



UNIVERSITI PUTRA MALAYSIA

***SYNTHESIS AND ELECTRICAL PROPERTIES OF BISMUTH
TANTALATE
BINARY MATERIALS***

KARTIKA BINTI FIRMAN

FS 2018 32



**SYNTHESIS AND ELECTRICAL PROPERTIES OF BISMUTH TANTALATE
BINARY MATERIALS**

By

KARTIKA BINTI FIRMAN

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

January 2018

All material contained within the thesis, including without limitation text, logos, icons, photographs and all other artwork, is copyright material of Universiti Putra Malaysia unless otherwise stated. Use may be made of any material contained within the thesis for non-commercial purposes from the copyright holder. Commercial use of material may only be made with the express, prior, written permission of Universiti Putra Malaysia.

Copyright © Universiti Putra Malaysia



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

SYNTHESIS AND ELECTRICAL PROPERTIES OF BISMUTH TANTALATE BINARY MATERIALS

By

KARTIKA BINTI FIRMAN

January 2018

Chairman : Tan Kar Ban, PhD
Faculty : Science

Phase-pure bismuth tantalate fluorites were successfully prepared via conventional solid-state method at 900 °C in 24 – 48 hours. The solid solution was proposed with the general formula of $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ ($0 \leq x \leq 0.184$), wherein the formation mechanism involved a one-to-one replacement of Ta^{5+} cation by Bi^{3+} cation within ~4.6 mol% difference. These samples crystallised in a cubic symmetry, space group Fm-3m with lattice constants, $a=b=c$ in the range 5.4477(± 0.0037) – 5.4580(± 0.0039) Å. A slight increment in the unit cell was discernible with increasing Bi_2O_3 content and this may attribute to the incorporation of relatively larger Bi^{3+} cation in the host structure. The linear correlation between lattice parameter and composition variable showed that the Vegard's Law was obeyed. Both TGA and DTA analyses showed $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ samples to be thermally stable as neither phase transition nor weight loss was observed within ~28–1000 °C. The correct stoichiometry of sample was confirmed using inductively coupled-plasma optical emission spectroscopy (ICP-OES), in which a close agreement between experimental and theoretical values had been achieved. Electrical properties of $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ solid solution samples were measured over the frequency range 5 Hz – 13 MHz. At intermediate temperatures, ~350 – 850 °C, $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ solid solution was a modest oxide ion conductor with conductivity, $\sim 10^{-6} - 10^{-3} \text{ S cm}^{-1}$; the activation energy was in the range 0.98 – 1.08 eV. Bi-rich sample, $\text{Bi}_{3.184}\text{Ta}_{0.816}\text{O}_{6.816}$ exhibited the highest conductivity of $\sim 1.50 \times 10^{-3} \text{ S cm}^{-1}$ at 650 °C. The improved electrical conductivity could be a result of the structural change in terms of the grain size, surface morphology and oxygen vacancies with increasing bismuth content.

Solid solutions with general formula of $\text{Bi}_3\text{Ta}_{1-x}\text{Ln}_x\text{O}_{7-x}$ (Ln = Nd, Gd and La) had been successfully prepared. The formation mechanism involved a proportion amount of Ta^{5+} cation replaced by Ln^{3+} cation with creation of oxygen vacancy

for charge compensation. Therefore, the overall charge electroneutrality of the system was preserved through a mechanism: $\text{Ln}^{3+} \leftrightarrow \text{Ta}^{5+} + \text{O}^{2-}$. The solid solution limit was up to $x = 0.2$ for Nd-doped $\text{Bi}_3\text{Ta}_{1-x}\text{Nd}_x\text{O}_{7-x}$, with a slight increased lattice constants, $a=b=c$ in the range $5.4477(\pm 0.0037) - 5.4682(\pm 0.0009)$ Å. The increment of unit cell may attribute to the larger Nd^{3+} ionic radius of 0.983 Å if compare to Ta^{5+} of 0.64 Å at 6-fold coordination. Meanwhile, only limited solid solution range, i.e. $x = 0.1$ for both Gd- and La-series. The recorded lattice constants, $a=b=c$ were $5.4635(\pm 0.0002)$ and $5.4687(\pm 0.0002)$ Å, respectively. $\text{Bi}_3\text{Ta}_{0.8}\text{Nd}_{0.2}\text{O}_{6.8}$ exhibited the highest conductivity for the doped lanthanide series at all temperatures, i.e. ~ 350 to 850 °C. The recorded conductivity was $9.26 \times 10^{-3} \text{ S cm}^{-1}$ at 650 °C.

A selection of pentavalent cations was introduced at either Bi-site or Ta-site of Bi_3TaO_7 . However, only substitution of Ta-site was able to yield new solid solution using Nb^{5+} and V^{5+} , respectively. The solid solution mechanism is proposed to be a one-to-one replacement of Ta by Nb or V, with the general formula of $\text{Bi}_3\text{Ta}_{1-x}\text{M}_x\text{O}_7$ ($\text{M} = \text{V}$ or Nb). The solid solution limit for Nb-doped $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ was up to $x = 0.5$. $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ solid solution adopted similar defective fluorite structure, space group Fm-3m with lattice parameters, $a=b=c$ in the range $5.4477(\pm 0.0037) - 5.4654(\pm 0.0011)$ Å. The Nb-doped samples showed an increase in electrical conductivity with increasing Nb content; $\text{Bi}_3\text{Ta}_{0.5}\text{Nb}_{0.5}\text{O}_7$ exhibited the highest conductivity, $\sim 5.96 \times 10^{-3} \text{ S cm}^{-1}$ at 650 °C. The enhanced electrical conductivity for $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ solid solution may attribute to the large and well-connected grains that could reduce the impedance barrier for the charge transfer in samples. On the other hand, a limited solid solution range of $x = 0.1$ was attainable for $\text{Bi}_3\text{Ta}_{1-x}\text{V}_x\text{O}_7$ solid solution with lattice parameters, $a=b=c$, $5.4559 (\pm 0.0011)$ Å. The ionic conductivity exhibited by $\text{Bi}_3\text{Ta}_{0.9}\text{V}_{0.1}\text{O}_7$ was $\sim 4.17 \times 10^{-3} \text{ S cm}^{-1}$ at 650 °C with activation energy of 1.01 eV.

On the other hand, tungsten substituted solid solution, $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7+(x/2)}$ ($0 \leq x \leq 0.2$) with lattice constants, $a=b=c$ in the range $5.4477(\pm 0.0037) - 5.4668(\pm 0.0001)$ Å. The conductivity values of $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7+(x/2)}$ solid solution, $x = 0.1$ and $x = 0.2$ were $\sim 5.15 \times 10^{-3} \text{ S cm}^{-1}$ and $\sim 6.78 \times 10^{-3} \text{ S cm}^{-1}$ at 650 °C, respectively. These conductivity values appeared to be comparable to other doped series, e.g. Nb, V, and slightly higher than that of the parent phase. The relatively higher conductivity of tungsten doped samples may somewhat correlate to minor contribution of electronic conductivity that resulted from the variable oxidation state of tungsten.

In conclusion, Bi_3TaO_7 and related materials were successfully synthesised by solid-state reaction at the optimised conditions. These materials exhibited interesting oxide ionic conductivity that may attribute to the high concentration of oxygen vacancy in the host lattice. The structural and electrical properties of Bi_3TaO_7 and related materials had been demonstrated to be highly dependent on the composition and crystal structure.

