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PREPARATION AND CHARACTERIZATION OF MONO-DIMENSIONAL OXIDE ION CONDUCTORS IN $Bi_2O_3MoO_3$ SYSTEM

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By

LIM CHIA MENG

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PREPARATION AND CHARACTERIZATION OF MONO-DIMENSIONAL OXIDE ION CONDUCTORS IN $Bi_2O_3MoO_3$ SYSTEM

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A new family of mono-dimensional oxide ion conductors with a formula xBi_2O_3: MoO_3 has been prepared by three different methods: solid state, mechanochemical and *n*-butylamine method. X-ray powder diffraction (XRPD) analysis showed that materials with compositions $Bi_xMo_{10}O_\delta$ ($25.5 \leq x \leq 27.5$) prepared by solid state method formed high-temperature (HT) phase after heating at 800°C for 48 hours. With mechanochemical and *n*-butylamine methods, the lower limit of solid solution was $x = 25$. In the mechanochemical method, HT-$Bi_{26}Mo_{10}O_{69}$ was obtained after milling at 1400 rpm for 1 hour, followed by heating at 800°C for only 1 hour or 750°C for 24 hours. With *n*-butylamine method, the reaction product had to be heated at 800°C for 48 hours to yield a phase pure HT-$Bi_{26}Mo_{10}O_{69}$. All the peaks in the XRPD patterns of HT-phase materials can be fully indexed in a monoclinic symmetry with space group $P2/c$. Materials of compositions $27 \leq x \leq 31$ appears to form a low-temperature (LT) phase after being heated at 650°C for 48 hours. For LT-phase materials, the XRPD patterns were fully indexed in a monoclinic symmetry with space group $P2_1/a$.

Electrical properties of phase pure materials were determined using impedance spectroscopy. From the results, HT-$Bi_{26}Mo_{10}O_{69}$ prepared by mechanochemical and *n*-butylamine methods exhibited higher conductivity values compared to that prepared via solid-state method in the temperature range of 200-300^{o}C. HT-$Bi_{27}Mo_{10}O_{70.5}$ prepared by solid state method exhibited highest conductivity among the HT-phase solid solutions. There was, however, no difference in conductivity for HT-$Bi_{27}Mo_{10}O_{70.5}$ prepared by the three different methods. The high-temperature polymorph of $Bi_{27}Mo_{10}O_{70.5}$ exhibited higher conductivity than the low-temperature polymorph.

Doping was carried out on the Mo site of HT-$Bi_{27}Mo_{10}O_{70.5}$ with selected dopants, i.e. Al, Cr, Ge, Si, Sn, Zr, As, Nb, Sb and W. All dopants could be introduced into $Bi_{27}Mo_{10}O_{70.5}$ with rather limited solid solutions. $Bi_{27}Mo_{9.5}Zr_{0.5}O_{70}$ gave a conductivity value one order higher than the parent material $Bi_{27}Mo_{10}O_{70.5}$. No significant difference in conductivity was observed for other doped materials compared to the parent material $Bi_{27}Mo_{10}O_{70.5}$.

The stoichiometric composition of phase pure materials was confirmed by inductively coupled plasma-optical emission spectrometry (ICP-OES). The phase transition of triclinic-monoclinic for HT-$Bi_xMO_{10}O_\delta$ ($25.5 \leq x \leq 27$) was observed in differential thermal analysis (DTA) and differential scanning calorimetry (DSC). No thermal event was observed for doped materials, except $Bi_{27}Mo_{9.8}W_{0.2}O_{70.5}$. No weight loss of phase pure materials was observed in the thermogravimetric analysis (TGA).

Scanning electron microscopy (SEM) experiments showed that the grain size of single phase materials was in the range of 10 – 20 μm, with low porosity. The straight-line plots of density versus x in $Bi_xMo_{10}O_\delta$ solid solutions indicated that Vegard's law was obeyed. Absorptions in the far IR region (400 – 1000 cm^{-1}) due to the vibration of Mo-O bond were observed in Fourier-transform infrared (FT-IR) spectroscopy.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN DAN PENCIRIAN SATU DIMENSI KONDUKTOR ION OKSIDA DALAM $Bi_2O_3MoO_3$ SISTEM

