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Subsolidus phase equilibria and electrical properties of pyrochlores in the Bi_2O_3–CuO–Ta_2O_5 ternary system

M.P. Chon [a], K.B. Tan [a, *], C.C. Khaw [b], Z. Zainal [a], Y.H. Taufiq-Yap [a], S.K. Chen [c], P.Y. Tan [a]

[a] Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
[b] Department of Mechanical and Materials Engineering, Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, 43000 Bandar Sungai Long, Kajang, Selangor, Malaysia
[c] Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

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ABSTRACT

Subsolidus phase relations had been determined for the Bi_2O_3–CuO–Ta_2O_5 (BCT) system over the temperature range 700–950 °C in air. Two structurally distinct ternary phases of different symmetries, a cubic pyrochlore and a monoclinic zirconolite were observed. Phase-pure pyrochlores existed in a unique boomerang-shaped area, which could be described using the general formula, $Bi_{2.48+y}Cu_{1.92-x}Ta_{3.6+x-y}O_{14.64+3x/2-y}$: $0.00(1) \leq x \leq 0.80(1)$ and $0.00\ (1) \leq y \leq 0.60(1)$, respectively. BCT subsolidus pyrochlores exhibited low electrical conductivities, 10^{-7}–10^{-6} S cm^{-1}, moderate dielectric constants, ε', ~60–80 and low dielectric losses, tan δ, ~0.01–0.20 at 1 MHz and ambient temperature, ~28 °C. The recorded low activation energies, 0.32–0.40 eV suggesting these electroceramics were of semiconductor-type at elevated temperatures.

1. Introduction

The pyrochlore structure is often represented by a general formula of $A_2B_2O_7$ or $A_2O'\cdot B_2O_6$. A broad range of chemical substitutions at the A, B and O crystallographic sites could produce hundreds of compositions with a specific set of desired properties for various electrical, magnetic and optical applications. The A element could be a rare earth cation with inert lone pair electrons and B element could be a transition metal with variable oxidation states and/or a post transition metal. The pyrochlore also shows great tolerance towards high vacancy concentration at the A and O′ sites that may facilitate the cationic migration throughout the lattice. To date, ternary systems in the complex family of bismuth-based pyrochlores, e.g. Bi_2O_3–ZnO–Nb_2O_5 (BZN) and Bi_2O_3–ZnO–Ta_2O_5 (BZT) have captured much attention due to their excellent composition-dependent dielectric properties. These pyrochlore analogues appeared to be the research subjects of several independent groups [1–6].

Early studies since 1970's have demonstrated that BZN pyrochlores could be a promising candidate for the multilayer ceramic capacitor (MLCC) application due to their firing temperature [7–9]. Two distinct phases were found in the BZN system: (i) a cubic phase (α-phase), $(Bi_{1.5}Zn)(ZnNb_{1.5})O_7$ with a high ε', ~150 and a negative temperature coefficient of capacitance (TCC), ~–400 ppm/°C and (ii) a monoclinic zirconolite phase (β-phase), $Bi_2Zn_{2/3}Nb_{4/3}O_7$ with a low ε', ~80 and a positive TCC (~200 ppm/°C). Through judicious control between these two phases, the resulted TCC could achieve a value close to zero that show a good thermal-independent electrical characteristic [10,11]. Similar characteristics were found in the BZT pyrochlores; however, the dielectric properties were less attractive due to their relatively lower ε', ~80 [9]. In this context, the phenomena responsible for the high ε' is worthwhile further investigation, especially it remains elusive and yet to be fully characterised at this stage. It has been proposed that inhomogeneity of cationic distribution at the A site could be the reason for high polarisation that leads on to high ε', specifically both Bi^{3+} and Zn^{2+} cations are having very different ionic radii and crystallo-chemical requirements. In addition, asymmetrically chemical bonds may have formed due to the presence of lone pair electrons from heavy p-block elements, e.g. Bi^{3+} with their oxidation states that are two less than the group valency [2,12,13]. In order to understand the low temperature electrical behaviour of these pyrochlores, equivalent electrical circuits fitting method had been used to model the data collected in the cryogenic condition, 10–320 K. The relaxor behaviour was somewhat related with the

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* Corresponding author.
E-mail address: tankarban@upm.edu.my (K.B. Tan).

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formation of nano polar domains [14].

