UNIVERSITI PUTRA MALAYSIA

SYNTHESIS, CHARACTERISATION AND ELECTRICAL PROPERTIES OF PYROCHLORE MATERIALS IN Bi2O3-CuO-M2O5 (M = Ta AND Nb) TERNARY SYSTEMS

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By

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SYNTHESIS, CHARACTERISATION AND ELECTRICAL PROPERTIES OF PYROCHLORE MATERIALS IN Bi_2O_3-CuO-M_2O_5 (M = Ta AND Nb) TERNARY SYSTEMS

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Chairman: Tan Kar Ban, PhD

Faculty: Science

Detailed investigations of phase diagrams and electrical properties of novel pyrochlores in the Bi_2O_3-CuO-M_2O_5 (M = Ta and Nb) ternary systems were presented. The materials were synthesised through solid state reaction. Careful phase identification using X-ray diffraction analysis was performed to confirm the phase purities of the prepared materials and to determine the subsolidus areas in these systems. The Gibbs' phase rule approach and disappearing phase method were applied for the construction of the phase diagrams. The complete subsolidus ternary phase diagrams of the BCN and BCT systems were determined using various samples which were prepared over a wide range of temperatures, i.e. 700°C-925°C and 700-950°C, respectively. Phase-pure BCN pyrochlores were found to crystallise in cubic symmetry, space group *Fd*3*m*, No. 227 with lattice constants in the range of 10.4855 (5) < x < 10.5321 (3). The mechanism of this limited subsolidus series could be represented by a general formula, $Bi_{3.08-x}Cu_{1.84+2x/9}Nb_{3.08+7x/9}O_{14.16+6x/9}$ ($0 \leq x \leq 0.36$).

The cubic pyrochlore subsolidus area of BCT system could be described through two compositional variables in an overall general formula of $Bi_{2.48+y}Cu_{1.92-x}Ta_{3.6+x-y}O_{14.64+3x/2-y}$: 0.00 (1) ≤ x ≤ 0.80 (1) and 0.00 (1) ≤ y ≤ 0.60 (1), respectively. On the other hand, other binary phases of $Bi_7Ta_3O_{18}$, $CuTa_2O_6$ were prepared and characterised systematically for their phase formation, structural and electrical performance.

Interesting electrical properties were found in BCT cubic pyrochlores for which these materials exhibited semiconducting behaviour with recorded activation energies 0.3-0.4 eV. The dielectric constant, ε' of BCT material was ~75 with high dielectric losses, in the order of 10^{-2}-10^{-1} at room temperature and frequency of 1 MHz. A structurally related monoclinic phase $Bi_{1.92}Cu_{0.08}(Cu_{0.3}Ta_{0.7})_2O_{7.06}$ was discovered and high ε', ~70 and dielectric loss were also recorded. The ac electrical conductivity of the material corresponded well to power-law frequency dependence with distinctive features of conductivity in different frequency regimes.

The cubic phase of BCN materials had a relatively lower activation energy range, 0.2-0.4 eV. Similar electrical behaviour was observed in BCN pyrochlores as to their

comparable electrical conductivities to those BCT materials. Meanwhile, the ε' of BCN materials in the range of 45-70 and high dielectric losses (tan δ) of 0.04-0.12 were found.

Scanning electron microscopy was performed in order to study the surface morphologies of the prepared single phase materials. The spherulite shaped grains were randomly distributed with visible pores observed in the materials. Fourier transform infrared spectroscopy (FTIR) was used to qualitatively identify the bond stretching and bending vibration modes of the pyrochlores. Meanwhile, Raman spectroscopy was employed as a complement technique for structural analysis. Thermal analyses showed no phase transition and weight loss in BCT and BCN materials. Good stoichiometry for the prepared compositions was also confirmed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) by which a close agreement between the experimental and theoretical values were obtained, neither loss of Bi nor Cu was a problem during synthesis.