Oleh

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Konduktor ion oksida jenis mono-dimensi dalam keluarga baru dengan formula xBi_2O_3: MoO_3 telah disediakan dengan tiga cara yang berlainan: tindak balas keadaan pepejal, mekanokimia dan *n*-butilamina. Analisis pembelauan serbuk sinar-x (XRPD) menunjukkan bahawa bahan-bahan dengan komposisi $Bi_xMo_{10}O_\delta$ ($1.275 \leq x \leq 1.375$) yang disintesis melalui cara tindak balas keadaan pepejal adalah dalam fasa suhu tinggi (HT-phase) selepas dipanaskan pada 800°C selama 48 jam. Manakala dengan cara-cara mekanokimia dan *n*-butilamina, larutan pepejal terendah mempunyai komposisi dengan $x = 1.25$. Bahan-bahan berkomposisi $1.35 \leq x \leq 1.55$ adalah dalam fasa suhu rendah (LT-phase) selepas dipanaskan pada 650°C selama 48 jam. HT-$Bi_{26}Mo_{10}O_{69}$ (bahan induk) telah dihasilkan selepas penginciran pada 1400 rpm selama 1 jam, diikuti dengan pemanasan pada 800°C selama 1 jam atau 750°C selama 24 jam. Dengan cara *n*-butilamina, bahan tindak balas perlu dipanaskan pada 800°C selama 48 jam untuk menghasilkan fasa tulen HT-$Bi_{26}Mo_{10}O_{69}$. Semua puncak dalam data XRPD bagi bahan-bahan berfasa suhu tinggi boleh diindeks sepenuhnya dalam simetri monoklinik dengan kumpulan ruang $P2/c$. Untuk bahan-

bahan berfasa suhu rendah, XRPD data telah diindeks sepenuhnya dalam simetri monoklinik dengan kumpulan ruang $P2_1/a$.

Kekonduksian bagi bahan-bahan berfasa tulen telah diukur dengan menggunakan spektroskopi impedans. HT-$Bi_{26}Mo_{10}O_{69}$ yang disediakan melalui cara-cara mekanikal kimia dan *n*-butilamina telah menunjukkan nilai kekonduksian yang tertinggi pada suhu antara 200-300^oC berbanding dengan HT-$Bi_{26}Mo_{10}O_{69}$ yang disediakan melalui cara tindak balas keadaan pepejal. HT-$Bi_{27}Mo_{10}O_{70.5}$ menunjukkan kekonduksian tertinggi antara bahan-bahan berfasa suhu tinggi yang disediakan melalui cara tindak balas keadaan pepejal. Namun, tiada perbezaan kekonduksian antara bahan-bahan berkomposisi HT-$Bi_{27}Mo_{10}O_{70.5}$ yang disediakan melalui tiga cara yang berlainan. $Bi_{27}Mo_{10}O_{70.5}$ berfasa suhu tinggi menunjukkan kekonduksian yang tinggi berbanding dengan $Bi_{27}Mo_{10}O_{70.5}$ berfasa suhu rendah.

Proses pendopan dengan pelbagai dopan, termasuk Al, Cr, Ge, Si, Sn, Zr, As, Nb, Sb dan W, telah dijalankan untuk HT-$Bi_{27}Mo_{10}O_{70.5}$. Semua jenis dopan boleh didopkan ke dalam $Bi_{27}Mo_{10}O_{70.5}$ dengan larutan pepejal yang agak terhad. $Bi_{27}Mo_{9.5}Zr_{0.5}O_{70}$ memberikan nilai kekonduksian satu tertib lebih tinggi berbanding dengan bahan induk $Bi_{27}Mo_{10}O_{70.5}$. Tiada perbezaan yang ketara dalam kekonduksian bagi bahan-bahan didopkan berbanding bahan induk $Bi_{27}Mo_{10}O_{70.5}$.

Komposisi stoikiometri bagi bahan-bahan berfasa tulen telah ditentukan melalui eksperimen plasma aruhan gandaan-spektroskopi penyebaran optik (ICP-OES). Perubahan fasa antara trikilnik –monoklinik bagi HT-$Bi_xMO_{10}O_\delta$ ($25.5 \leq x \leq 27$) telah didapati dalam analisis pembezaan terma (DTA) dan kalorimetri pembezaan pengimbasan (DSC). Tiada peristiwa terma bagi bahan-bahan didopkan, kecuali $Bi_{27}Mo_{9.8}W_{0.2}O_{70.5}$. Didapati tiada kehilangan jisim bagi bahan-bahan berfasa tulen dalam analisis thermogravimetri (TGA).