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

SINTESIS DAN SIFAT ELEKTRIK BAHAN-BAHAN DI DALAM SISTEM BINARI BISMUT TANTALATE

Oleh

KARTIKA BINTI FIRMAN

Januari 2018

Pengerusi : Tan Kar Ban, PhD
Fakulti : Sains

Bismut tantalate fluorit yang berfasa tulen telah disintesis melalui tindak balas keadaan pepejal pada suhu 900 °C, dalam masa 24 – 48 jam. Larutan pepejal ini dicadangkan dengan satu formula umum, $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ ($0 \leq x \leq 0.184$), di mana pembentukan mekanisme melibatkan penggantian satu kation Ta^{5+} dengan satu kation Bi^{3+} dalam perbezaan peratusan ~4.6 mol%. Sampel-sampel tersebut mengablur dalam struktur simetri kubik, kumpulan ruang Fm-3m dan pemalar kekisi, $a=b=c$ yang berada dalam julat 5.4477(± 0.0037) – 5.4580(± 0.0039) Å. Peningkatan sel unit yang tidak ketara telah diperhatikan dengan kuantiti Bi_2O_3 yang semakin meningkat. Pemerhatian ini mungkin disebabkan oleh kation Bi^{3+} yang bersaiz lebih besar di dalam struktur perumah. Sifat korelasi yang linear di antara parameter kekisi dengan komposisi menunjukkan bahawa Hukum Vegard telah dipatuhi. Kedua-dua analisis TGA dan DTA menunjukkan sampel $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ adalah stabil secara terma memandangkan tidak ada sebarang peralihan fasa mahupun pengurangan berat yang diperhatikan dalam julat suhu ~28 – 1000 °C. Komposisi stoikiometri sampel yang tepat telah ditentukan dengan spektroskopi pancaran atomik plasma ganding induktif (ICP-OES), di mana persetujuan yang rapat antara nilai eksperimen dan teori telah tercapai. Sifat elektrik larutan pepejal $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ telah diukur dalam julat frekuensi 5 Hz – 13 MHz. Pada perantaraan suhu, ~350 – 850 °C, larutan pepejal $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ merupakan konduktor ion oksida yang sederhana dengan kekonduksian, $\sim 10^{-6}$ – $10^{-3} \text{ S cm}^{-1}$; tenaga pengaktifan adalah di dalam julat 0.98 – 1.08 eV. Sampel yang kaya dengan bismut, $\text{Bi}_{3.184}\text{Ta}_{0.816}\text{O}_{6.816}$ mempunyai nilai kekonduksian yang paling tinggi, $\sim 1.50 \times 10^{-3} \text{ S cm}^{-1}$ pada suhu 650 °C. Peningkatan dalam kekonduksian elektrik adalah hasil daripada perubahan struktur dari segi saiz butiran, morfologi permukaan dan kekosongan oksigen yang disebabkan oleh kandungan bismut yang meningkat.

Larutan pepejal dengan formula umum, $\text{Bi}_3\text{Ta}_{1-x}\text{Ln}_x\text{O}_{7-x}$ ($\text{Ln} = \text{Nd}, \text{Gd}, \text{dan La}$) telah berjaya disediakan. Mekanisme pembentukan melibatkan satu amaun perkadaran kation Ta^{5+} digantikan oleh kation Ln^{3+} dan penghasilan kekosongan oksigen demi pampasan cas. Oleh itu, cas elektoneutral keseluruhan dalam sistem ini dapat dikekalkan melalui mekanisme: $\text{Ln}^{3+} \leftrightarrow \text{Ta}^{5+} + \text{O}^{2-}$. Had larutan pepejal adalah sehingga $x = 0.2$ untuk Nd-terdop $\text{Bi}_3\text{Ta}_{1-x}\text{Nd}_x\text{O}_{7-x}$, yang menunjukkan sedikit peningkatan dalam pemalar kekisi, $a=b=c$ dalam julat $5.4477(\pm 0.0037) - 5.4682(\pm 0.0009)$ Å. Peningkatan pemalar kekisi mungkin disebabkan oleh saiz jejari ion Nd^{3+} yang lebih besar iaitu 0.983 Å jika dibandingkan dengan Ta^{5+} , iaitu 0.64 Å pada koordinasi enam. Sementara itu, had larutan pepejal sangat terbatas, iaitu $x = 0.1$ untuk kedua-dua siri Gd- dan La-. Pemalar kekisi mereka, $a=b=c$ adalah $5.4635(\pm 0.0002)$ dan $5.4687(\pm 0.0002)$ Å. $\text{Bi}_3\text{Ta}_{0.8}\text{Nd}_{0.2}\text{O}_{6.8}$ menunjukkan kekonduksian yang tertinggi pada ke semua suhu yang dikaji dalam siri lantanid terdop dari suhu ~ 350 ke 850 °C. Nilai kekonduksiannya yang direkodkan pada suhu 650 °C ialah $9.26 \times 10^{-3} \text{ S cm}^{-1}$.

Kation pentavalensi telah diperkenalkan dalam Bi_3TaO_7 sama ada pada tapak Bi atau Ta. Akan tetapi, hanya penggantian pada tapak Ta boleh menghasilkan larutan pepejal yang baru dengan menggunakan Nb^{5+} dan V^{5+} . Mekanisme larutan pepejal dicadangkan sebagai penggantian satu kepada satu Ta oleh Nb atau V, dengan formula umum $\text{Bi}_3\text{Ta}_{1-x}\text{M}_x\text{O}_7$ ($\text{M} = \text{V}$ atau Nb). Had larutan pepejal untuk Nb-terdop $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ adalah sehingga $x = 0.5$. Larutan pepejal $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ juga mempunyai struktur fluorit yang tercacat, kumpulan ruang Fm-3m dengan pemalar kekisi, $a=b=c$ di dalam julat nilai $5.4477(\pm 0.0037) - 5.4654(\pm 0.0011)$ Å. Sampel Nb-terdop menunjukkan peningkatan kekonduksian elektrik yang seiring dengan pertambahan komposisi Nb; $\text{Bi}_3\text{Ta}_{0.5}\text{Nb}_{0.5}\text{O}_7$ mempunyai kekonduksian yang tertinggi, $\sim 5.96 \times 10^{-3} \text{ S cm}^{-1}$ pada suhu 650 °C. Peningkatan kekonduksian elektrik dalam larutan pepejal $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ mungkin disebabkan oleh saiz butiran yang besar dan rapat sehingga rintangan impedans untuk pemindahan cas di dalam sampel dapat dikurangkan. Sebaliknya, had larutan pepejal terbatas untuk $\text{Bi}_3\text{Ta}_{1-x}\text{V}_x\text{O}_7$, iaitu $x = 0.1$ dengan pemalar kekisi, $a=b=c$, $5.4559 (\pm 0.0011)$ Å. Kekonduksian ion yang diperolehi oleh $\text{Bi}_3\text{Ta}_{0.9}\text{V}_{0.1}\text{O}_7$ ialah $\sim 4.17 \times 10^{-3} \text{ S cm}^{-1}$ pada suhu 650 °C dengan tenaga pengaktifan 1.01 eV .

Selain itu, larutan pepejal penggantian tungsten (wolfram), $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7+(x/2)}$ ($0 \leq x \leq 0.2$) dengan pemalar kekisi, $a=b=c$ dalam julat nilai $5.4477(\pm 0.0037) - 5.4668(\pm 0.0001)$ Å telah disediakan. Nilai kekonduksian larutan pepejal $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7+(x/2)}$, $x = 0.1$ dan $x = 0.2$ adalah $\sim 5.15 \times 10^{-3} \text{ S cm}^{-1}$ dan $\sim 6.78 \times 10^{-3} \text{ S cm}^{-1}$ pada suhu 650 °C. Nilai-nilai kekonduksian tersebut adalah setanding dengan siri terdop yang lain, seperti Nb, V, walaupun hanya sedikit lebih tinggi daripada fasa induk. Kekonduksian yang lebih tinggi untuk sampel wolfram-terdop mungkin berkaitan rapat dengan kekonduksian elektron yang terhasil daripada perubahan keadaan pengoksidaan wolfram.

Sebagai kesimpulan, Bi_3TaO_7 dan bahan-bahan berkaitan telah berjaya disintesis melalui tindak balas keadaan pepejal pada keadaan yang optimum. Bahan-bahan ini mempunyai kekonduksian ion oksida yang disebabkan oleh kekosongan oksigen yang tinggi di dalam kekisi perumah. Didapati juga sifat struktur dan elektrik bagi Bi_3TaO_7 serta bahan-bahan berkaitan adalah sangat bergantung terhadap komposisi bahan dan struktur hablur.



ACKNOWLEDGEMENTS

In the name of Allah, the Most Gracious and the Most Merciful. Alhamdulillah, all praises to Allah for His greatness and for giving me the strength to complete this thesis.

I am wholeheartedly thankful and indebted to my supervisor, Associate Professor Dr. Tan Kar Ban for his invaluable advises, unfailing helps, motivational supports, and patience throughout the entire course of this project. I would like to extend my sincere appreciation to Dr. Khaw Chwin Chieh, Professor Dr. Zulkarnain Zainal, and Dr. Tan Yen Ping for their constructive suggestions and discussions.

My deepest gratitude also dedicated to the staff of the Department of Chemistry, UPM especially Madam Zaidina (XRD), Madam Haslina (TGA/DTA), Madam Rusnani Amirudin (FTIR), Madam Nurhidayu (ICP-OES), and Madam Siti Fairouz (ICP-OES) for their technical assistance in data collection. I would also like to express my sincere thanks to the staffs at the Electron Microscopy Unit, Institute of Bioscience (IBS) for their kind assistance.

My heartfelt appreciation goes to my family members, especially my mother, Mrs. Jumiaty Sugio and my father, Mr. Firman Asis for their continuous supports and courage throughout my study. They are my role models who have given me all the motivation. My parents have inspired me in every aspect and their love encourages me to go through all difficult times. Thank you for always being there when I need you all.