Divalent cations (M), e.g. Zn, Mg, Ni, Ca, Pb and pentavalent cations (N), e.g. Ta and Sb were chemically introduced into selected BCN and BCT materials. A complete substitutional solid solution, $Bi_{3.08}Cu_{1.84-x}Zn_xTa_{3.08}O_{14.16}$ ($0.0 \leq x \leq 1.84$) was obtained; however, only a narrower solid solution limit was found in the BCN system with general formula, $Bi_{2.72}Cu_{1.92-x}Zn_xNb_{3.36}O_{14.40}$ ($0.0 \leq x \leq 0.4$). The recorded activation energies for Zn substituted BCT pyrochlores were in the range of 0.40-1.4 eV. Extensive solid solutions were also found for the Ta replacement by Sb dopant in the BCT system. The resulted activation energies did not change significantly but remained reasonably low, i.e. in the range of 0.30-0.35 eV.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
Sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS, PENCIRIAN DAN SIFAT ELEKTRIK BAHAN PIROKLOR DALAM SISTEM TERNARI Bi_2O_3-CuO-M_2O_5 (M = Ta DAN Nb)

Oleh

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Penyelidikan mengenai gambar rajah fasa dan sifat elektrik dalam sistem baru ternari piroklor Bi_2O_3-CuO-M_2O_5 (M = Ta dan Nb) telan dikaji dengan teliti. Bahan piroklor telah disintesis melalui tindak balas dalam keadaan pepejal. Data pembelauan sinar X telah digunakan untuk mengenal pasti ketulenan fasa dan untuk menentukan kawasan *subsolidus* bagi kedua-dua sistem. Gambar rajah fasa ternari bagi sistem BCT dan BCN dibina dengan menggunakan aturan fasa Gibbs' dan kaedah fasa menghilang. Sampel-sampel yang disintesis dalam julat suhu antara 700°C-925°C dan 700-950°C telah digunakan untuk melengkapkan gambar rajah fasa sistem ternari *subsolidus* BCN dan BCT. Piroklor BCN fasa tulen menghablur dalam simetri kubik, kumpulan ruang *Fd*3*m*, No. 227 dengan pemalar kekisi dalam lingkungan 10.4855 (5) < x < 10.5321 (3). Mekanisme untuk siri *subsolidus* yang terhad ini boleh diwakilkan dengan formula am $Bi_{3.08-x}Cu_{1.84+2x/9}Nb_{3.08+7x/9}O_{14.16+6x/9}$ ($0 \leq x \leq 0.36$).

Kawasan *subsolidus* piroklor BCT dapat digambarkan melalui dua pembolehubah komposisi dengan formula am $Bi_{2.48+y}Cu_{1.92-x}Ta_{3.6+x-y}O_{14.64+3x/2-y}$: 0.00 (1) ≤ x ≤ 0.80 (1) and 0.00 (1) ≤ y ≤ 0.60 (1). Selain itu, fasa binari $Bi_7Ta_3O_{18}$, $CuTa_2O_6$ telah disintesis dan ciri-ciri pembentukan fasa, struktur dan sifat elektrik juga dikaji dengan sistematik.

Sifat elecktrik piroklor BCT menunjukkan ciri semikonduktor dengan tenaga pengaktifan antara 0.3-0.4 eV. Pemalar dielektrik bagi bahan BCT adalah ~75 dan kehilangan dielektrik yang agak tinggi, iaitu dalam lingkungan 10^{-2}-10^{-1} pada suhu bilik dan frekuensi 1 MHz. Fasa struktur yang berkaitan dengan fasa monoklinik $Bi_{1.92}Cu_{0.08}(Cu_{0.3}Ta_{0.7})_2O_{7.06}$ telah ditemui dan mempunyai pemalar dielektrik pukal, ~70 serta kehilangan dielektrik yang tinggi. AC kekonduksian elecktrik ini berkait rapat dengan hukum kuasa yang bergantung pada frekuensi di mana kekonduksian dalam rejim frekuensi yang berbeza boleh diwakili dengan ciri-ciri tersendiri.