Ujian imbasan elektron mikrograf (SEM) menunjukkan saiz butir-butiran bagi setiap bahan adalah dalam lingkungan 10 – 20 μm, dengan keliangan yang rendah. Plot gengan garisan lurus untuk ketumpatan lawan nilai x dalam larutan pepejal $Bi_xMo_{10}O_\delta$ menunjukkan bahawa Hukum Vegard adalah dipatuhi. Penyerapan dalam IR berlingkungan jauh (400 – 1000 cm^{-1}) yang disebabkan oleh getaran ikatan Mo-O telah didapati dalam spektroskopi inframerah transformasi Fourier (FT-IR).

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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.

LIM CHIA MENG

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TABLE OF CONTENTS

Page

ABSTRACT ii
ABSTRAK v
ACKNOWLEDGEMENTS viii
APPROVAL x
DECLARATION xi
LIST OF TABLES xv
LIST OF FIGURES xvii
LIST OF ABBREVIATIONS xxiv

CHAPTER

1. INTRODUCTION

1.1 Solid State Chemistry 1
1.2 Solid Solutions 2
1.3 Solid Electrolytes and Oxide Ion Conductors 3
1.4 Applications of Oxide Ion Conductor 8
  1.4.1 Oxygen Sensors 8
  1.4.2 Solid Oxide Fuel Cells (SOFCs) 9
1.5 Objectives 11

2. LITERATURE REVIEW

2.1 Bismuth-based Oxide Ion Conductors 13
2.2 $Bi_{26}Mo_{10}O_{69}$ Family 19
  2.2.1 Synthesis Conditions 19
  2.2.2 Polymorphism 21
  2.2.3 Structure 23
  2.2.4 Introduction of Dopants 31

3. EXPERIMENTAL

3.1 Sample Preparation 35
  3.1.1 General Principle of Solid State Reaction 35
  3.1.2 Solid State Reaction with Manual Mixing 35
  3.1.3 Synthesis with Mechanochemical and *n*-butylamine Mixing 37
3.2 Pellet Preparation 40
3.3 Characterization 40
  3.3.1 X-ray Powder Diffraction (XRPD) 41
  3.3.2 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) 44
  3.3.3 Thermal Analysis 45
  3.3.4 Scanning Electron Microscopy (SEM) 47
  3.3.5 Density Measurement 48
  3.3.6 Fourier-transform Infrared Spectroscopy (FT-IR) 48
  3.3.7 Electrical Properties 49
  3.4 Estimation of Errors 62

4. RESULTS AND DISCUSSION

4.1 Phase Formation 63
  4.1.1 Solid State Synthesis 63
    4.1.1.1 Parent Material $Bi_{26}Mo_{10}O_{69}$ 63
    4.1.1.2 $Bi_{26}Mo_{10}O_{69}$ Solid Solutions 67
  4.1.2 Mechanochemical Synthesis 74
    4.1.2.1 Parent Material $Bi_{26}Mo_{10}O_{69}$ 74
    4.1.2.2 $Bi_{26}Mo_{10}O_{69}$ Solid Solutions 77
  4.1.3 *n*-butylamine Synthesis 83
    4.1.3.1 Parent Material $Bi_{26}Mo_{10}O_{69}$ 83
    4.1.3.2 $Bi_{26}Mo_{10}O_{69}$ Solid Solutions 83
  4.1.4 Low-temperature (LT) phase Materials 87
    4.1.4.1 LT-$Bi_{30}Mo_{10}O_{75}$ 87
    4.1.4.2 LT-$Bi_{30}Mo_{10}O_{75}$ Solid Solutions 91
  4.1.5 Elemental Analysis 96
  4.1.6 Thermal Analyses 100
    4.1.6.1 Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) 100
    4.1.6.2 Thermogravimetric analysis (TGA) 113
  4.1.7 Scanning Electron Microscopy 113
    4.1.7.1 Parent Material $Bi_{26}Mo_{10}O_{69}$ 113
    4.1.7.2 $Bi_{26}Mo_{10}O_{69}$ Solid Solutions 116
    4.1.7.3 Low-temperature phase Materials 126
  4.1.8 Density Measurement 126
  4.1.9 Fourier-transform Infrared Spectroscopy (FT-IR) 129
  4.1.10 Summary 134
4.2 Electrical Properties of $Bi_{26}Mo_{10}O_{69}$ Solid Solutions 137
  4.2.1 $Bi_{26}Mo_{10}O_{69}$ Solid Solutions Prepared Via Solid State Synthesis 137
  4.2.2 $Bi_{26}Mo_{10}O_{69}$ Solid Solutions Prepared Via Mechanochemical Synthesis 155
  4.2.3 $Bi_{26}Mo_{10}O_{69}$ Solid Solutions Prepared Via *n*-butylamine Synthesis 162
  4.2.4 Low-temperature phase Materials 166
  4.2.5 Summary 169
4.3 Doped Materials 171
  4.3.1 Phase Formation 171
  4.3.2 Elemental Analysis 188
  4.3.3 Thermal Analysis 190
    4.3.3.1 Differential Thermal Analysis (DTA) 190
    4.3.3.2 Thermogravimetric analysis (TGA) 191
  4.3.4 Scanning Electron Microscopy (SEM) 199
  4.3.5 Density Measurement 199
  4.3.6 Electrical Properties of Doped Materials 205
  4.3.7 Summary 227