Not to be forgotten, I would like to thank my friends in the laboratory 128, Miss Nurul Adayu Mat Dasin, Miss Syafiqah Shaari, Miss Syazmimi Mohd Razi, Miss Rohayu Md Noor, Miss Chan Siew Ling, Mr. Mohd Khaizarul Hanafi, and my lab seniors, Dr. Tan Phei Yi and Dr. Chon Mun Ping for all their knowledge sharing, guidance, and helps. Special notes dedicated to Mr. Faisal Sawi, Mr. Kennedy Sarnang, and housemates for the prayers, supports and concerns. Lastly, the financial support from the Ministry of Higher Education, Malaysia (MOHE) through Fundamental Research Grant Scheme (FRGS) is also gratefully acknowledged.

TABLE OF CONTENTS

ABSTRACT	Page
ABSTRAK	i
ACKNOWLEDGEMENTS	iii
APPROVAL	vi
DECLARATION	vii
LIST OF TABLES	viii
LIST OF FIGURES	xiii
LIST OF ABBREVIATIONS	xv
	xx
 CHAPTER	
1. INTRODUCTION	1
1.1 Solid State Ionics	1
1.2 Solid Electrolytes	2
1.3 Bismuth Oxide	3
1.4 Electrical Properties	4
1.5 Problem Statement	5
1.6 Objectives	5
 2. LITERATURE REVIEW	7
2.1 Bi ₂ O ₃ and Its Crystallochemical Properties	7
2.2 The Structure of α-Bi ₂ O ₃	8
2.3 The Structure of δ-Bi ₂ O ₃	8
2.4 The Structure of β-Bi ₂ O ₃	9
2.5 The Structure of γ-Bi ₂ O ₃	10
2.6 Bi-based Oxide Ion Conductor	11
2.7 Doped Bi ₂ O ₃ Systems	14
2.7.1 Niobium-Doped Bi ₂ O ₃ System	15
2.7.2 Tantalum-Doped Bi ₂ O ₃ System	18
2.7.3 Antimony-Doped Bi ₂ O ₃ System	21
 3. METHODOLOGY	23
3.1 Synthesis	23
3.1.1 General Principle of Solid State Reaction	23
3.1.2 Synthesis of Bismuth Tantalate Materials	23
3.1.3 Chemically Doped Bismuth Tantalate Materials	24
3.2 Pellet Preparation	24
3.3 Sample Characterisations	24
3.3.1 X-Ray Powder Diffraction (XRD)	25
3.3.2 Thermal Gravimetric Analysis (TGA)	27
3.3.3 Differential Thermal Analysis (DTA)	27
3.3.4 Scanning Electron Microscopy (SEM)	28
3.3.5 Fourier Transform Infrared Spectroscopy (FTIR)	28
3.3.6 Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES)	29

3.3.7	AC Impedance Spectroscopy	29
3.3.7.1	General Concepts Interpretation of AC Impedance Spectroscopy	30
4.	RESULTS AND DISCUSSION	34
4.1	Phase Formation and Electrical Properties of Bismuth Tantalate Fluorites	34
4.1.1	XRD Patterns of $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ Solid Solution	35
4.1.2	Thermal Analyses and Elemental Analyses	41
4.1.3	Surface Morphology and Crystallite Size Studies	43
4.1.4	Fourier Transform Infrared Spectroscopy (FT-IR)	47
4.1.5	AC Impedance Analyses	50
4.2	Structural and Electrical Properties of the Nb-Substituted Bismuth Tantalate Fluorites	57
4.2.1	XRD Patterns of $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ Solid Solution	57
4.2.2	Thermal Analyses and Elemental Analyses	59
4.2.3	Surface Morphology and Crystallite Size Studies	61
4.2.4	Fourier Transform Infrared Spectroscopy (FT-IR)	65
4.2.5	AC Impedance Analyses	66
4.3	Phase Formation and Electrical Properties of V^{5+} - and W^{6+} -doped $\text{Bi}_3\text{Ta}_{1-x}\text{M}_x\text{O}_{7-\delta}$	73
4.3.1	XRD Patterns of V- and W-Doped $\text{Bi}_3\text{Ta}_{1-x}\text{M}_x\text{O}_{7-\delta}$ (M = V, W) Series	73
4.3.2	Thermal Analyses	78
4.3.3	Surface Morphology and Crystallite Size Studies	78
4.3.4	Fourier Transform Infrared Spectroscopy (FT-IR)	80
4.3.5	AC Impedance Analyses	83
4.4	Phase Formation and Electrical Properties of Ln-doped $\text{Bi}_3\text{Ta}_{1-x}\text{Ln}_x\text{O}_{7-x}$ (Ln = Nd^{3+} , Gd^{3+} , La^{3+})	89
4.4.1	XRD Patterns of Ln-doped $\text{Bi}_3\text{Ta}_{1-x}\text{Ln}_x\text{O}_{7-x}$ Series	91
4.4.2	Thermal Analyses	94
4.4.3	Surface Morphology and Crystallite Size Studies	94
4.4.4	Fourier Transform Infrared Spectroscopy (FT-IR)	99
4.4.5	AC Impedance Analyses	99
5.	CONCLUSIONS	107
	FURTHER WORK	109
	REFERENCES	110
	APPENDICES	116
	BIODATA OF STUDENT	127
	PUBLICATION	128

LIST OF TABLES

Table		Page
1.1	Typical electrical conductivity of electronic and ionic materials	1
2.1	Structural data of the Bi_2O_3 phases	8
2.2	Electrolytes studied for SOFC	14
2.3	Conductivities (σ_{300} and σ_{600}) and activation energies (E_a) of Bi_xNbO_6 , $2.5 \leq x \leq 6$ solid solution and YSZ	18
2.4	Several phases and intermediate compounds in the tantalum-stabilised bismuth system	20
2.5	Comparison of microwave dielectric properties of Bi_3SbO_7 ceramics reported in Pang <i>et al.</i> and Manier <i>et al.</i> 's work	22
3.1	The capacitance values and their possible interpretations	33
4.1	Summary of compositions, phases and heat treatment conditions in the Bi_2O_3 – Ta_2O_5 binary system	37
4.2	Elemental analyses by ICP-OES and EDX	43
4.3	Internal strains and crystallite sizes of $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ ($0 \leq x \leq 0.184$) by Scherrer and W-H methods	49
4.4	Vibrational frequencies of the absorption bands of Bi–O and Ta–O bonds in $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ ($0 \leq x \leq 0.184$) solid solution	49
4.5	Ionic conductivity values of Bi_3NbO_7 , Bi_3TaO_7 and $\text{Bi}_{3.184}\text{Ta}_{0.816}\text{O}_{7.816}$ at different temperatures	56
4.6	Elemental analyses of $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ solid solution by ICP-OES	62
4.7	Internal strains and crystallite sizes of $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ ($0 \leq x \leq 0.5$) by Scherrer and W-H methods	64
4.8	Ionic conductivity values for Bi_3NbO_7 and $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ ($0 \leq x \leq 0.5$) at different temperatures	72
4.9	Internal strains and crystallite sizes of $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7+x/2}$ ($0 \leq x \leq 0.2$) and $\text{Bi}_3\text{Ta}_{0.9}\text{V}_{0.1}\text{O}_7$ by Scherrer and W-H methods	88

4.10	Ionic conductivity values of Bi_3TaO_7 , $\text{Bi}_3\text{Ta}_{0.9}\text{V}_{0.1}\text{O}_7$, and $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7+x/2}$ ($0 \leq x \leq 0.2$) solid solution at different temperatures	88
4.11	Internal strains and crystallite sizes of $\text{Bi}_3\text{Ta}_{1-x}\text{Nd}_x\text{O}_{7-x}$ ($0 \leq x \leq 0.2$) and $\text{Bi}_3\text{Ta}_{1-x}\text{Ln}_x\text{O}_{7-x}$ ($\text{Ln} = \text{La}, \text{Gd}; 0 \leq x \leq 0.1$) solid solutions by Scherrer and W-H methods	106
4.12	Ionic conductivities of Bi_3TaO_7 and $\text{Bi}_3\text{Ta}_{1-x}\text{Ln}_x\text{O}_{7-x}$ ($\text{Ln} = \text{Nd}, \text{Gd}, \text{La}$) at different temperatures	106