Fasa kubik BCN mempunyai tenaga pengaktifan yang rendah, 0.2-0.4 eV. Sifat elektrik yang ditunjukkan oleh kubik BCN adalah setanding dengan kubik piroklor BCT. Sementara itu, pemalar dielektrik, ε' kubik BCN adalah dalam lingkungan 45-70 manakala bagi nilai kehilangan dielektrik yang tinggi (tan δ), 0.04-0.12 telah dicatatkan.

Mikroskopi elektron pengimbas telah digunakan untuk mengkaji morfologi permukaan untuk sampel fasa tulen. Butiran berbentuk sferulit yang berliang dapat dilihat di atas permukaan sampel. Fourier spektroskopi inframerah (FTIR) digunakan untuk mengenal pasti regangan ikatan dan mod getaran lenturan piroklor. Selain daripada itu, specktroskopi Raman juga digunakan untuk menganalisa struktur piroklor. Analisis terma untuk piroklor BCT dan BCN tidak menunjukkan sebarang peralihan fasa dan kehilangan berat sampel. Komposisi stoikiometri untuk sampel yang dikaji juga turut dianalisa dengan spektroskopi pancaran atomik plasma ganding induktif (ICP-AES). Nilai eksperimen yang diperoleh adalah setanding dengan nilai teori sampel dan menunjukkan kehilangan Bi atau Cu tidak ketara.

Kation divalen (M) seperti Zn, Mg, Ni, Ca, Pb dan kation pentavalen (N) Ta dan Sb telah didopkan ke dalam piroklor BCN dan BCT yang terpilih. Penggantian larutan pepejal yang lengkap dalam piroklor BCT $Bi_{3.08}Cu_{1.84-x}M_xTa_{3.08}O_{14.16}$ ($0.0 \leq x \leq 1.84$) telah disediakan, namun larutan pepejal dalam sistem BCN dengan formula umum $Bi_{2.72}Cu_{1.92-x}Zn_xNb_{3.36}O_{14.40}$ adalah terhad ($0.0 \leq x \leq 0.4$). Tenaga pengaktifan yang dicatatkan dalam piroklor yang diganti dengan Zn berada dalam lingkungan 0.40-1.4 eV. Bagi penggantian kation pentavalen Sb ke bahan BCT, had larutan pepejal yang terbentuk adalah ekstensif. Tenaga pengaktifan tidak menunjukkan perubahan yang ketara dan berada pada tahap rendah, iaitu 0.30-0.35 eV.

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I certify that a Thesis Examination Committee has met on 28th April 2015 to conduct the final examination of Chon Mun Ping on her thesis entitled "Synthesis, Characterisation and Electrical Properties of Pyrochlore Materials in Bi_2O_3-CuO-M_2O_5 (M = Ta, Nb) Ternary Systems" 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 Doctor of Philosophy.

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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 Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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TABLE OF CONTENTS

