PREPARATION AND CHARACTERISATION OF BISMUTH ZINC TANTALATE PYROCHLORE MATERIALS

By

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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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Chairman: Professor Zulkarnain Zainal, PhD

Faculty : Science

Pyrochlore materials in Bi_2O_3-ZnO-Ta_2O_5 ternary system were synthesized by solid-state reaction at 1050^{o}C for 48 hours. The X-ray diffraction (XRD) pattern of the material of composition $Bi_3Zn_2Ta_3O_{14}$ could be fully indexed on a cubic cell with a = 10.5437(9) Å. A study on the phase formation mechanism indicated that Bi_2O_3 played an important role only in the initial stage of the formation of the pyrochlore phase. The subsolidus phase diagram of Bi_2O_3-ZnO-Ta_2O_5 in the region of the cubic pyrochlore has been determined at 1050^{o}C. This phase forms a solid solution area that includes the ideal composition P, $Bi_3Zn_2Ta_3O_{14}$. Density measurement was used to identify the possible mechanism of solid solution formation. The solid solution area in the phase diagram can be described by the combination of two mechanisms: $Bi_3Zn_{2-x}Ta_3O_{14-x}$ and $Bi_{3+y}Zn_2Ta_{3-y}O_{14-y}$, to yield the formula $Bi_{3+y}Zn_{2-x}Ta_{3-y}O_{14-x-y}$, $-0.20 \leq y \leq 0.16$ and $0.00 \leq x \leq 0.40$. XRD in combination with neutron diffraction data were used for Rietveld Refinement for the elucidation of the crystal structure of selected materials. The results show that there is a degree of insensitivity of the refinement to certain changes in the cation content and the oxygen stoichiometry is refined to a value similar to the expected

values.

Various possible sources of error and variation in permittivity measurements were investigated and the results showed that pellet density was the parameter that had the greatest effect on the determination of capacitance value. Optimisation of sintering conditions was carried out to obtain pellets with highest density and capacitance value. Cubic $Bi_3Zn_2Ta_3O_{14}$ (BZT) has ε' of 58, dielectric loss (tan δ) of 0.0023 at 30^oC and 1 MHz; temperature coefficient of capacitance (TCC) of -156 ppm/^oC in the range of 30^oC to 300^oC at 1 MHz. Slight variations of permittivity and dielectric loss with compositions were observed in the solid solutions. Conductivities of the solid solutions are higher than that of BZT with activation energy, E_a, in the range of 1.55 – 1.67 eV. The structurally related monoclinic phase $Bi_2(Zn_{1/3}Ta_{2/3})_2O_7$ has ε' of 62, tan δ of 0.0084 at 30^oC and 1 MHz and TCC of +110 ppm/^oC in the range of 30^oC to 300^oC at 1 MHz. The conductivity at 649^oC is 6.68 x10^{-6} ohm^{-1} cm^{-1} with E_a = 1.75 eV.

Chemical doping using divalent, tetravalent, trivalent, tetra/hexavalent and pentavalent cations was carried out in the search for better performance materials; only di-, tetra- and pentavalent dopants could be successfully introduced into BZT. Results show that permittivity and dielectric loss of di- and tetravalent doped solid solutions did not vary greatly with dopant concentration. On the other hand, ε' and tan δ greatly increased or decreased with variations in composition for pentavalent doped materials. Conductivities of the doped materials are higher than that of $Bi_3Zn_2Ta_3O_{14}$ with E_a of 1.36 – 1.62 eV.

Elemental analysis using inductively-coupled plasma optical emission spectrometry (ICP-OES) confirmed the stoichiometric compositions of single phase materials. Fourier transform infra red (FTIR) spectroscopy was used to identify functional groups of the materials and Raman spectroscopy was used as a complement to FTIR. Four absorption bands were observed in FTIR and Raman spectra which can be assigned to different bond stretching or bending modes. There is a correlation between the frequency of the absorption bands and dopant concentration in pentavalent doped materials. Thermal analysis showed no phase transition and weight loss in the temperature range of 35 to 1000^{o}C. Scanning Electron Microscopy was performed to study the morphology of the materials. All the materials show grains of polyhedral shapes which are randomly distributed with visible open pores in the materials.