LIST OF FIGURES

Figure		Page
2.1	The stable and metastable regions found in Bi_2O_3	7
2.2	The projection of the α - Bi_2O_3 structure on the [010] plane. The position parameters in the $\langle 010 \rangle$ direction are multiplied by 100	9
2.3	Structure models for fluorite related δ - Bi_2O_3 ; (a) Sillen model; (b) Gattow model; (c) Willis model	10
2.4	(a) Schematic diagram of solid oxide fuel cells (SOFC); (b) Cross section of a first-generation anode-supported cell	12
2.4	Schematic diagram of solid oxide fuel cells (SOFC) showing; (c) oxide ion conducting electrolyte, and (d) proton conducting electrolyte during its operation	13
2.5	(a) The (unrefined) metal atom plus oxygen atom vacancy ordering model for the Bi_2O_3 - Nb_2O_5 Type II solid solution at the composition $\text{Bi}_8\text{Nb}_2\text{O}_{17}$. Bismuth atoms are darker than niobium atoms, and the oxygen atoms are black. NbO_6 octahedra were shown	16
2.5	(b) The (unrefined) metal atom plus oxygen atom vacancy ordering model for Type III Bi_3NbO_7 . Bismuth atoms are darker than niobium atoms, and the oxygen atoms are black. NbO_6 octahedra were shown	17
2.6	(a) Thermal ellipsoid plot showing proposed coordination geometry for Ta^{5+} in Bi_3TaO_7 ; (b) Proposed chains of corner sharing tantalate octahedra in Bi_3TaO_7	19
3.1	Flow diagram of the sample preparation and characterisation	26
3.2	Cole-Cole plot	32
4.1	XRD patterns of phases in the Bi_2O_3 - Ta_2O_5 system ($\bullet$ - Bi_3TaO_7 and $\times$ - δ - Bi_2O_3)	36
4.2	Identified phases in the Bi-rich region of Bi_2O_3 - Ta_2O_5 binary system	39
4.3	XRD patterns of Bi_3TaO_7 solid solution	39
4.4	Variation of lattice parameter as a function of composition	41

in $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ solid solution. Inset of figure shows a shift in (1 1 1) diffraction plane

4.5	(a) TGA thermograms of $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ solid solution	42
4.5	(b) DTA thermograms of $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ solid solution	42
4.6	W-H plots of $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ solid solution	44
4.7	Comparison between crystallite sizes, D calculated by (i) Scherrer and (ii) Williamson-Hall method, and the internal strains of $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ solid solution, $0 \leq x \leq 0.184$	45
4.8	SEM images of $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ at 15 k magnification	46
4.9	The particle size distribution of $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ solid solution at 8 k magnification	47
4.10	FT-IR spectra of $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ solid solution	48
4.11	(a) Complex Cole-Cole plots of Bi_3TaO_7 at different temperatures. Insets of figure show spike was observed at 500 °C and 550 °C	51
4.11	(b) Complex Cole-Cole plots of $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ solid solution at temperature 400 °C	52
4.12	Combined spectroscopic plots of Z'' and M'' of Bi_3TaO_7 as a function of frequency at temperature of 450 °C	53
4.13	Imaginary part of impedance plots, Z'' of Bi_3TaO_7 as a function of frequency at different temperatures for Bi_3TaO_7	54
4.14	Real admittance plots, Y' of Bi_3TaO_7 as a function of frequency at various temperatures	55
4.15	Arrhenius conductivity plot of $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ solid solution	56
4.16	XRD patterns of phases in the $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ system	58
4.17	Variation of lattice parameter as a function of composition in $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ solid solution	59
4.18	(a) TGA thermograms of $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ solid solution	60
4.18	(b) DTA thermograms of $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ solid solution	60
4.19	The particle size distribution of $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ solid solution at 8 k magnification	61

4.20	VPSEM images of $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$, where $0 \leq x \leq 0.5$ at 8 k magnification	63
4.21	W-H plots of $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ solid solution, $0 \leq x \leq 0.5$	64
4.22	Comparison between crystallite sizes, D calculated by (i) Scherrer and (ii) Williamson-Hall method, and the internal strains of $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ solid solution, $0 \leq x \leq 0.5$	65
4.23	FT-IR spectra of $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$, ($0 \leq x \leq 0.5$) solid solution	66
4.24	(a) Complex Cole-Cole plots of $\text{Bi}_3\text{Ta}_{1-x}\text{Nb}_x\text{O}_7$ solid solution, where $0 \leq x \leq 0.5$ at temperature 450°C	68
4.24	(b) Complex Cole-Cole plots of $\text{Bi}_3\text{Ta}_{0.5}\text{Nb}_{0.5}\text{O}_7$ at different temperatures. Insets of figure show spike was observed at temperature 500°C and 550°C	68
4.25	Imaginary part of impedance plots, Z'' as a function of frequency at different temperatures for $\text{Bi}_3\text{Ta}_{0.5}\text{Nb}_{0.5}\text{O}_7$	69
4.26	Combined spectroscopic plots of Z'' and M'' as a function of frequency at temperature of 450°C	70
4.27	Real admittance plots, Y' as a function of frequency at various temperatures for $\text{Bi}_3\text{Ta}_{0.5}\text{Nb}_{0.5}\text{O}_7$	70
4.28	Arrhenius conductivity plot for $\text{Bi}_{3+x}\text{Ta}_{1-x}\text{O}_{7-x}$ solid solution, $0 \leq x \leq 0.5$	71
4.29	XRD patterns for $\text{Bi}_{3-x}\text{W}_x\text{TaO}_{7-(3x/2)}$ ($0 \leq x \leq 0.2$) and $\text{Bi}_{3-x}\text{V}_x\text{TaO}_{7-x}$ ($0 \leq x \leq 0.2$)	74
4.30	(a) XRD patterns of $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7-x}$ ($0.1 \leq x \leq 0.3$)	75
4.30	(b) XRD patterns of $\text{Bi}_3\text{Ta}_{1-x}\text{V}_x\text{O}_7$ ($0.1 \leq x \leq 0.3$)	76
4.31	Variation of lattice constant as a function of composition in $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7+x/2}$ ($0 \leq x \leq 0.2$) and $\text{Bi}_3\text{Ta}_{1-x}\text{V}_x\text{O}_7$ ($0 \leq x \leq 0.1$) samples	77
4.32	(a) TGA thermograms of $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7+x}$ ($0 \leq x \leq 0.2$) and $\text{Bi}_3\text{Ta}_{1-x}\text{V}_x\text{O}_7$ ($x = 0.1$) solid solutions	79
4.32	(b) DTA thermograms of $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7+x}$ ($0 \leq x \leq 0.2$) and $\text{Bi}_3\text{Ta}_{1-x}\text{V}_x\text{O}_7$ ($x = 0.1$) solid solutions	79
4.33	Williamson-Hall plots of $\text{Bi}_3\text{Ta}_{0.9}\text{V}_{0.1}\text{O}_7$ ($0 \leq x \leq 0.1$) and $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7-x}$ ($0 \leq x \leq 0.2$) solid solutions	80

4.34	VPSEM micrographs of $\text{Bi}_3\text{Ta}_{0.9}\text{V}_{0.1}\text{O}_7$ ($0 \leq x \leq 0.1$) and $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7-x}$ ($0 \leq x \leq 0.2$) solid solutions at 5 k magnification	81
4.35	The histograms of the particle size distribution of the $\text{Bi}_3\text{Ta}_{0.9}\text{V}_{0.1}\text{O}_7$ ($0 \leq x \leq 0.1$) and $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7-x}$ ($0 \leq x \leq 0.2$) solid solutions at 5 k magnification	82
4.36	FT-IR spectra of $\text{Bi}_3\text{Ta}_{0.9}\text{V}_{0.1}\text{O}_7$ and $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7+x/2}$ ($0 \leq x \leq 0.2$) solid solutions	82
4.37	(a) Cole-Cole plots of $\text{Bi}_3\text{Ta}_{0.9}\text{V}_{0.1}\text{O}_7$ and $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7+x/2}$ ($0 \leq x \leq 0.2$) solid solutions at 450 °C	83
4.37	(b) Cole-Cole plots of $\text{Bi}_3\text{Ta}_{0.8}\text{W}_{0.2}\text{O}_{7.1}$ at various temperatures	84
4.38	Imaginary part of impedance plots, $-Z''$ of $\text{Bi}_3\text{Ta}_{0.8}\text{W}_{0.2}\text{O}_{7.10}$ as a function of frequency at different temperatures	86
4.39	(a) Real admittance plot, Y' of $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7+x/2}$ ($x = 0.2$) as a function of frequency at various temperatures	86
4.39	(b) Real admittance plot, Y' of $\text{Bi}_3\text{Ta}_{0.9}\text{V}_{0.1}\text{O}_7$ and $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7+x/2}$ ($0 \leq x \leq 0.2$) solid solution as a function of frequency at 450 °C	87
4.40	Arrhenius conductivity plots of $\text{Bi}_3\text{Ta}_{0.9}\text{V}_{0.1}\text{O}_7$ ($0 \leq x \leq 0.1$) and $\text{Bi}_3\text{Ta}_{1-x}\text{W}_x\text{O}_{7-x}$ ($0 \leq x \leq 0.2$) solid solution	89
4.41	XRD patterns for $\text{Bi}_{3-x}\text{TaLn}_x\text{O}_{7-x}$ ($\text{Ln} = \text{Nd, La, Gd, Er, Yb}$) at $x = 0.1$	90
4.42	(a) XRD patterns for $\text{Bi}_3\text{Ta}_{1-x}\text{Nd}_x\text{O}_{7-x}$ ($0.1 \leq x \leq 0.3$)	92
4.42	(b) XRD patterns for $\text{Bi}_3\text{Ta}_{1-x}\text{La}_x\text{O}_{7-x}$ ($0.1 \leq x \leq 0.3$)	92
4.42	(c) XRD patterns for $\text{Bi}_3\text{Ta}_{1-x}\text{Gd}_x\text{O}_{7-x}$ ($0.1 \leq x \leq 0.3$)	93
4.42	(d) XRD patterns for $\text{Bi}_3\text{Ta}_{1-x}\text{Ln}_x\text{O}_{7-x}$ ($\text{Ln} = \text{Er, Yb}$) at $x = 0.1$	93
4.43	Variation of lattice parameter as a function of composition in $\text{Bi}_3\text{Ta}_{1-x}\text{Ln}_x\text{O}_{7-x}$ ($\text{Ln} = \text{La, Nd, Gd}$) samples	94
4.44	(a) TGA thermograms of Bi_3TaO_7 and $\text{Bi}_3\text{Ta}_{1-x}\text{Ln}_x\text{O}_{7-x}$ ($\text{Ln} = \text{Nd, La, Gd}$) compositions	95