CHAPTER 4
RESULTS AND DISCUSSION

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVATIONS

AC	Alternating current
BCN	Bismuth copper niobate
BCT	Bismuth copper tantalate
BMN	Bismuth magnesium niobate
BMT	Bismuth magnesium tantalate
BZN	Bismuth zinc niobate
BZT	Bismuth zinc tantalate
CSD	Chemical solution deposition
CVD	Chemical vapour deposition
dc	Direct current
DTA	Differential thermal analysis
fcc	Faced-centred cubic
FTIR or IR	Fourier transform infrared spectroscopy
FWHM/ β	Full width at half maximum
HTB	Hexagonal tungsten bronze
ICDD	International Centre for Diffraction Data
ICP-AES	Inductively coupled plasma-atomic emission spectroscopy
LTCC	Low temperature co-fired ceramic
MHD	Magnetohydrodynamic
MLCC	Multilayer ceramic capacitor
PLD	Pulsed laser deposition
RS	Raman spectroscopy
SEM	Scanning electron microscopy
SOFC	Sold oxide fuel cells
TCC	Temperature coefficient of capacitance
TGA	Thermogravimetry analysis
WD	Working distance
XRD	X-ray diffraction
a,b,c/ α, β	Lattice constants/ angles for each symmetry
A	Area
A	Temperature dependent constant
A* or Y*	Admittance
A' or Y'	Real part of admittance
A'' or Y''	Imaginary part of admittance
C_b	Bulk capacitance
C_{gb}	Grain boundary capacitance
C_o	Vacuum capacitance
D	Coherent scattering length
d	Interplanar spacing/ d-spacing
ε	Internal strain
ε*	Complex permittivity
ε'	Relative permittivity/ dielectric constant
ε''	Imaginary part of permittivity
ε_o	Permittivity of free space
E_a	activation energy for conduction
GF	Geometrical factors
h, k, l	Miller indices

j	Imaginary component
k_B	Boltzman's constant
l	Thickness
M*	Complex modulus
M'/M''	Real part of modulus/ Imaginary part of modulus
MC	Microwave ceramics
Q	Dissipation factor/ quality factor
R_b	Bulk Resistance
R_{gb}	Grain boundary Resistance
T	Crystallite size (Scherrer method)
tan δ	Dielectric loss
T_c	Critical temperature
TCC	Temperature coefficient of capacitance
TCε'	Temperature coefficient of permittivity
Z	Unit formula
Z*	Complex impedance
Z'/Z''	Real part of impedance/ Imaginary part of impedance
σ/ σ_0/ σ_{ac}	Conductivity/ dc conductivity/ ac conductivity
σ_0	pre-exponential factor
τ	Impedance relaxation frequency or relaxation time
θ	Bragg angle
λ	Wavelength
ν	Wavenumber
ω	Angular frequency
ω_{max}	frequency of maximum loss

CHAPTER 1

INTRODUCTION

1.1 Electroceramics

Research advancement in the field of electroceramics is driven by their technological applications. Microelectronics are the superior form of the ceramic substances whose properties and applications are found in many areas, such as power conversion and storage, communications, computation, automation, consumer products and medical industries. Electroceramics are widely applied in insulating materials, high dielectric capacitors, ultrasonic transducers, resistors, thin film capacitors and communications filters, solid oxide fuel cells (SOFC) and batteries. Therefore, their unique functional capabilities provide a wide spectrum of electrical and microelectronic devices and other related applications.

In fact, the advanced functional components are made of integrated materials which are useful in the miniaturised systems where interfaces of the materials play a crucial role. The integration of electroceramic thin films onto the substrates and the combination of bulk ceramics of different kinds or other materials such as glasses, metals or polymers are common in the evolution of multifunctional components. The objectives of electrical and electronic components miniaturisation are to produce materials with the specific properties, required shapes and sizes within the specified dimensional tolerances and at reasonable cost. Electroceramics have experienced the progression from microtechnology towards nanotechnology. The nanosize effects and the application of new characterisation techniques that reveal the nanometric scale features are therefore of the realm of research (Setter *et al.*, 2000).

Practically, these materials are produced by conventional powder processing, tape casting or screen printing techniques and then followed by sintering processes. In the late 1980s, these techniques were progressively supplemented by thin film deposition techniques such as sputtering, pulsed laser deposition (PLD), chemical solution deposition (CSD) and the chemical vapour deposition (CVD). During the deposition processes, these materials are prepared on a microscopic scale without powder processing as an intermediate step because the synthesised temperatures are below the typical sintering temperatures of the bulk ceramics (Setter *et al.*, 2000).

