PHASE DIAGRAM, AND STRUCTURAL AND ELECTRICAL PROPERTIES OF PYROCHLORES IN Bi_2O_3-ZnO-Nb_2O_5 TERNARY SYSTEM

By

TAN KAR BAN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Doctor of Philosophy

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For My Wonderful Papa, Mama, Brother and Lee Chuen

With Love

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Chairman: Professor Zulkarnain Zainal, PhD

Faculty: Science

A comprehensive investigation of phase diagram, structural and electrical properties of pyrochlores in Bi_2O_3-ZnO-Nb_2O_5 ternary system was presented. A thorough and complete literature review was carried out in order to gather background information on bismuth zinc niobate (BZN) phases and related materials. Thus, a better understanding in the phase formation, research problems, electrical and thermal properties of the investigated materials and their potential application is achieved.

BZN pyrochlores and related materials were prepared via conventional solid state reaction at sintering temperatures ranging from 700 ^{o}C to 1200 ^{o}C using high purity oxides. Analysis and characterization were performed using a combination of techniques including diffraction, microscopy, spectroscopy, thermal analysis and physical property measurements. X-ray diffraction (XRD) was used for phase identity and purity determination. Detailed analysis was carried out on single phase materials. The surface structure and morphology were characterized using scanning electron microscopy (SEM). Structural analysis was carried out using Fourier-transform infrared spectroscopy (FT-IR), Raman spectroscopy and

Rietveld refinement using neutron and X-ray diffraction data. Electrical properties were determined by a.c impedance spectroscopy in the frequency range of 5 Hz to 13 MHz and temperature range of ~28 ^{o}C to 850 ^{o}C. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were employed to study thermal properties. Other analysis such as inductively coupled plasma atomic emission spectrometry (ICP-AES) and density measurement were carried out on selected samples.

A complete phase diagram including two solid solution areas for cubic and monoclinic phases in BZN ternary system has been constructed. The cubic pyrochlore solid solutions do not include the so-called ideal composition P, $Bi_3Zn_2Nb_3O_{14}$. It may be described in terms of two compositional variables: ZnO deficiency compared to P together with variable Bi: Nb ratio with general formula, $Bi_{3+y}Zn_{2-x}Nb_{3-y}O_{14-x-y}$: $-0.11(1) \leq y \leq 0.14(1)$ and $-0.03(1) \leq x \leq 0.31(1)$.

Selected BZN materials have been characterized by a.c impedance spectroscopy. These materials exhibited excellent dielectric properties: permitivity, $\varepsilon' = \sim 80$-100, dielectric loss ($\tan \delta$) = ~ 0.002 - 0.009 and temperature coefficient, Tcc = ~ 400 ppm/^{o}C, at ~28 ^{o}C in the frequency region of $1x10^5$ Hz. Chemical doping was carried out in order to elucidate relative ability of cubic pyrochlore $Bi_3Zn_{1.84}Nb_3O_{13.84}$ to accommodate various dopants in forming new solid solutions and in the search for better performance materials. However, chemically doped BZN materials did not show extensive solid solutions limit or significant improvement in electrical properties.

In conclusion two structurally related phases i.e. cubic and monoclinic phases exist in the BZN ternary system. These materials display interesting electrical properties: the cubic phase, P has a large negative temperature coefficient of permittivity while the monoclinic phase, M has a positive value for the temperature dependency. Given the opposite signs of the temperature coefficients of these phases, it may be possible to make composites of P and M so as to achieve controllable or almost zero temperature coefficient of capacitance (TCC) values. In addition both of these phases have high dielectric constants. Hence, these materials have potential applications in high frequency multilayer devices including LC filters and low temperature, co-fired ceramic, LTCC system.

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

GAMBARAJAH FASA, DAN SIFAT STRUKTUR DAN ELEKTRIK BAGI PYROCHLORES DALAM SISTEM TERNARI Bi_2O_3-ZnO-Nb_2O_5

Oleh
Tan Kar Ban

Februari 2007

Pengerusi: Profesor Zulkarnain Zainal, PhD

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Penyelidikan mengenai gambarajah fasa, struktur dan sifat elektrik dalam sistem ternari Bi_2O_3- ZnO-Nb_2O_5 telah dipersembahkan. Sorotan literatur yang lengkap dan meluas telah dilakukan untuk pengumpulan maklumat-maklumat yang penting. Justeru itu, perfahaman yang menyeluruh mengenai pembentukan fasa, masalah penyelidikan, sifat terma dan elektrik dalam bahan yang dikaji dapat dicapai.