4.44	(b) DTA thermograms of Bi_3TaO_7 and $\text{Bi}_3\text{Ta}_{1-x}\text{Ln}_x\text{O}_{7-x}$ compositions	95
4.45	Williamson-Hall plots of $\text{Bi}_3\text{Ta}_{1-x}\text{Nd}_x\text{O}_{7-x}$ ($0 \leq x \leq 0.2$) and $\text{Bi}_3\text{Ta}_{1-x}\text{Ln}_x\text{O}_{7-x}$ ($\text{Ln} = \text{La, Gd}; 0 \leq x \leq 0.1$) solid solutions	96
4.46	The histograms of the particle size distribution for $\text{Bi}_3\text{Ta}_{1-x}\text{Ln}_x\text{O}_{7-x}$ solid solution at 5 k magnification	97
4.47	VPSEM micrographs of (a) Nd-doped; $x = 0.1$; (b) Nd-doped; $x = 0.2$; (c) La-doped; $x = 0.1$; (d) Gd-doped; $x = 0.1$ at 5 k magnification	98
4.48	FT-IR spectra of $\text{Bi}_3\text{Ta}_{1-x}\text{Ln}_x\text{O}_{7-x}$ solid solutions	99
4.49	(a) Cole-Cole plots of the $\text{Bi}_3\text{Ta}_{1-x}\text{Ln}_x\text{O}_{7-x}$ ($\text{Ln} = \text{Nd, Gd, La}$), $0 \leq x \leq 0.1$ solid solution at 450°C	100
4.49	(b) Cole-Cole plots of the $\text{Bi}_3\text{Ta}_{1-x}\text{Nd}_x\text{O}_{7-x}$ ($0 \leq x \leq 0.2$) solid solution at 450°C	101
4.49	(c) Cole-Cole plots of the $\text{Bi}_3\text{Ta}_{0.8}\text{Nd}_{0.2}\text{O}_{6.8}$ at different temperatures	102
4.50	Imaginary part of impedance plots, Z'' of $\text{Bi}_3\text{Ta}_{1-x}\text{Nd}_x\text{O}_{7-x}$ ($x = 0.2$) as a function of frequency at different temperatures	103
4.51	(a) Real admittance plot, Y' of the $\text{Bi}_3\text{Ta}_{1-x}\text{Nd}_x\text{O}_{7-x}$ ($x = 0.2$) as a function of frequency at various temperatures	103
4.51	(b) Real admittance plot, Y' of the Bi_3TaO_7 and $\text{Bi}_3\text{Ta}_{1-x}\text{Ln}_x\text{O}_{7-x}$ ($\text{Ln} = \text{Nd, Gd, La}$) as a function of frequency at 450°C	104
4.52	Arrhenius conductivity plots of $\text{Bi}_3\text{Ta}_{1-x}\text{Ln}_x\text{O}_{7-x}$ solid solution as a function of temperatures	105

LIST OF ABBREVIATIONS

SOFC	Solid oxide fuel cell
σ	Conductivity
Ω	Ohm
fcc	Face-centered cubic
Bcc	Body- centered cubic
Ea	Activation energy
ε'	Dielectric constant
ε	Lattice strain
D	Crystallite size
LTCC	Low temperature co-fired ceramics
τ_f	Resonant frequency
f	Frequency
TCF	Temperature coefficient of resonant frequency
TGA	Thermogravimetric analysis
DTA	Differential thermal analysis
SEM	Scanning electron microscopy
FTIR	Fourier transform infrared frequency
AC	Alternating current
ICDD	International center for diffraction data
L	Thickness
d	Diameter
R	Radius
Z^*	Complex impedance
Z'	Real part of impedance
Z''	Imaginary part of impedance
A^*, Y^*	Admittance
M^*	Electric modulus
ω	Angular frequency
C	Capacitance
R	Resistance
S	Siemen unit
Z	Formula unit
h, k, l	Miller indices
λ	Wavelength
a, b, c	Lattice constant

CHAPTER 1

INTRODUCTION

1.1 Solid State Ionics

Solid state ionic is a study of ionic migration phenomenon by jumping or hopping of charge carrier into vacancy or interstitial sites in the crystal structure. The transportation of charge carriers by electric field is known as electrical conduction. Electrical conduction has two types of mechanism, which are either electronic or ionic conduction that basically depends on the nature of electrical properties in materials. The current carriers for electronic conduction are electrons which responsible for the electrical characteristics of metals, semiconductors, and superconductors. Meanwhile, the current carriers for ionic conduction are charged ions which occur in materials that known variously as solid electrolytes, superionic conductors or fast ion conductors. Those materials exhibit electronic and ionic conductivity have typical values as summarised in Table 1.1.

In many years, there are exhaustive investigations had been performed on oxide ion conductors owing to their high technological applications that have high economical interest. Solid oxide ion conductors are a very interesting group of solid electrolytes with which these materials are applied for numerous applications including oxygen sensors, solid oxide fuel cells (SOFCs), dense ceramic membranes for oxygen separation, and various types of sensors (Ng *et al.*, 2009; Sammes *et al.*, 1999). Oxide ion conducting solid electrolytes play important role in electrochemical cell for measuring oxygen activities and the thermodynamic data in solid, liquid and gaseous phases.

Table 1.1: Typical electrical conductivity of electronic and ionic materials
(West, 1999)

Conduction mechanism	Material	Conductivity, σ ($\text{ohm}^{-1} \text{cm}^{-1}$)
Ionic	Ionic crystals	$< 10^{-18} - 10^{-4}$
	Solid electrolytes	$10^{-3} - 10^1$
	Strong (liquid) electrolytes	$10^{-3} - 10^1$
Electronic	Metals	$10^{-1} - 10^5$
	Semiconductors	$10^{-5} - 10^2$
	Insulators	$< 10^{-12}$

1.2 Solid Electrolytes

In the area of solid state ionics, solid electrolytes or also known as fast ionic conductors are important due to their applications in batteries, solid oxide fuel cells and various sensors. Solid electrolytes are the crystal solids which have cations and anions that are free to move throughout crystal structure and thus conducting electric current. The cations are ionic bonded to anions at the lattice sites in ionic solids. Solid electrolytes are the intermediate solid structure between typical ionic solids and liquid electrolytes. Normal crystalline solid has a regular network structure with immobile ions, in which all ions are fixed at their lattice sites, while all ions are mobile in liquid electrolytes. Solid electrolytes with highly mobile ions, which have high values of ionic conductivity as high as $1 \Omega^{-1} \text{ cm}^{-1}$, are due to the rapid diffusion of ionic species through a lattice formed by immobile counter ions. The high mobility of ionic species within their crystal structures is the major feature that distinguishes materials that can act as solid electrolytes.

Most of ions in crystalline solids are trapped at their lattice sites, vibrate, and have no tendency to escape from their lattice sites. They need high activation energy to change position in the lattice and therefore, exhibit low conductivity value. Solid electrolytes that allowing the phenomena of electrical charge transport by the motion of ions in solids have low conductivity at low temperature, but possessing high conductivity at high temperature. At elevated temperature, the ions have greater thermal energy causing them to vibrate more vigorously and thus leading to high ionic migration.