Electroceramics are in general comprised of dielectrics, conductive, magnetic and optical ceramics. Examples for the dielectrics are piezo, pyro, ferroelectrics whereas the superconductors, conductors and semiconductors with both ionically and/or electronically are categorised as conductive ceramics. The primary distinction between a dielectric (or insulator) and a semiconductor lies in the difference between their energy band gap in which the latter has a smaller energy band gap and the dominant charge carriers are generated mainly by thermal excitation in the bulk under normal ranges of temperature and pressure ranges (Kwan, 2004). In dielectric, charge carriers are mainly injected from the electrical contacts or other external sources simply because the band gap of dielectric is relatively larger and therefore, higher amount of energy is required for the band-to-band transition. The occurrence of dielectric

phenomena are the interaction between the free charges with the external forces, such as electric fields, magnetic fields, electromagnetic waves, mechanical stress or temperature. For non-magnetic dielectric materials, the phenomena are encompassed by mainly electric polarisation, resonance, relaxation, energy storage, energy dissipation, thermal, mechanical, optical effects and their interrelations. In general, electroceramics offer a wide variety of functions, notably in microelectronics and communication components. The fabrication and miniaturisation of electrical and electronic devices are prevalent which had made much fascination in the research development of electroceramics.

1.2 Electrical Conduction

Electrical conduction is primarily governed by the manner of generating charge carriers in a material. 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 (Kwan, 2004) which outlined as below:

i) Intrinsic conductivity: Charge carriers are developed in the material based on its chemical structure.

ii) Extrinsic conductivity: Charge carriers are initiated by material impurities, which may be introduced by fabrication processes or deliberately doped into it for a distinct purpose.

iii) Injection-controlled conductivity: Charge carriers are injected into the material mainly from metallic electrodes via a metal-material interface.

The electrical conductivity follows the empirical equation as given in Equation (1.1)

$$\sigma = \sigma_0 \exp(-E_\sigma/kT) \qquad (1.1)$$

where σ_0 is the pre-exponential factor, E_σ 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 under certain condition, it may involve both ionic and electronic conductions (Kwan, 2004).

Generally, the fundamental charge carriers are the cations, anions, electrons and electron holes and the total conductivity is given as

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

where σ_c, σ_a, σ_n, σ_p are the cation, anion, electron and electron hole conductivities, respectively. The individual conductivity may be written in terms of their transport numbers:

$$(t): \sigma_c = t_c\sigma,\ \sigma_a = t_a\sigma,\ \sigma_n = t_n\sigma \text{ and } \sigma_p = t_p\sigma \qquad (1.3)$$

and the sum of the transport numbers of all the charge carriers are equivalent to unity:

$$t_c + t_a + t_n + t_p = 1 \qquad (1.4)$$

The summation of ionic conductivity (1.5) and electronic conductivity (1.6) gives rise to the total electrical conductivity (1.7) (Manning, 1962).

$$\sigma_{ion} = \sigma_c + \sigma_a \qquad (1.5)$$

$$\sigma_{el} = \sigma_n + \sigma_p \qquad (1.6)$$

$$\sigma = \sigma_{ion} + \sigma_{el} \qquad (1.7)$$

It is common that only one type of charge carrier prevails the charge transport and the contribution from minority carriers is insignificant. The mobilities of electrons and electron holes in oxides are generally several orders of magnitude ($\sim 10^4$-10^8) greater than those of the ions. In some cases, the oxide may still be essentially an electronic conductor though the concentration of electron or electrons holes is lower than that of the ionic charge carriers. The relative importance of ionic and electronic conductivities will always vary incredibly with temperature and oxygen partial pressure (Manning, 1962).

In fact, most metal oxides are electronic conductors at elevated temperatures. The conductivities of these oxides increase with increasing temperature and the reason is due to the increase of the number of electronic defects with temperature. Transition metal monoxides are metallic conductors for which their conductivities decrease with increasing temperature as the mobility of electronic defects decrease with increasing temperature. For certain oxides, e.g. p-conducting acceptor-doped perovskites demonstrate metallic-like conductivity in which the conductivity decreases with temperature and the depreciation of conductivity is attributed to decreased number of electron holes with increasing temperature, thus the conductivity cannot be classified as metallic (Manning, 1962).