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

PENYEDIAAN DAN PENCIRIAN DALAM BAHAN PIROKLOR BISMUTH ZINK TANTALAT

Oleh

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Februari 2007

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Dalam kajian ini, bahan-bahan piroklor dalam sistem ternari $Bi_3Zn_2Ta_3O_{14}$ disintesis melalui tindak balas keadaan pepejal pada 1050^oC selama 48 jam. Data pembelauan sinar X (XRD) untuk satu bahan dengan komposisi $Bi_3Zn_2Ta_3O_{14}$ boleh diindeks sepenuhnya bagi satu sel kubus dengan a = 10.5437(9) Å. Kajian mekanisme pembetukan fasa menunjukkan bahawa Bi_2O_3 memainkan peranan penting dalam langkah permulaan bagi pembetukan fasa piroklor. Gambarajah fasa subsolidus untuk sistem Bi_2O_3-ZnO-Ta_2O_5 dalam kawasan piroklor kubus telah ditentukan pada 1050^oC. Fasa ini membentuk satu kawasan larutan pepejal yang termasuk komposisi unggul P, $Bi_3Zn_2Ta_3O_{14}$. Ukuran ketumpatan telah digunakan untuk menentukan mekanisme pembetukan larutan pepejal yang mungkin. Kawasan larutan pepejal dalam gambarajah fasa boleh digambarkan dengan kombinasi dua mekanisme: $Bi_3Zn_{2-x}Ta_3O_{14-x}$ dan $Bi_{3+y}Zn_2Ta_{3-y}O_{14-y}$, untuk menghasilkan formula $Bi_{3+y}Zn_{2-x}Ta_{3-y}O_{14-x-y}$, $-0.20 \leq y \leq 0.16$ and $0.00 \leq x \leq 0.40$. XRD dengan kombinasi data pembelauan neutron digunakan dalam 'Rietveld Refinement' untuk elusidasi struktur hablur bagi bahan -bahan terpilih. Keputusan menunjukkan bahawa terdapat satu darjah ketidakpekaan terhadap penukaran

tertentu dalam kandungan kation dan stoikiometri oksigen telah dihalusi ke satu nilai yang sama dengan nilai yang dijangkakan.

Pelbagai sumber ralat yang mungkin dan variasi dalam ukuran permitiviti disiasat dan keputusan menunjukkan bahawa ketumpatan pelet merupakan parameter terpenting yang berkaitan dengan nilai kapasitan. Optimisasi keadaan pengsinteran dilakukan untuk mendapatkan pelet dengan ketumpatan dan nilai kapasitan tertinggi. $Bi_3Zn_2Ta_3O_{14}$ (BZT) kubus mempunyai ε' dengan nilai 58, kehilangan dielektrik (tan δ) sebanyak 0.0023 pada 30^oC dan 1 MHz; pekali suhu kapasitan (TCC) sebanyak -156 ppm/^oC dalam lingkungan 30^oC hingga 300^oC pada 1 MHz. Sedikit variasi untuk permitiviti dan kehilangan dielektrik diperhatikan dalam larutan pepejal. Kekonduksian larutan pepejal lebih tinggi berbanding dengan BZT dengan tenaga pengaktifan, E_a, dalam linkungan 1.55 – 1.67 eV. Fasa monoklinik $Bi_2(Zn_{1/3}Ta_{2/3})_2O_7$ mempunyai ε' dengan nilai 62, tan δ sebanyak 0.0084 pada 30^oC dan 1 MHz dan TCC sebanyak +110 ppm/^oC dalam lingkungan 30^oC hingga 300^oC pada 1 MHz. Kekonduksian pada 649^oC adalah 6.68×10^{-6} ohm^{-1} cm^{-1} dengan E_a = 1.75 eV.

Pendopan kimia dengan menggunakan kation divalens, tetravalens, trivalens, tetra/heksaavalens dan pentavalens telah dilakukan dengan tujuan untuk mencari bahan dengan prestasi yang lebih baik dan hanya dopan di-, tetra and pentavalens telah berjaya didopkan ke dalam BZT. Keputusan menunjukkan bahawa permitiviti dan kehilangan dielektrik tidak banyak berubah bagi larutan pepejal yang didopkan dengan di- dan tetravalens dengan kepekatan dopan. Bagi larutan pepejal yang terhasil dengan dopan pentavalens, ε' dan tan δ meningkat dengan banyak atau

menurun dengan komposisi bahan yang didopkan. Kekonduksian bagi bahan yang didop adalah lebih tinggi dariapada $Bi_3Zn_2Ta_3O_{14}$ dengan E_a yang tinggi, 1.36 – 1.62 eV.

Analisis unsur menggunakan spektrometri pancaran optik plasma ganding-induktif (ICP-OES) mengesahkan komposisi stoikiometri bagi bahan fasa tunggal. Spektroskopi Fourier Inframerah (FTIR) digunakan untuk mengenalpasti kumpulan berfungsi bahan dan spektroskopi Raman digunakan sebagai tambahan kepada FTIR. Empat jalur penyerapan diperhatikan dalam spektrum FTIR dan Raman yang boleh dilabelkan sama ada mod ikatan regangan atau bengkokan. Terdapat korelasi di antara frekuensi jalur penyerapan dan kepekatan bagi bahan yang didopkan dengan dopan pentavalens. Analisis terma menunjukkan bahawa tiada peralihan fasa dan kehilangan berat dalam lingkungan suhu 35 hingga 1000^{o}C. Mikroskopi Pengimbasan Elektron telah dilakukan untuk mengkaji morfologi bahan. Semua bahan menunjukkan butir berbentuk polihedron yang tersusun secara rawak dengan liang terbuka pada bahan tersebut.

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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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KHAW CHWIN CHIEH

Date: 6 MAC 2007

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