It is noteworthy to highlight that the movement of trapped charged ions into the adjacent lattice sites could be due to the ionic conduction, migration, hopping, or diffusion mechanisms. The minimum requirement for the ionic conduction to occur is either by the presence of vacant sites, that enabling the adjacent ions to hop into that vacancies and leaving their own sites vacant, or by having ions in interstitial sites which can hop into the adjacent interstitial sites. Two important factors that could facilitate the ionic conduction are high temperatures and high concentration of crystal defects, with vacancies or interstitials. Ions or atoms cannot escape from their lattice sites, but can only move via crystal defects. At high temperatures, the ions in crystal lattice have greater thermal energy that causes them to vibrate vigorously and makes the ionic conduction is easier, as mentioned earlier. This factor meets one of significant conditions required by ionic conduction to occur, that a large number of same species ions should be mobile. Other conditions that must be satisfied by significant ionic conduction to occur in crystals are as follows (West, 1999):

1. A large number of empty sites are available for the mobile ions to jump into. This is essentially a corollary of having large number of mobile ions since ions can be mobile only if there are empty sites available for them to occupy.

2. The empty and occupied sites should have similar potential energies with a low activation barrier for jumping between neighboring sites.
3. The structure should have a 3D framework permeated by open channels through which mobile ions may migrate.
4. The anion framework should be highly polarizable.

1.3 Bismuth oxide

One of the oxide conductors that captured much attention is bismuth-based electrolytes as these materials could demonstrate high ionic conductivity as high as $1 \Omega^{-1} \text{ cm}^{-1}$ at 750°C . Bismuth oxide, Bi_2O_3 could exist in four polymorphic forms, which are monoclinic α -, tetragonal β -, body centered cubic γ -, and face centered cubic δ -phase. The δ - Bi_2O_3 is the most interesting phase among other polymorphs of bismuth oxides, since it shows very high oxide ion conductivity, $1 \Omega^{-1} \text{ cm}^{-1}$ at 750°C , whereas the other polymorphs only exhibit low ionic conductivity. The polymorph δ - Bi_2O_3 with an oxygen-deficient fluorite-type crystal structure is known as one of the best oxide ion conductors, due to its high concentration of intrinsic oxygen vacancies in the structure that contributes to the ionic conduction properties (Castro *et al.*, 1998; Ling *et al.*, 1998; Struzik *et al.*, 2012; Zhou 1992).

The preservation of δ - Bi_2O_3 with the fluorite structure to lower temperatures is of great research interest. However, this δ - Bi_2O_3 is only stable in a limited temperature range, i.e. 725°C up to its melting point of 825°C (Shuk *et al.*, 1996). This phase requires thermal quenching in order to bring down to room temperature for certain practical applications. It is believed that the instability of δ - Bi_2O_3 phase mainly resulted from high oxygen vacancies, i.e. 25% of the anionic sites, are vacant (Zhou, 1992). Therefore, chemical substitution of Bi by a variety of cations may help to stabilise the cubic δ -phase. For example, Ta^{5+} is such a cation, with the Bi_2O_3 – Ta_2O_5 system could yield a number of ordered fluorite type phase. Bi_3TaO_7 is one of phases that had been extensively studied for its structural properties by various researchers; but, still only limited information is available on its electrical properties.

It is worthwhile to highlight that a solid solution is referred as a crystalline phase that can have variable compositions. Two simple types of solid solution are substitutional solid solution and interstitial solid solution. Substitutional solid solutions need replacement of atom or homovalent ion in the host structure by another species, while the interstitial solid solution involves the introduced species occupies a site that is either empty or no ion/atoms are left out. In order to form substitutional solid solutions, there are prerequisites that must be met, i.e. the ions that replace each other must have same charge and similar ionic radius. Meanwhile, ions that are substituted by other ions of different charges and the additional changes may involve the creation of vacancies or

interstitial (ionic compensation) or electrons or holes (electronic compensation) are known as heterovalent or aliovalent substitution, where these are solid solutions require a more complex formation mechanism. In addition, two substitutions could take place simultaneously and the substituting ions may be of different charge, providing that overall electroneutrality is preserved (West, 1999).

Practically, solid solution in $\text{Bi}_2\text{O}_3\text{--Ta}_2\text{O}_5$ system could be formed by substitution of cations at Bi or Ta sites. Certainly, the substitution may lead to the formation of vacancies, holes, or interstitial oxygen that may contribute to the interesting electrical properties.

1.4 Electrical Properties

In this study, the electrical properties of prepared materials are of the main focus, i.e. the electrical conductivity and the dielectric behavior. Electrical conduction is primarily governed by the manner of generating charge carriers in materials. The electrical conductivities of the materials are ranging from superconductors through those of metals, semiconductors, and highly resistive insulators. Electrical conductivity can be divided into three different categories which are intrinsic, extrinsic, and injected-controlled conductivity. It is categorised as intrinsic conductivity if the charge carriers are developed in the material based on its chemical structure. On the contrary, the extrinsic conductivity takes place if the charge carriers are initiated by introducing impurities either through fabrication processes or doping activity into material for a distinct purpose. Meanwhile, injected-controlled conductivity occurred if the charge carriers are injected into material, mainly from metallic electrodes via a metal-material interface. The electrical conductivity follows the Arrhenius equation as given below:

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad (1.1)$$

Where σ_0 is the pre-exponential factor, E_a is the activation energy, k is the Boltzman constant, and T is the temperature in Kelvin. In reality, the electrical conduction involves various transport processes and may involve both ionic and electronic conductions, under certain condition. Generally, the fundamental charge carriers involving cations, anions, electrons, and electron holes and all these carriers contribute to the total conductivity in a material as shown below:

$$\sigma = \sigma_c + \sigma_a + \sigma_n + \sigma_p \quad (1.2)$$

$$\sigma = \sigma_{\text{ion}} + \sigma_{\text{el}} \quad (1.3)$$

Where σ_c , σ_a , σ_n and σ_p are the cation, anion, electron, and electron hole conductivities, respectively. The summation of σ_c and σ_a gives ionic conductivity value, while the summation of σ_n and σ_p gives the electronic conductivity value. The summation of both ionic and electronic conductivities then gives rise to the total electrical conductivity, Equation (1.3). It is common that only one type of

charge carrier prevails the charge transport and the contribution from minority carriers are insignificant. The mobilities of electrons and electron holes in oxides are generally several orders of magnitude greater than those of the ions (Wang *et al.*, 2006; Bo *et al.*, 2006).

On the contrary, dielectric material has a unit set of electrical characteristics that dependent on its dielectric properties. Measurements on these dielectric properties could provide scientists and engineers with valuable information to properly incorporate the material into its intended application for more solid designs and could provide the critical design parameter information for many electronic applications.

1.5 Problem Statement

Exhaustive investigation has been performed on bismuth based oxide ion conductors owing to their applications in various technological devices. The δ - Bi_2O_3 exhibits high oxide ion conductivity properties due to its fluorite-type sesquioxide lattice with high concentration of oxygen vacancies. However, the large number of vacancies in the structure causes a long-range order easily occurs at low temperature and undergoes a phase transition on cooling, accompanied by a dramatic three orders of magnitude lowering of its conductivity (Fruth *et al.*, 2004). Therefore, the δ -phase requires thermal quenching in order to bring down to room temperature for certain practical applications. The substitution for Bi^{3+} by another cation through chemical doping, e.g. W^{6+} , Ta^{5+} , Nb^{5+} , Sb^{3+} , Y^{3+} could prevent the long-range ordering being established on cooling. One material that has been studied by many researchers is Bi_3NbO_7 due to its interesting polymorphic structures and electrical properties. Such phase possesses good ionic conductivity and the resulted Ta-analogue, Bi_3TaO_7 could have comparable electrical performance especially both phases have an ordered fluorite structure. However, there is only limited information available on the structural and electrical properties of Bi_3TaO_7 . An attempt to enhance the electrical properties of Bi_3TaO_7 materials by chemical doping is also part of the investigation. Therefore, the focus of this study is to develop an understanding of the correlation between compositions and the electrical properties of various phases and related solid solution in the Bi_2O_3 – Ta_2O_5 system.

1.6 Objectives

The key objectives of this work are outlined as below:

1. To synthesise phase pure bismuth tantalate Bi_3TaO_7 and its solid solution using conventional solid state method.

2. To perform characterisations on the crystal structure, surface morphology, thermal stability, and the electrical properties of the phase pure samples through a series of systematic investigations.

3. To enhance the electrical properties of prepared materials through chemical doping at the Ta-site of Bi_3TaO_7 with suitable metal oxides, e.g. Nd^{3+} , Gd^{3+} , La^{3+} , Nb^{5+} , V^{5+} , and W^{6+} .



