UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND ELECTRICAL PROPERTIES OF BISMUTH TANTALATE BINARY MATERIALS

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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**

January 2018

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

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KARTIKA BINTI FIRMAN

January 2018

Chairman : Tan Kar Ban, PhD
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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 $Bi_{3+x}Ta_{1-x}O_{7-x}$ ($0 \leq x \leq 0.184$), 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 $Bi_{3+x}Ta_{1-x}O_{7-x}$ 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 $Bi_{3+x}Ta_{1-x}O_{7-x}$ solid solution samples were measured over the frequency range 5 Hz – 13 MHz. At intermediate temperatures, ~350 – 850 ˚C, $Bi_{3+x}Ta_{1-x}O_{7-x}$ solid solution was a modest oxide ion conductor with conductivity, ~10^{-6} – 10^{-3} S cm^{-1}; the activation energy was in the range 0.98 – 1.08 eV. Bi-rich sample, $Bi_{3.184}Ta_{0.816}O_{6.816}$ exhibited the highest conductivity of ~1.50x10^{-3} 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 $Bi_3Ta_{1-x}Ln_xO_{7-x}$ (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: $Ln^{3+} \leftrightarrow Ta^{5+} + O^{2}$. The solid solution limit was up to x = 0.2 for Nd-doped $Bi_3Ta_{1-x}Nd_xO_{7-x}$, with a slight increased lattice constants, a=b=c in the range 5.4477(±0.0037) – 5.4682(±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(±0.0002) and 5.4687(±0.0002) Å, respectively. $Bi_3Ta_{0.8}Nd_{0.2}O_{6.8}$ exhibited the highest conductivity for the doped lanthanide series at all temperatures, i.e. ~350 to 850 ˚C. The recorded conductivity was 9.26×10^{-3} 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 $Bi_3Ta_{1-x}M_xO_7$ (M = V or Nb). The solid solution limit for Nb–doped $Bi_3Ta_{1-x}Nb_xO_7$ was up to x = 0.5. $Bi_3Ta_{1-x}Nb_xO_7$solid solution adopted similar defective fluorite structure, space group Fm-3m with lattice parameters, a=b=c in the range 5.4477(±0.0037) – 5.4654(±0.0011) Å.The Nb-doped samples showed an increase in electrical conductivity with increasing Nb content; $Bi_3Ta_{0.5}Nb_{0.5}O_7$ exhibited the highest conductivity, ~5.96×10^{-3} S cm^{-1} at 650 ˚C. The enhanced electrical conductivity for $Bi_3Ta_{1-x}Nb_xO_7$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 $Bi_3Ta_{1-x}V_xO_7$solid solution with lattice parameters, a=b=c, 5.4559 ((±0.0011) Å. The ionic conductivity exhibited by $Bi_3Ta_{0.9}V_{0.1}O_7$ was ~4.17×10^{-3} S cm^{-1} at 650 ˚C with activation energy of 1.01 eV.

On the other hand, tungsten substituted solid solution, $Bi_3Ta_{1-x}W_xO_{7+(x/2)}$ ($0 \leq x \leq 0.2$) with lattice constants, a=b=c in the range 5.4477(±0.0037) – 5.4668(±0.0001) Å. The conductivity values of $Bi_3Ta_{1-x}W_xO_{7+(x/2)}$ solid solution, x = 0.1 and x = 0.2 were ~5.15×10^{-3} S cm^{-1} and ~6.78×10^{-3} 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