5. CONCLUSIONS 231

FURTHER WORK 235
REFERENCES 236
APPENDICES 244
BIODATA OF THE AUTHOR 249

LIST OF TABLES

Table **Page**

2.1 Conductivity of each phase of Bi_2O_3 at 650°C 14

3.1 Wavelength used and detection limits of elements in ICP-OES analysis 45

3.2 Capacitance values and their possible interpretations 58

3.3 Estimation of errors for experimental parameters 62

4.1 The lattice parameters of HT-phase materials $Bi_xMo_{10}O_\delta$ $(25.5 \leq x \leq 27.5)$ prepared via solid state method 67

4.2 Phase assemblage of $Bi_xMo_{10}O_\delta$ $(25 \leq x \leq 28)$ prepared via solid state method 68

4.3 Phase assemblage of $Bi_xMo_{10}O_\delta$ $(24.5 \leq x \leq 28)$ prepared via mechanochemical method 82

4.4 The lattice parameters of HT-phase materials $Bi_xMo_{10}O_\delta$ $(25 \leq x \leq 27.5)$ prepared via mechanochemical method 82

4.5 Phase assemblage of $Bi_xMo_{10}O_\delta$ $(24.5 \leq x \leq 28)$ prepared via *n*-butylamine method 86

4.6 The lattice parameters of HT-phase materials $Bi_xMo_{10}O_\delta$ $(25 \leq x \leq 27.5)$ prepared via *n*-butylamine method 87

4.7 Phase assemblage of $Bi_xMo_{10}O_\delta$ $(26 \leq x \leq 32)$ 94

4.8 The lattice parameters of LT-phase materials $Bi_xMo_{10}O_\delta$ $(27 \leq x \leq 31)$ 95

4.9 Elemental concentrations of HT-$Bi_xMo_{10}O_\delta$ $(1.275 \leq x \leq 1.375)$ synthesized via solid state method 97

4.10 Elemental concentrations of HT-$Bi_xMo_{10}O_\delta$ $(1.25 \leq x \leq 1.375)$ synthesized via mechanochemical method 98

4.11 Elemental concentrations of HT-$Bi_xMo_{10}O_\delta$ $(1.25 \leq x \leq 1.375)$ synthesized via *n*-butylamine method 99

4.12 Elemental concentrations of selected LT-$Bi_xMo_{10}O_\delta$ 100

4.13 The phase transition temperatures of DTA and DSC for HT-$Bi_xMo_{10}O_\delta$ $(25.5 \leq x \leq 27.5)$ prepared via solid state method 102

4.14 The phase transition temperatures of DTA and DSC for HT-$Bi_xMo_{10}O_\delta$ $(25 \leq x \leq 27.5)$ prepared via mechanochemical method 104

4.15 The phase transition temperatures of DTA and DSC for HT-$Bi_xMo_{10}O_\delta$ ($25 \leq x \leq 27.5$) prepared via *n*-butylamine method 108

4.16 Densities of HT-$Bi_xMo_{10}O_\delta$ ($25.5 \leq x \leq 27.5$) prepared via solid state method 128

4.17 Densities of HT-$Bi_xMo_{10}O_\delta$ ($25.5 \leq x \leq 27.5$) prepared via mechanochemical method 129

4.18 Densities of HT-$Bi_xMo_{10}O_\delta$ ($25 \leq x \leq 27.5$) prepared via *n*-butylamine method 129

4.19 Conductivity (σ_{250} and σ_{600}) and activation energy (E_a) of $Bi_xMo_{10}O_\delta$ ($25.5 \leq x \leq 26.5$) 149