REFERENCES

- Abrahams, I., Krok, F., Struzik, M. and Dygas, J. (2008). Defect structure and electrical conductivity in Bi_3TaO_7 . *Solid State Ionics*, 179: 1013-1017.
- Abram, E., Sinclair, D. and West, A.R. (2001). Electrode-contact spreading resistance phenomena in doped-lanthanum gallate ceramics. *Journal of Electroceramics*, 7: 179-188.
- Adam, M.S., Matthew, G.K., Benjamin, A.N., Shaul, A. and Shannon, W.B. (2014). A planar-defect-driven growth mechanism of oxygen deficient tungsten oxide nanowires. *Journal of Materials Chemistry A*, 2: 6121-6129.
- Almeida, C.G., Andrade, H.M.C., Mascarenhas, A.J.S. and Silva, L.A. (2010). Synthesis of nanosized $\beta\text{-BiTaO}_4$ by the polymeric precursor method. *Materials Letters*, 64: 1088–1090.
- Aurivillius, B. and Malmros, G. (1972). Crystal structure of $\beta\text{-Bi}_2\text{O}_3$. *Transactions of the Royal Institute of Technology*, 291: 545–562.
- Bak, K.Y., Tan, K.B., Khaw, C.C., Zainal, Z., Tan, P.Y. and Chon, M.P. (2014). Structural and electrical properties of Nb-substituted $\text{LiTa}_{1-x}\text{Nb}_x\text{O}_3$. *Sains Malaysiana*, 43: 1573-1582.
- Battle, P.D., Catlow, C.R.A., Drennan, J. and Murray A.D. (1983). The structural properties of the oxygen conducting δ phase of Bi_2O_3 . *Journal of Physics C: Solid State Physics*, 16: 561.
- Bo, W., Zhe, L., Xiqiang, H., Jipeng, M., Xueqing, S., Xianshuang, X. and Wenhui, S. (2006). Crystal structure, thermal expansion and electrical conductivity of perovskite oxides $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ($0.3 \leq x \leq 0.7$). *Journal of the European Ceramic Society*, 26: 2827–2832.
- Carrazan, S.R.G., Martin, C., Rives, V. and Vidal, R. (1996). An FT-IR spectroscopy study of the adsorption and oxidation of propene on multiphase Bi, Mo and Co catalysts. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 52:1107-1118.
- Castro, A. and Palem, D. (2002). Study of fluorite phases in the system $\text{Bi}_2\text{O}_3 - \text{Nb}_2\text{O}_5 - \text{Ta}_2\text{O}_5$. Synthesis by mechanochemical activation assisted methods. *Journal of Materials Chemistry*, 12: 2774–2780.
- Castro, A., Aguado, E., Rojo, J., Herrero, P., Enjalbert, R. and Galy, J. (1998). The new oxygen-deficient fluorite Bi_3NbO_7 : synthesis, electrical behavior and structural approach. *Materials Research Bulletin*, 33: 31-41.
- Chon, M.P., Tan, K.B., Khaw, C.C., Zainal, Z., Taufiq-Yap, Y., Chen, S.K. and Tan, P.Y. (2014). Investigation of the phase formation and dielectric

- properties of $\text{Bi}_7\text{Ta}_3\text{O}_{18}$. *Journal of Alloys and Compounds*, 590:479-485.
- Dhivya, L., Janani, N., Palanivel, B. and Murugan, R. (2013). Li^+ transport properties of W-substituted $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ cubic lithium garnets. *AIP Advances*, 3:821.
- Di, Z., Hong, W. and Xi, Y. (2007). Sintering behavior and dielectric properties of Bi_3NbO_7 ceramics prepared by mixed oxides and high-energy ball-milling methods. *Journal of the American Ceramic Society*, 90: 327–329.
- Egorysheva, A.V., Ellert, O.G., Zubavichus, Y.V., Gajtko, O.M., Efimov, N.N., Svetogorov, R.D. and Murzin, V.Y. (2015). New complex bismuth oxides in the $\text{Bi}_2\text{O}_3\text{-NiO-Sb}_2\text{O}_5$ system and their properties. *Journal of Solid State Chemistry*, 225: 97–104.
- Fielicke, A., Meijer, G., Von Helden, G. (2003). Infrared multiple photon dissociation spectroscopy of transition metal oxide cluster cations. *European Physical Journal D: Atomic, Molecular, Optical and Plasma Physics*, 24: 69-72.
- Fruth, V., Ianculescu, A., Berger, D., Preda, S., Voicu, G., Tenea, E. and Popa, M. (2006). Synthesis, structure and properties of doped Bi_2O_3 . *Journal of the European Ceramic Society*, 26: 3011-3016.
- Gattow, V.G. and Schroder, H. (1962). Die kristallstruktur der hochtemperaturremodifikation von wismut (III)-oxid ($\delta\text{-Bi}_2\text{O}_3$). *Zeitschrift für Anorganische und Allgemeine Chemie*, 318: 176-189.
- Gonçalves, N., Carvalho, J., Lima, Z. and Sasaki, J. (2012). Size-strain study of NiO nanoparticles by X-ray powder diffraction line broadening. *Materials Letters*, 72: 36-38.
- Hagenmuller, P. (1983). Predictive character of solid state chemistry: Relation between structure, chemical bonding and physical properties of solids. *Proceedings of the Indian Academy of Sciences: Chemical Sciences*, 92: 1-26.
- Harwig, H.A. (1978). On the structure of bismuthsesquioxide: the α , β , γ , and δ -phase. *Zeitschrift für Anorganische und Allgemeine Chemie*, 444: 151-166.
- Harwig, H.A. and Gerards, A.G. (1978). Electrical properties of the α , β , γ , and δ phases of bismuth sesquioxide. *Journal of Solid State Chemistry*, 26: 265–274.
- Hornig, W.S. and Hess, P.C. (2000). Partition coefficients of Nb and Ta between rutile and anhydrous haplogranite melts. *Contributions to Mineral and Petrology*, 138: 176-185.

- Irmawati, R., Nasriah, M.N., Taufiq-Yap, Y. and Hamid, S.A. (2004). Characterization of bismuth oxide catalysts prepared from bismuth trinitrate pentahydrate: Influence of bismuth concentration. *Catalysis Today*, 93: 701-709.
- Irvine, J.T., Sinclair, D.C. and West, A.R. (1990). Electroceramics: Characterization by impedance spectroscopy. *Advanced Materials*, 2: 132-138.
- Jaiswal, N., Kumar, D., Parkash, O. and Upadhyay, S. (2015). Ceria ($\text{La}^{3+}/\text{Sr}^{2+}$)/carbonates nanocomposite electrolytes with high electrical conductivity for low-temperature SOFCs. *International Journal of Applied Ceramic Technology*, 12: 1080-1087.
- Kagata, H., Inoue, T., Kato, J., and Kameyama, I. (1992). Low-fire bismuth-based dielectric ceramics for microwave use. *Japanese Journal of Applied Physics*, 31: 3152–3155.
- Kan, Y.M., Zhang, G.J., Wang, P.L. and Cheng, Y.B. (2008). Preparation and properties of neodymium-modified bismuth titanate ceramics. *Journal of the European Ceramic Society*, 28: 1641-1647.
- Kilner, J.A. and Burriel, M. (2014). Materials for intermediate-temperature solid-oxide fuel cells. *Annual Review of Materials Research*, 44: 365–393.
- Levin, E.M., and Roth, R.S. (1964). Polymorphism of bismuth sesquioxide. II. Effect of oxide additions on the polymorphism of Bi_2O_3 . *Journal of Research of the National Bureau of Standards—A. Physics and Chemistry*, 68A: 197–206.
- Li, M., Pietrowski, M.J., De Souza, R.A., Zhang, H., Reaney, I.M., Cook, S.N., Kilner, J.A. and Sinclair, D.C. (2014). A family of oxide ion conductors based on the ferroelectric perovskite $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. *Nature Materials*, 13: 31-35.
- Lin, S.E. and Wei, W.C.J. (2011). Long-term degradation of Ta_2O_5 -doped Bi_2O_3 systems. *Journal of the European Ceramic Society*, 31: 3081-3086.
- Ling, C.D. (1999). Structural relationships among bismuth-rich phases in the $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$, $\text{Bi}_2\text{O}_3\text{--Ta}_2\text{O}_5$, $\text{Bi}_2\text{O}_3\text{--MoO}_3$, and $\text{Bi}_2\text{O}_3\text{--WO}_3$ systems. *Journal of Solid State Chemistry*, 148: 380-405.
- Ling, C.D. and Johnson, M. (2004). Modelling, refinement and analysis of the “Type III” $\delta\text{-Bi}_2\text{O}_3$ -related superstructure in the $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$ system. *Journal of Solid State Chemistry*, 177: 1838-1846.
- Ling, C.D., Withers, R.L., Schmid, S. and Thompson, J.G. (1998). A review of bismuth-rich binary oxides in the systems $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$, $\text{Bi}_2\text{O}_3\text{--Ta}_2\text{O}_5$, $\text{Bi}_2\text{O}_3\text{--MoO}_3$, and $\text{Bi}_2\text{O}_3\text{--WO}_3$. *Journal of Solid State Chemistry*, 137: 42-61.