The electronic conductivity, σ_{el} of a semiconducting oxide is given in Equation (1.6). As mentioned earlier, one type of charge carrier will usually dominate and in some cases where an oxide is close to stoichiometric, both n- and p-typed conductivity may contribute significantly to the electronic conductivity.

1.3 Dielectric Materials and Type of Polarisations

The important electrical property of dielectric materials is relative permittivity (ε'), which is also known as dielectric constant. It relies greatly on the frequency of the alternating electric field or the rate of the change of the time-varying field. Likewise, the chemical structure and the imperfections such as defects of the materials, as well as some other physical parameters including temperature and pressure play a significant role in determining the dielectric properties (West, 1999). A dielectric material is made up of atoms or molecules that possess one or more basic types of electric polarisation, including electronic, atomic (or ionic), dipolar and interface/space charge polarisations. The application of an electric field causes the formation and movement of dipoles is called polarisation. When an electric field is applied to the material, dipoles within the atomic or molecular structure are induced and aligned with the direction of that applied

field. Any permanent dipoles that are previously present in the material are also aligned with that particular field. In this case, the material is said to be polarised. The degree of the overall polarisation is affected by the time variation of the electric field as each type of the polarisation requires time to perform.

1.3.1 Electronic Polarisation

It is always present in atoms or molecules in all kinds of materials. When the atom is located in an electric field, the charged particles experience an electric force as a result of which the centre of the negative charge cloud is displaced with respect to the nucleus. A dipole moment is induced by electric field and the atom is said to be electronically polarised (Raju, 2003).

1.3.2 Atomic/Ionic Polarisation

It is sometimes referred as vibrational polarisation due to the distortion of the normal lattice vibration and the electric field causes the atoms or ions of a polyatomic molecule to be displaced relative to each other. In other words, this is the displacement of positive ions with respect to negative ions and the induced dipole moment is slightly dependent on temperature (Kwan, 2004).

1.3.3 Dipolar/Orientational Polarisation

This polarisation is different from the electronic and ionic polarisations in which it can occur even when an external electric field is not applied and this happens only in materials consisting of molecules or particles with a permanent dipole moment. The electric field causes the reorientation of the dipoles toward the direction of the field. When an electric field is applied to a polar dielectric, the following steps will take place:

i) The distance between the centres of the negative and positive electric charges increases slightly and the dipole moment becomes greater due to the action of electric field because the dipole experiences tension.

ii) The dipoles turn so that the positively charged end faces the negative electrode and the negatively charged end faces the positively electrode. The sum of the individual dipole moments will now not be equal to zero (Rajput, 2004).

1.3.4 Space Charge Polarisation

The space charge or translational polarisation is observed in materials containing intrinsic free charges such as ions, holes or electrons. This polarisation is caused by the accumulation of charges at the multiphase of dielectrics. When one of the phases has a higher resistivity than the other, the charge moves on the surface when the material is placed in an electric field. This usually found in ferrites and semiconductors at elevated temperatures (Raju, 2003).

1.4 Overview of Pyrochlore and Applications

Oxides are the biggest family of solid state materials. Different types of oxides emerge from a wide variety of structures, bonding characters and compositions and these parameters have strong correlation with their physical and electrical properties. With general knowledge on the chemical nature of different elements, the information is used to design new materials with the desired properties for many applications.

Examples of mixed metal oxides with the formula $A_2B_2O_7$ are oxide pyrochlores which show good chemical and thermal stability. Pyrochlore oxides are useful in various devices and applications due to their broad spectrum of properties such as electrical, magnetic, dielectric, optical and catalytic behaviour. These properties are generally controlled by the factors, i.e. ionic size, polarisability of the ions, electronic configuration and the preparative conditions. They could be viewed as doubled unit cells of derivative fluorite structure, AO_2 for which the cationic sites are differentiated into both A and B sites. As a consequence, hundreds of different compositions of pyrochlores with various properties could be yielded. Pyrochlore structure has great tolerance towards vacancies and therefore, defect pyrochlores with vacancies in A and/or O sites can attribute to many compounds in this family.