4.20 Conductivity (σ_{500}) and activation energy (E_a) of selected LT-phase materials 168

4.21 The coordination number (CN), charge, and ionic radius of the dopants 171

4.22 Phase assemblage of single phase doped materials 185

4.23 The lattice parameters of single phase doped materials with general formula $Bi_{27}Mo_{10-x}M_xO_\delta$ (M = dopant) 187

4.24 Elemental concentrations of $Bi_{27}Mo_{10-x}Nb_xO_\delta$ ($0 \leq x \leq 0.20$) 189

4.25 Elemental concentrations of $Bi_{27}Mo_{10-x}As_xO_\delta$ ($0 \leq x \leq 1.70$) 189

4.26 Elemental concentrations of $Bi_{27}Mo_{10-x}Zr_xO_\delta$ ($0 \leq x \leq 0.50$) 190

4.27 The DTA phase transition temperatures for HT-$Bi_{27}Mo_{10}O_{70.5}$ and $Bi_{27}Mo_{9.8}W_{0.2}O_{70.5}$ 191

4.28 Densities of Cr-doped materials, $Bi_{27}Mo_{10-x}Cr_xO_\delta$ ($0 \leq x \leq 1.40$) 204

4.29 Densities of W-doped materials, $Bi_{27}Mo_{10-x}W_xO_\delta$ ($0 \leq x \leq 1.10$) 204

4.30 Conductivity (σ_{250} and σ_{600}) and activation energies (E_a) of doped materials 226

LIST OF FIGURES

Figure **Page**

1.1 Electrical conductivities of selected common substances and representative solid electrolytes (Greenblatt, 1994) 5

1.2 Schematic operation of SOFC (Fisher,1999) 11

2.1 (a, b) projection of $Bi_{26}Mo_{10}O_{69}$ structure with $[Bi_{12}O_{14}]_\infty$ columns extending along the twofold axis (Vannier *et al*., 1996) 24

2.2 (b, c) projection of $Bi_{26}Mo_{10}O_{69}$ (Vannier *et al*., 1996) 24

2.3 (a, c) projection of $Bi_{26}Mo_{10}O_{69}$ (Vannier *et al*., 1996) 25

2.4 $[Bi_{12}O_{14}]$ rose (Vannier *et al*., 1996) 26

2.5 Bi(1)-Bi(6) and Mo surroundings (Vannier *et al*., 1996) 26

2.6 Bi(7) surrounding (Vannier *et al*., 1996) 27

2.7 $Bi_{26}Mo_{10}O_{69}$ structure. The shaded zone indicates the area where oxygen diffusion is likely to take place (Vannier *et al*., 2000) 28

3.1 Flow chart for the samples synthesis process 37

3.2 Flow chart for sample preparation and characterization 41

3.3 Principle of X-ray diffraction 43

3.4 Admittance bridge 50

3.5 Impedance bridge 50

3.6 Semi-circle and spike in a cole-cole plot (West, 1984) 54

3.7 Equivalent circuit for a polycrystalline solid electrolyte; C_{dl} – electrode double-layer capacitance; C_b, R_b –bulk crystals; C_{gb}, R_{gb} – grain boundaries 55

3.8 Semi-circles in a complex plane plot (Irvine *et al*., 1990) 56

3.9 Brickwork model of grain boundary regions in a ceramic placed between metal electrodes (Irvine *et al*., 1990) 57

3.10 Impedance diagram due to a blocking interface: (a) a perfectly smooth interface; (b) rough electrode or due to Warburg impedance (Armstrong and Todd, 1995) 59

3.11 (a) A complex Z* plot and (b) the respective Z'' and M'' spectroscopic plots 60

4.1 XRPD patterns showing phase evolution of $Bi_{26}Mo_{10}O_{69}$ with synthesis temperature 64

4.2 XRPD pattern of $Bi_{26}Mo_{10}O_{69}$ 66

4.3 XRPD patterns of $Bi_xMo_{10}O_\delta$ ($25 \leq x \leq 28$) prepared via solid state method 69

4.4 Variation of lattice parameter, a, with x in $Bi_xMo_{10}O_\delta$ solid solutions prepared via solid state method 71

4.5 Variation of lattice parameter, b, with x in $Bi_xMo_{10}O_\delta$ solid solutions prepared via solid state method 72