- Mahato, N., Banerjee, A., Gupta, A., Omar, S. and Balani, K. (2015). Progress in material selection for solid oxide fuel cell technology: A review. *Progress in Materials Science*, 72: 141-337.
- Manier, M., Mercurio, J., Mercurio, D. and Frit, B. (1986). Dielectric materials of the Bi_3SbO_7 type. *Journal de Physique Colloques*, 47: 907-911.
- McDevitt, N.T. and Baun, W.L. (1964). Infrared absorption study of metal oxides in the low frequency region ($700\text{--}240\text{ cm}^{-1}$). *Spectrochimica Acta*, 20: 799-808.
- Meenakshi, M., Sivakumar, R., Perumal, P. and Sanjeeviraja, C. (2016). Studies on electrochromic properties of RF sputtered Vanadium Oxide: Tungsten Oxide thin films. *Materials Today: Proceedings*, 3S: S30-S39.
- Ng, S.N., Tan, Y.P. and Taufiq-Yap, Y. (2008). Preparation and characterization of bismuth-niobium oxide ion conductors. *Journal of Physical Science*, 20: 75-86.
- Ng, S.N., Tan, Y.P. and Taufiq-Yap, Y. (2009). Mechanochemical synthesis and characterization of bismuth-niobium oxide ion conductors. *Journal of Physical Science*, 20: 75-86.
- Nobre, M.A.L. and Lanfredi, S. (2001). New evidence of grain boundary phenomenon in $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ ceramic: an analysis by impedance spectroscopy. *Materials Letters*, 50: 322-327.
- Nobre, M.A.L. and Lanfredi, S. (2003). Dielectric spectroscopy on $\text{Bi}_3\text{Zn}_2\text{Sb}_3\text{O}_{14}$ ceramic: an approach based on the complex impedance. *Journal of Physics and Chemistry of Solids*, 64: 2457-2464.
- Pal, V., Dwivedi, R.K. and Thakur, O.P. (2014). Effect of neodymium substitution on structural and ferroelectric properties of BNT ceramics. *Materials Research Bulletin*, 51: 189-196.
- Pang, L.X., Di, Z., Hong, W., Ying, W., Jing, G. and Yue-Hua, C. (2011). Phase evolution and microwave dielectric properties of Bi_3SbO_7 ceramic. *Journal of Physics and Chemistry of Solids*, 72: 882-885.
- Pirnat, U. and Suvorov, D. (2007). Dielectric properties and phase transitions of $\text{Bi}_3\text{Nb}_{1-x}\text{Ta}_x\text{O}_7$ fluorite-type dielectrics. *Journal of the European Ceramic Society*, 27: 3843-3846.
- Saito, T. and Miida, R. (1999). Crystal structure and ionic conductivity in Bi_2O_3 -rich $\text{Bi}_2\text{O}_3\text{--Ta}_2\text{O}_5$ sintered oxides. *Japanese Journal of Applied Physics*, 38: 4838-4842.
- Salje, E., Carley, A.F. and Roberts, M.W. (1979). The effect of reduction and temperature on the electronic core levels of tungsten and molybdenum in WO_3 and $\text{W}_x\text{Mo}_{1-x}\text{O}_3$ – A photoelectron spectroscopic study. *Journal of Solid State Chemistry*, 29: 237-251.

- Sammes, N.M., Tompsett, G.A., Näfe, H. and Aldinger, F. (1999). Bismuth based oxide electrolytes-structure and ionic conductivity. *Journal of the European Ceramic Society*, 19:1801-1826.
- Schumb, W.C. and Rittner, E.S. (1943). Polymorphism of bismuth trioxide. *Journal of the American Chemical Society*, 65: 1055-1060.
- Shuk, P., Wiemhöfer, H.D., Guth, U., Göpel, W. and M. Greenblatt. (1996). Oxide ion conducting solid electrolytes based on Bi_2O_3 . *Solid State Ionics*, 89: 179-196.
- Silija, P., Yaakob, Z., Suraja, V., Binitha, N.N. and Akmal, Z.S. (2012). An enthusiastic glance in to the visible responsive photocatalysts for energy production and pollutant removal, with species emphasis on titania. *International Journal of Photoenergy*, 2012: 1-19.
- Sillen, L.G. (1937). X-ray studies on bismuth trioxide. *Arkiv for Kemi, Mineralogi och Geologi*, 12: 1-15.
- Sinclair, D.C., Morrison, F.D. and West, A.R. (2000). Application of combined impedance and electric modulus spectroscopy to characterise electroceramics. *International Ceramics*, 2: 33-38.
- Struzik, M., Liu, X., Abrahams, I., Krok, F., Malys, M. and Dygas, J.R. (2012). Defect structure and electrical conductivity in the pseudo-binary system $\text{Bi}_3\text{TaO}_7\text{--Bi}_3\text{NbO}_7$. *Solid State Ionics*, 218: 25-30.
- Takahashi, T. and Iwahara, H. (1978). Oxide ion conductors based on bismuthsesquioxide. *Materials Research Bulletin*, 13: 1447–1553.
- Tan, K.B., Chon, M.P., Khaw, C.C., Zainal, Z., Taufiq-Yap, Y. and Tan, P. 2014. Novel monoclinic zirconolite in $\text{Bi}_2\text{O}_3\text{--CuO--Ta}_2\text{O}_5$ ternary system: Phase equilibria, structural and electrical properties. *Journal of Alloys and Compounds*, 592: 140-149.
- Tan, M.Y., Tan, K.B., Zainal, Z., Khaw, C.C. and Chen, S.K. (2012). Subsolidus formation and impedance spectroscopy studies of materials in the $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Y}_2\text{O}_3)_x$ binary system. *Ceramics International*, 38: 3403-3409.
- Turkoglu, O. and Belenli, I. (2003). Electrical conductivity of $\gamma\text{-Bi}_2\text{O}_3\text{--V}_2\text{O}_5$ solid solution. *Journal of Thermal Analysis and Calorimetry*, 73: 1001-1012.
- Valant, M. and Suvorov, D. (2000). Chemical compatibility between silver electrodes and low-firing binary-oxide compounds-Conceptual study. *Journal of the American Ceramic Society*, 83: 2721-2729.
- Wang, X., Corbel, G., Kodjikian, S., Fang, Q. and Lacorre, P. (2006). Isothermal kinetic of phase transformation and mixed electrical conductivity in Bi_3NbO_7 . *Journal of Solid State Chemistry*, 179: 3338-3346.

- West, A.R. (1999). Electrical properties. In basic solid state chemistry, ed. A.R. West, pp 226-311. New York: John Wiley & Sons, Ltd.
- Yaremchenko, A.A., Kharton, V.V., Naumovich, E.N. and Marques, F.M.B. (2000). Physicochemical and transport properties of BICUVOX-based ceramics. *Journal of Electroceramics*, 4: 233-242.
- Yaremchenko, A.A., Kharton, V.V., Naumovich, E.N., Tonoyan, A.A. and Samokhval, V.V. (1998). Oxygen ionic transport in Bi_2O_3 -based oxide: II. The $\text{Bi}_2\text{O}_3\text{-ZrO}_2\text{-Y}_2\text{O}_3$ and $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-Ho}_2\text{O}_3$ solid solutions. *Journal of Solid State Electrochemistry*, 2: 308-314.
- Yuman, P., Zuju, M., Junjie, H. and Kechen, W. (2017). A first-principles study of anionic (S) and cationic (V/Nb) doped $\text{Sr}_2\text{Ta}_2\text{O}_7$ for visible light photocatalysis. *RSC Advances*, 7: 40922.
- Zak, A.K., Majid, W.A., Abrishami, M.E. and Yousefi, R. (2011). X-ray analysis of ZnO nanoparticles by Williamson–Hall and size–strain plot methods. *Solid State Sciences*, 13: 251-256.
- Zhang, G., Li, M., Yu, S., Zhang, S., Huang, B. and Yu, J. (2010). Synthesis of nanometer-size Bi_3TaO_7 and its visible-light photocatalytic activity for the degradation of a 4BS dye. *Journal of Colloid and Interface Science*, 345: 467-473.
- Zhou, W.(1992). Structural chemistry and physical properties of some ternary oxides in the $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ system. *Journal of Solid State Chemistry*, 101: 1-17.
- Zhou, W. (1994). Defect fluorite superstructures in the $\text{Bi}_2\text{O}_3\text{-WO}_3$ system. *Journal of Solid State Chemistry*, 108: 381-394.
- Zhou, W., Jefferson, D. and Thomas, J. (1987). A new structure type in the $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5$ system. *Journal of Solid State Chemistry*, 70: 129-136.