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Januari 2018

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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, $Bi_{3+x}Ta_{1-x}O_{7-x}$ ($0 \leq x \leq 0.184$), di mana pembentukan mekanisme melibatkan penggantian satu kation Ta^{5+} dengan satu kation Bi^{3+} dalam perbezaan peratusan ~4.6 mol%. Sampel-sampel tersebut menghablur 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 $Bi_{3+x}Ta_{1-x}O_{7-x}$ 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 telahditentukan 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 $Bi_{3+x}Ta_{1-x}O_{7-x}$ telah diukur dalam julat frekuensi 5 Hz – 13 MHz. Pada perantaraan suhu, ~350 – 850 ˚C, larutan pepejal $Bi_{3+x}Ta_{1-x}O_{7-x}$ merupakan konduktor ion oksida yang sederhana dengan kekonduksian, ~10^{-6} – 10^{-3} S cm^{-1}; tenaga pengaktifan adalah di dalam julat 0.98 – 1.08 eV. Sampel yang kaya dengan bismut, $Bi_{3.184}Ta_{0.816}O_{6.816}$ mempunyai nilai kekonduksian yang paling tinggi, ~1.50×10^{-3} 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, $Bi_3Ta_{1-x}Ln_xO_{7-x}$ (Ln = Nd, Gd,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: $Ln^{3+} \leftrightarrow Ta^{5+} + O^{2-}$. Had larutan pepejal adalah sehingga x = 0.2 untuk Nd-terdop $Bi_3Ta_{1-x}Nd_xO_{7-x}$, yang menunjukkan sedikit peningkatan dalam pemalar kekisi, a=b=c dalam julat 5.4477(±0.0037) – 5.4682(±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(±0.0002) dan 5.4687(±0.0002) Å. $Bi_3Ta_{0.8}Nd_{0.2}O_{6.8}$ 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 9.26×10^{-3} 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 $Bi_3Ta_{1-x}M_xO_7$ (M = V atau Nb). Had larutan pepejal untuk Nb–terdop $Bi_3Ta_{1-x}Nb_xO_7$ adalah sehingga x = 0.5. Larutan pepejal $Bi_3Ta_{1-x}Nb_xO_7$ juga mempunyai struktur fluorit yang tercacat, kumpulan ruang Fm-3m dengan pemalar kekisi, a=b=c di dalam julat nilai 5.4477(±0.0037) – 5.4654(±0.0011) Å. Sampel Nb-terdop menunjukkan peningkatan kekonduksian elektrik yang seiring dengan pertambahan komposisi Nb; $Bi_3Ta_{0.5}Nb_{0.5}O_7$ mempunyai kekonduksian yang tertinggi, ~5.96×10^{-3} S cm^{-1} pada suhu 650 ˚C. Peningkatan kekonduksian elektrik dalam larutan pepejal $Bi_3Ta_{1-x}Nb_xO_7$ 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 $Bi_3Ta_{1-x}V_xO_7$, iaitu x = 0.1 dengan pemalar kekisi, a=b=c, 5.4559 ((±0.0011) Å. Kekonduksian ion yang diperolehi oleh $Bi_3Ta_{0.9}V_{0.1}O_7$ ialah ~4.17×10^{-3} S cm^{-1} pada suhu 650 ˚C dengan tenaga pengaktifan 1.01 eV.

Selain itu, larutan pepejal penggantian tungsten (wolfram), $Bi_3Ta_{1-x}W_xO_{7+(x/2)}$ (0 ≤ x ≤ 0.2) dengan pemalar kekisi, a=b=c dalam julat nilai 5.4477(±0.0037) – 5.4668(±0.0001) Å telah disediakan. Nilai kekonduksian larutan pepejal $Bi_3Ta_{1-x}W_xO_{7+(x/2)}$, x = 0.1 dan x = 0.2 adalah ~5.15×10^{-3} S cm^{-1} dan ~6.78×10^{-3} 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. Jumiati 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 Aidayu 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.

I certify that a Thesis Examination Committee has met on 22 January 2018 to conduct the final examination of Kartika binti Firman on her thesis entitled "Synthesis and Electrical Properties of Bismuth Tantalate Binary Materials" in accordance with 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 Science.

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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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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 (ohm^{-1} 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 Ω^{-1} 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 he 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 Ω^{-1} 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 Ω^{-1} 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 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 Bi_2O_3–Ta_2O_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:

$$\sigma = \sigma_0 \exp(-Ea/kT) \tag{1.1}$$

Where σ_0 is the pre-exponential factor, Ea 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:

$$\sigma = \sigma_c + \sigma_a + \sigma_n + \sigma_p \tag{1.2}$$

$$\sigma = \sigma_{ion} + \sigma_{el} \tag{1.3}$$

Where σ_c, σ_a, σ_n and $\sigma_p$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+}.

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