4.6 Variation of lattice parameter, c, with x in $Bi_xMo_{10}O_\delta$ solid solutions prepared via solid state method 73

4.7 Phase evolution of $Bi_{26}Mo_{10}O_{69}$ synthesized via mechanochemical method (1400 rpm for 1 hour) 75

4.8 Phase evolution of $Bi_{26}Mo_{10}O_{69}$ synthesized via mechanochemical method (700 and 1000 rpm for 1 hour) with synthesis temperature 76

4.9 XRPD patterns of $Bi_xMo_{10}O_\delta$ ($24.5 \leq x \leq 28$) prepared via mechanochemical method 78

4.10 Variation of lattice parameter, a, with x in $Bi_xMo_{10}O_\delta$ solid solutions prepared via mechanochemical method 79

4.11 Variation of lattice parameter, b, with x in $Bi_xMo_{10}O_\delta$ solid solutions prepared via mechanochemical method 80

4.12 Variation of lattice parameter, c, with x in $Bi_xMo_{10}O_\delta$ solid solutions prepared via mechanochemical method 81

4.13 Phase evolution of $Bi_{26}Mo_{10}O_{69}$ synthesized by *n*-butylamine method and heated at 800^{o}C with increasing duration 84

4.14 XRPD diffraction patterns of $Bi_xMo_{10}O_\delta$ ($24.5 \leq x \leq 28$) prepared via *n*-butylamine method 85

4.15 Variation of lattice parameter, a, with x in $Bi_xMo_{10}O_\delta$ solid solutions prepared via *n*-butylamine method 88

4.16 Variation of lattice parameter, b, with x in $Bi_xMo_{10}O_\delta$ solid solutions 89 prepared via *n*-butylamine method

4.17 Variation of lattice parameter, c, with x in $Bi_xMo_{10}O_\delta$ solid solutions prepared via *n*-butylamine method 90

4.18 XRPD diffraction patterns showing phase evolution of LT-$Bi_{30}Mo_{10}O_{75}$ with synthesis temperature 92

4.19 XRPD diffraction patterns of LT-phase $Bi_xMo_{10}O_\delta$ ($26 \leq x \leq 32$) 93

4.20 XRPD patterns of L-$Bi_6Mo_2O_{15}$ (i.e. LT-$Bi_{30}Mo_{10}O_{75}$) and $Bi_{10}Mo_3O_{24}$ 96

4.21 DTA thermograms of $Bi_{26}Mo_{10}O_{69}$ solid solutions prepared via solid state method 101

4.22 DSC thermograms of $Bi_{26}Mo_{10}O_{69}$ solid solutions prepared via solid state method 103

4.23 DTA thermograms of $Bi_{26}Mo_{10}O_{69}$ at various heating and cooling rate 105

4.24 DTA thermograms of $Bi_{26}Mo_{10}O_{69}$ solid solutions prepared via mechanochemical method 106

4.25 DTA thermograms of $Bi_{26}Mo_{10}O_{69}$ solid solutions prepared via and *n*-butylamine method 107

4.26 DSC thermograms of $Bi_{27}Mo_{10}O_{70.5}$ and $Bi_{27.5}Mo_{10}O_{71.25}$ prepared via mechanochemical method 109

4.27 DSC thermograms of $Bi_{27}Mo_{10}O_{70.5}$ and $Bi_{27.5}Mo_{10}O_{71.25}$ prepared via *n*-butylamine method 110

4.28 DTA thermograms of selected LT-phase materials 111

4.29 TGA thermograms of selected HT- and LT-phase materials prepared via solid state method 114

4.30 TGA thermograms of selected HT-phase materials prepared via mechanochemical (a to c) and *n*-butylamine (d and e) methods 115

4.31 SEM micrographs of HT-$Bi_{26}Mo_{10}O_{69}$ (in powder form) prepared by three different methods 117

4.32 SEM micrographs of grain sizes of HT-$Bi_{26}Mo_{10}O_{69}$ (in pellet form) prepared by three different methods 119

4.33 SEM micrograph of $Bi_{26}Mo_{10}O_{69}$ solid solutions prepared by solid state method 121

4.34 SEM micrograph of $Bi_{26}Mo_{10}O_{69}$ solid solutions prepared by mechanochemical method 123

4.35 SEM micrograph of $Bi_{26}Mo_{10}O_{69}$ solid solutions prepared by *n*-butylamine method 125

4.36 SEM micrograph of selected LT-phase materials 127

4.37 Variation of density with x in $Bi_xMo_{10}O_{69}$ of $Bi_xMo_{10}O_{69}$ solid solutions prepared via solid state method 130

