian yang paling tinggi, iaitu satu tertib lebih tinggi daripada YSZ yang sesuai digunakan sebagi elektrod dalam SOFC. Tenaga pengaktifannya juga hampir dengan YSZ iaitu 0.8 eV. Kekonduksian bagi $Bi_5Nb_{0.91}Zr_{0.09}O_{9.955}$ adalah lebih tinggi jika berbanding dengan bahan induk, manakala, tiada perbezaan yang ketara dalam kekonduksian bagi bahan-bahan lain yang didopkan berbanding dengan bahan induk Bi_5NbO_{10}.

Analisis perbezaan terma (DTA) menunjukkan tiada perubahan terma dan fasa bagi bahan dalam larutan pepejal Bi_xNbO_δ ($2.5 \le x \le 6$). Sementara, TGA menunjukkan bahan adalah stabil secara terma bagi julat suhu yang diuji. Analisis unsur yang dijalankan melalui plasma aruhan gandaan-spektroskopi penyebaran optik (ICP-OES) membuktikan komposisi stoikiometri bagi bahan berfasa tulen yang disediakan.

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I certify that a Thesis Examination Committee has met on 22 October 2009 to conduct the final examination of Ng Sin Nee on her thesis entitled "Preparation and Characteriszation of Bismuth Oxide Ion Conductors" in accordance the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Scence.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Date: 14 January 2010

DECLARATION

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

NG SIN NEE

Date: 26 January 2010

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS/ NOTATIONS/ GLOSSARY OF TERMS

3D	three dimensions
ac	alternating current
dc	direct current
DTA	differential thermal analysis
FT-IR	Fourier-transform infrared spectroscopy
ICDD	international centre for diffraction data
ICP-AES	inductivity coupled plasma-atomic emission spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standards
μ PDSM	micro powder diffraction search/ match
SEM	scanning electron microscopy
SOFC	solid oxide fuel cell
TGA	thermogravimetry analysis
XRD	x-ray diffraction
a,b,c,α,β,γ	lattice diffraction
A	area
A_w	Warbung coefficient
C	capacitance
C_b	bulk capacitance
C_{dl}	double-layer capacitance
C_{gb}	grain boundary capacitance
C_o	vacuum capacitance
d	d-spacing
D	density

e	charge of the conducting species
e_o	permittivity of free space
E	electric field
E_a	activation energy
ε'	relative permittivity
ε^*	complex permittivity
f	frequency
F	Faraday constant
h,k,l	Miller indices
I	current
j	flux of charge
J	density of the current
l	thickness
λ	wavelength
M	dopant introduced
M'	real part of modulus
M"	imaginary part of modulus
M^*	complex modulus
μ	mobility of the species
P'	partial pressure to be measured
P"	reference partial pressure
R	resistance
R	Boltzmann constant
R_b	bulk resistance