Pyrochlore materials can be used as solid electrolytes, oxygen electrodes, catalysts as well as in the active and passive electronic components e.g. high permittivity microwave filters, thermistors, gas sensor, switching elements and thick film resistors (Boivin *et al.*, 1998). Stoichiometric oxide pyrochlores containing elements in their maximum oxidation state and high ionic polarisability always exhibit good dielectric properties, e.g. $Cd_2Nb_2O_7$, $Ln_2Ti_2O_7$ are excellent ferroelectric materials. Dielectric constants are fairly large in many niobates, tantalates and titanates and these materials can be used as high permittivity ceramics (Tan *et al.*, 2005; Sreekantan *et al.*, 2008; Khaw *et al.*, 2009). Thermistors are commonly made from oxide components with spinel or related structure, e.g. Bi_2CrNbO_7 and Bi_2CrTaO_7 with the pyrochlore structures are used for temperature compensation, voltage stabilisation and current time relays. Many Pb- and Bi- containing precious metals are used to make thick film resistors with low and reproducible sheet resistance. These materials are unaffected by humidity and have negligibly small temperature coefficient of resistance (Van Loan, 1972).

Zirconate pyrochlores, e.g. $Pr_2Zr_2O_7$ doped with 10% In_2O_3 could also be the promising materials to be used as electrodes for open cycle magnetohydrodynamic (MHD) power generation schemes as they have excellent corrosion and shock resistance, good electronic and thermal conductivity (Meadowcroft, 1968). However, more experimentation and feasibility studies are required as the commercial utilisation of MHD power generation is still much in the experimental stages. On the other hand, pyrochlores materials are also applied in switching elements that show sudden and abnormally great change in electrical conductivity at a given temperature. The change in electrical conductivity can be caused by direct variation of temperature, the element by external source or by internal heating effects by the passage of current. Examples VO_2 and doped $BaTiO_3$ are both applied in switching elements for temperature sensitive electrical switches and fire extinguishers (Subramanian *et al.*, 1983).

Pyrochlores also play a crucial role in the nuclear waste disposal and the understanding of the detailed phase stability relationships enables a careful screening of additives for fixation of radioactive ions. Examples such as Ln, Zr, Mo, Ru are introduced into pyrochlore or the related crystalline phases for easy transportation, handling and disposal. Besides, pyrochlores are also used as microwave dielectrics in microwave resonators. The development of microwave dielectric materials depends strongly on the materials with high quality factor, Q (reciprocal of dielectric loss) (Q > 10,000). The recent device manufactures also emphasise on the process compatibility with low resistivity metals and allow low Q dielectrics (Q≈200). Ceramics in the bismuth zinc niobate (BZN) and bismuth zinc tantalate (BZT) ternary systems with pyrochlore structure are promising dielectrics because of their suitable Q values and the temperature coefficient of capacitance which can be compositionally tailor-made to a low value (Nino *et al.*, 2001; Youn *et al.*, 2002).