Bahan-bahan dalam sistem Bi_2O_3-ZnO-Nb_2O_5 (BZN) telah disediakan melalui tindak balas keadaan pepejal dengan penggunaan bahan mentah berketulenan tinggi di bawah suhu sintesis 700-1200 ^oC. Analisis dan pencirian telah dibuat melalui gabungan pembelauan, mikroskopik, spektroskopik, analisis terma dan pengukuran sifat fizikal. Pembelauan sinar-X (XRD) digunakan untuk penentuan identiti dan ketulenan fasa. Analisis yang selanjutnya dilakukan pada bahan yang berfasa tunggal. Struktur permukaan dan morfologi dikaji secara spektroskopi imbasan electron (SEM). Manakala, analisis struktur dilengkapkan dengan penggunaan spektroskopi inframerah transformasi Fourier (FT-IR), spektroskopi Raman dan Refimen Rietveld yang menggunakan data neutron dan XRD. Sifat

elektrik telah ditentukan dengan spektrokopi impedans ac dalam frekuensi 5 Hz – 13 MHz. Analisis pembezaan terma (DTA) dan analisis thermogravimetri (TGA) digunakan untuk kajian sifat terma. Analis-analisi yang lain termasuk plasma aruhan keduaan-spektroskopi penyebaran atom (ICP-AES) dan pengukuran ketumpatan telah dilakukan pada sampel yang selektif.

Gambarajah fasa yang lengkap merangkumi dua kawasan larutan pepejal bagi kubik dan monoklinik dalam sistem ternari BZN telah dilukiskan. Komposisi unggul P, $Bi_3Zn_2Nb_3O_{14}$ didapati tidak termasuk dalam larutan pepejal kubik. Secara keseluruhan, kawasan larutan pepejal kubik dapat diwakili dangen dua pembolehubah: Pengurangan ZnO daripada P dan variasi Bi:Nb dengan satu formula am, $Bi_{3+y}Zn_{2-x}Nb_{3-y}O_{14-x-y}$: $-0.11(1) \leq y \leq 0.14(1)$ dan $-0.03(1) \leq x \leq 0.31(1)$.

Bahan BZN yang selektif telah dikajikan dengan spektroskopi impedans a.c. Bahan-bahan ini menunjukkan ciri-ciri dielektrik yang unggul: ketelusan relatif, $\varepsilon' = \sim 80 - 100$, kerugian dielektrik $(\tan \delta) = \sim 0.002 - 0.009$ and pekali suhu, Tcc = ~ 400 ppm/^{o}C, at ~ 28 ^{o}C dalam lingkungan frekuensi $1x10^5$ Hz. Pendopan secara kimia telah dijalankan untuk mengkaji pembentukan larutan pepejal larutan yang baru dan juga sebagai isytihar untuk menerokai bahan yang lebih berprestasi. Akan tetapi, bahan-bahan yang didopkan menunjukkan larutan pepejal dan peningkatan sifat elektrik yang terhad.

Secara kesimpulan, dua fasa yang berstruktur kena-mengenai sama ada kubik dan monoklinik didapati wujud dalam sistem ternari BZN. Bahan-bahan ini

menunjukkan sifat elektrik yang manarik; fasa kubik, P yang mempunyai nilai pekali suhu yang amat negatif manakala fasa monoklinik, M mempunyai pekali suhu yang positif. Dengan tanda pekali suhu yang berlawanan, hasrat dan minat turut diberikan untuk penyediaan komposit yang mempunyai pekali suhu yang hampir sifar. Tambahan pula bahan bahan ini mempunyai nilai pemalar dielektrik yang tinggi. Justeru itu, BZN pyrochlore berpontensi digunakan sebagai alat berbilang lapis dalam frekuensi tinggi seperti penapis LC dan sistem seramik bersuhu rendah (LTCC).

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I certify that an Examination Committee met on 7 February 2007 to conduct the final examination of Tan Kar Ban on his Doctor of Philosophy thesis entitled "Phase Diagram, and Structural and Electrical Properties of Pyrochlores in Bi_2O_3-ZnO-Nb_2O_5 Ternary System" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regualtions 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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This thesis 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 are as follows:

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DECLARATION

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

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TAN KAR BAN

Date:

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