4.38 Variation of density with x in $Bi_xMo_{10}O_{69}$ of $Bi_xMo_{10}O_{69}$ solid solutions prepared via mechanochemical method 131

4.39 Variation of density with x in $Bi_xMo_{10}O_{69}$ of $Bi_xMo_{10}O_{69}$ solid solutions prepared via *n*-butylamine method 132

4.40 IR spectra of HT-$Bi_xMo_{10}O_\delta$ ($25.5 \leq x \leq 27.5$) 135

4.41 Complex impedance plane plots for HT-$Bi_{26}Mo_{10}O_{69}$ at (a) 300^oC (b) 500^oC (c) 850^oC 139

4.42 A combined Z” and M” spectroscopic plots for $Bi_{26}Mo_{10}O_{69}$ at 250^oC 141

4.43 A combined Z” and M” spectroscopic plots for $Bi_{27}Mo_{10}O_{70.5}$ at 250^oC 142

4.44 Complex plane plots of HT-$Bi_{26}Mo_{10}O_{69}$ at different voltages, at 550^oC 143

4.45 Complex plane plots of HT-$Bi_{27}Mo_{10}O_{70.5}$ at different voltages, at 550^oC 144

4.46 Arrhenius plots of HT-$Bi_{26}Mo_{10}O_{69}$ 146

4.47 Arrhenius plots of $Bi_xMo_{10}O_\delta$ ($25.5 \leq x \leq 27.5$) synthesized via solid state method (first cooling cycle) 147

4.48 Arrhenius plots of $Bi_{26}Mo_{10}O_{69}$ in two different atmospheres 151

4.49 Arrhenius plots of $Bi_{27}Mo_{10}O_{70.5}$ in two different atmospheres 152

4.50 Isothermal conductivity at 300^oC of HT-$Bi_{26}Mo_{10}O_{69}$ in different atmospheres 153

4.51 Isothermal conductivity at 300^oC of HT-$Bi_{27}Mo_{10}O_{70.5}$ in different atmospheres 154

4.52 Arrhenius plots of $Bi_xMo_{10}O_\delta$ ($25.5 \leq x \leq 27.5$) synthesized via mechanochemical method (first cooling cycle) 157

4.53 Complex impedance plane plot for HT-$Bi_{26}Mo_{10}O_{69}$ synthesized via mechanochemical method at 300^{o}C 158

4.54 A combined Z" and M" spectroscopic plots for HT-$Bi_{26}Mo_{10}O_{69}$ synthesized via mechanochemical method 159

4.55 Arrhenius plot of $Bi_{26}Mo_{10}O_{69}$ synthesized by conventional solid state and mechanochemical methods 161

4.56 Arrhenius plots of $Bi_xMo_{10}O_\delta$ ($25.5 \leq x \leq 27.5$) synthesized via *n*-butylamine method (first cooling cycle) 163