1.5 Formation of Pyrochlore and Solid Solution

A broad range of cations is substituted at the A and B sites of pyrochlores and this leads to hundreds of different compositions with various properties. In Bi_2O_3-ZnO-Nb_2O_5 (BZN) system, an ideal composition could be $Bi_3Zn_2Nb_3O_{14}$ in which it is presumed that the Zn cation is apportioned evenly at both A- and B- sites. Alternatively, the chemical formula of BZN could be written as $(Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O_6O'$. Bismuth-based pyrochlore structure has a great tolerance for accepting different ions at the A, B and O sites and the unambiguous correlation among the ionic radii of the A and B cations is crucial in order to maintain the stability of pyrochlores. Nevertheless, the stability of the pyrochlore structure also depends on the electronegativity of the cations, charge neutrality and thermodynamic stability of the competitive phases. The combination of A and B cations should yield the same average charge in order to maintain electroneutrality. The stability range has been stipulated by the cation radii ratio R_A/R_B. The substituted cations must have appropriate ionic radii to fit into the pyrochlore structure based on the upper and lower radius limits at which these values are given as $0.87 < r_A < 1.17$, $0.58 < r_B < 0.775$ Å and $0.96 < r_A < 1.29$, $0.54 < r_B < 0.76$ Å for $A_2^{3+}B_2^{4+}O_7$ and $A_2^{2+}B_2^{5+}O_7$ systems, respectively. The stability ranges are $1.46 < R_A/R_B < 1.80$ and $1.4 < R_A/R_B < 2.2$, respectively for the combinations of 3+, 4+ and 2+, 5+ cations (Subramanian *et al.*, 1983). In bismuth-based pyrochlores, the ionic radii of B cations, e.g. niobium, tantalum and antimony are comparable in which they are 0.64 Å for both Nb, Ta and 0.60 Å for Sb under 6 coordination environment. Hence, the weighted R_A/R_B average for both α-$(Bi_{1.5}Zn_{0.5})(Nb_{1.5}Zn_{0.5})O_6O'$ (BZN) and $(Bi_{1.5}Zn_{0.5})(Ta_{1.5}Zn_{0.5})O_6O'$ (BZT) is 1.66 and for $(Bi_{1.5}Zn_{0.5})(Sb_{1.5}Zn_{0.5})O_6O'$ (BZS) is 1.74, which are well within the stability limit for the pyrochlore structure (Mergen *et al.*, 1996; Shannon *et al.*, 1976).

It is worthwhile to highlight that a solid solution is referred as a crystalline phase that can have variable composition. Substitutional solid solutions and interstitial solid solutions are two simple types of solid solutions where the former replaces an atom or homovalent ion in the parent structure and the later involves the introduced species occupies a site that is either empty or no ions/atoms are left out. There are certain prerequisites that must be met to form substitutional solid solutions, i.e. the ions that replace each other must have same charge and similar size. Extensive solid solutions

generally form at high temperatures and the formation of solid solutions at lower temperatures may be more restricted or barely prevailed (West, 1999).

Meanwhile, ions that are substituted by other ions of different charges and additional changes involving creation of vacancies or interstitials (ionic compensation) or electrons or holes (electronic compensation) are known as heterovalent or aliovalent substitution, where these are solid solutions with 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 of pyrochlores could be formed by substitution of cations at either A or B site of $A_2B_2O_7$. Inevitably, the substitution may lead to the formation of vacancies, holes or interstitial oxygen that may be related to the interesting electrical properties.

1.6 Problem Statement

Intensive research has been focused on the materials of Bi_2O_3-ZnO-Nb_2O_5/Ta_2O_5 systems due to their interesting dielectric properties. In this project, copper is chosen as the alternative substituent for zinc and investigation of the structural, phase relations and electrical properties of pyrochlores in the Bi_2O_3-CuO-Nb_2O_5/Ta_2O_5 (BCN/BCT) systems is considerably limited. It is important to study the phase compatibilities between binary and/or ternary phases in both systems especially to determine the most appropriate condition for sample preparation. An attempt to enhance the electrical properties of the prepared materials by chemical doping is also part of the investigation. The focus of this study is, therefore, to develop an understanding of the correlation between electrical properties and compositions in these complicated ternary systems.

1.7 Objectives

1. To synthesise new pyrochlore phases and to construct the phase diagrams of Bi_2O_3-CuO-M_2O_5 (M = Nb and Ta) ternary systems using conventional solid state method.
2. To identify the phase purities and to investigate the thermal and structural properties of single phase materials using physical and chemical techniques.
3. To determine the electrical properties of the prepared samples using ac impedance spectroscopy.
4. To enhance the electrical properties and solubility of the pyrochlores through chemical doping.

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