4.57 Arrhenius plot of $Bi_{26}Mo_{10}O_{69}$ synthesized by conventional solid state and *n*-butylamine methods 165

4.58 Arrhenius plots of these selected LT-phase materials and selected HT-phase materials (first cooling cycle) 167

4.59 XRPD diffraction patterns of Al-doped solid solutions, $Bi_{27}Mo_{10-x}Al_xO_\delta$ ($0 \leq x \leq 0.40$) 173

4.60 XRPD diffraction patterns of Si-doped solid solutions, $Bi_{27}Mo_{10-x}Si_xO_\delta$ ($0 \leq x \leq 1.0$) 174

4.61 XRPD diffraction patterns of Sb-doped solid solutions, $Bi_{27}Mo_{10-x}Sb_xO_\delta$ ($0 \leq x \leq 0.2$) 175

4.62 XRPD diffraction patterns of Nb-doped solid solutions, $Bi_{27}Mo_{10-x}Nb_xO_\delta$ ($0 \leq x \leq 0.2$) 176

4.63 XRPD diffraction patterns of Ge-doped solid solutions, $Bi_{27}Mo_{10-x}Ge_xO_\delta$ ($0 \leq x \leq 0.2$) 177

4.64 XRPD diffraction patterns of Cr-doped solid solutions, $Bi_{27}Mo_{10-x}Cr_xO_\delta$ ($0 \leq x \leq 1.4$) 178

4.65 XRPD diffraction patterns of As-doped solid solutions, $Bi_{27}Mo_{10-x}As_xO_\delta$ ($0 \leq x \leq 0.5$) 180

4.66 XRPD diffraction patterns of Sn-doped solid solutions, $Bi_{27}Mo_{10-x}Sn_xO_\delta$ ($0 \leq x \leq 0.5$) 181

4.67 XRPD diffraction patterns of Zr-doped solid solutions, $Bi_{27}Mo_{10-x}Zr_xO_\delta$ ($0 \leq x \leq 0.5$) 182

4.68 XRPD diffraction patterns of W-doped solid solutions, 183

$Bi_{27}Mo_{10-x}W_xO_\delta$ $(0 \leq x \leq 1.1)$

4.69 DTA thermograms of Ge- and Al-doped solid solutions 192

4.70 DTA thermograms of Sb- and Sn-doped solid solutions 193

4.71 DTA thermograms of Nb- and Zr-doped solid solutions 194

4.72 DTA thermograms of W-doped solid solutions 195

4.73 DTA thermograms of Si- and Cr-doped solid solutions 196

4.74 DTA thermograms of As-doped solid solutions 197

4.75 TGA thermograms of selected doped materials 198

4.76 SEM micrograph of selected W-doped materials 200

4.77 SEM micrograph of selected Zr-doped materials 201

4.78 Density measurement of Cr-doped solid solutions ($Bi_{27}Mo_{10-x}Cr_xO_\delta$, $0 \leq x \leq 1.40$) 202

4.79 Density measurement of W-doped solid solutions ($Bi_{27}Mo_{10-x}W_xO_\delta$, $0 \leq x \leq 1.10$) 203

4.80 Complex impedance plane plots of $Bi_{27}Mo_{9.5}Zr_{0.5}O_{70}$ at (a) 300°C (b) 500°C (c) 850°C 206

4.81 Complex impedance plane plots of Bi27Mo9.5As0.5O70.25 at (a) 300oC (b) 500^{o}C (c) 850^{o}C 208

4.82 A combined Z” and M” spectroscopic plots for $Bi_{27}Mo_{9.5}Zr_{0.5}O_{70}$ at 250^{o}C 209

4.83 A combined Z” and M” spectroscopic plots for $Bi_{27}Mo_{9.5}As_{0.5}O_{70.25}$ at 250^{o}C 210

4.84 Complex plane plots of $Bi_{27}Mo_{9.5}Zr_{0.5}O_{70}$ at different voltages, at 550^{o}C 212

4.85 Arrhenius plots of W-doped materials 213

4.86 Arrhenius plots of Zr-doped materials 215

4.87 Arrhenius plots of Cr-doped materials 216

4.88 Arrhenius plots of Si-doped materials 217

4.89 Arrhenius plots of Ge-doped materials 218

4.90 Arrhenius plots of Sb-doped materials 220

4.91 Arrhenius plots of Nb-doped materials 221

4.92 Arrhenius plots of Sn-doped materials 222

4.93 Arrhenius plots of Al-doped materials 223

4.94 Arrhenius plots of As-doped materials 225

4.95 Arrhenius plots of $Bi_{27}Mo_{9.5}Zr_{0.5}O_{70}$ in two different atmospheres 228

4.96 Isothermal conductivity at 300^{o}C of $Bi_{27}Mo_{9.5}Zr_{0.5}O_{70}$ in different atmospheres 229

LIST OF ABBREVIATIONS/NOTATIONS/GLOSSARY OF TERMS

ac	alternating current
BIMEVOX	bismuth metal **v**anadium oxide
dc	direct current
DTA	differential thermal analysis
DSC	differential scanning calorimetry
FT-IR	fourier-transform infrared spectroscopy
HT-	high-temperature
ICDD	international centre for diffraction data
ICP-OES	inductively coupled plasma-optical emission spectrometry
LT-	low-temperature
ppb	parts per billion
OFN	oxygen free nitrogen
SEM	scanning electron microscopy
SD	standard deviations
SOFCs	solid oxide fuel cells
TGA	thermogravimetry analysis
XRPD	x-ray powder diffraction
YSZ	yittria stabilized zirconia
a, b, c	cell parameters
A	area
A*	complex admittance
c	velocity of light
C	capacitance
C_b	bulk capacitance