A great deal of effort had been directed at the synthesis and characterisation of novel pyrochlore phases using a wide range of transition metals, e.g. Co, Ni, Fe, Mn and Mg. Careful control of composition variables, synthetic condition and selection of dopants are of crucial factors in order to optimise and yield new phases with interesting electrical properties. Hence, chemical doping was attempted to substitute Zn cation in the BZN/BZT pyrochlores through initial screening of phase formation and electrical properties [15–22]. Alternatively, high-temperature firing was applied to increase the subsolidus solution limit of samples if their weight losses could remain negligibly small. On the other hand, ball milling or sol–gel methods were preferred as they offered nano-powdered samples at relatively lower temperatures [21,22].

Detailed knowledge of the structure-property relations for the individual phases is limited, but is especially important if these pyrochlore phases have variable composition and is essential in order to control and optimise the properties. In this work, Cu-substituted pyrochlore system was comprehensively studied with main objectives: (i) To investigate the chemical reaction and formation pathway, (ii) To determine the optimum synthetic conditions for the BCT pyrochlores and related phases, (iii) To construct the ternary phase diagram for better understanding towards phase relations, mechanisms and compatibilities, and (iv) To summarise the correlation between composition, structure and electrical property in the BCT system.

2. Experimental procedures

Approximately 200 compositions were prepared through solid state reaction using reagent grade oxides: Bi_2O_3 (99.9%, Acros Organics), CuO (99.7%, Alfa Aesar) and Ta_2O_5 (99.85%, Alfa Aesar). Chemicals were dried for 2 h at 300 °C (Bi_2O_3) and 600 °C (CuO, Ta_2O_5), respectively. Stoichiometric quantities of oxides, ~3–4 g were homogenised in sufficient acetone using an agate mortar and pestle. Pyrochlores were heated in a step-wise cycle, with lower temperature stages of 300 °C and 600 °C for 3 h each, in order to allow initial chemical reaction and to minimise losses of Bi and Cu. Meanwhile, intermediate regrinding was performed throughout firing as to bring fresh surface for reaction. The synthesis temperature was varied over the temperature range 700°C–950 °C depending on the Bi and Cu content. In order to ensure thermal equilibrium of sample, procedure of repeatedly heating with 25 °C incremental rate and/or longer duration was used until no further detectable phase change. X-ray data were collected using a Shimadzu X-ray powder diffractometer (XRD-6000, CuKα radiation, $\lambda = 1.5418$ Å) in the 2θ range 10–70° at 2°/min. Monophasic pyrochlores were refined and indexed by the *Chekcell* software using slow scan XRD data collected at 0.1°/min. Selected samples were further analysed by a STOE STADI-P diffractometer (Darmstadt, Germany) with a linear position sensitive detector operating in transmission mode, with Ge monochromator, CuKα1 (1.5406 Å) radiation, step size 0.01° and 2θ range 10–70° which controlled by the WinXpow software.

The absorption bands of pyrochlore materials were determined by ATR (Attenuated Total Reflectance) method using Fourier transform infrared spectrometer, Perkin Elmer 100 series in the frequency range 1500–50 cm^{-1}. The chemical compositions were analysed using inductively coupled plasma-optical emission spectrometer, Perkin Elmer Optima 2000DV. ~0.1 g of sample was dissolved in a 250 ml mixture of concentrated hydrofluoric acid and 5% nitric acid. Sample triplicates were diluted by 5 times to 80 ppm and the concentrations were determined using standard calibration procedure. The BCT crystalline powders were cold pressed into pellets at the pressure ~4.0 tons and sintered at 950 °C. The geometry of the pellets was typically 7.50 (±0.20) mm in diameter and 1.80–2.50 mm in thickness. Pellets were coated with gold using Polaron E5100 series sputter coater before their morphologies were examined using scanning electron microscope, LEO 1455 VPSEM. The optimum working distance (WD) was fixed within 15 mm with operating voltage at 20 kV. Impedance measurements were performed using pellets with platinum electrodes. The data were collected by a Hewlett–Packard Impedance Analyser, HP 4192A (Tokyo, Japan) from room temperature to 600 °C in frequency range 5 Hz–13 MHz at an applied voltage 0.1 V. A thermal equilibrium time of 20 min was allowed for each measurement interval of 50 °C over a heat-cool cycle. Impedance data were normalised by the sample's geometrical factor and were corrected for the blank capacitance of the jig prior to data analysis using ZView™ software.

3. Results and discussion

3.1. Subsolidus pyrochlores in the Bi_2O_3–CuO–Ta_2O_5 (BCT) system

Pyrochlore phases with excellent electrical properties could be prepared by varying their chemical constituents, compositions and synthetic methods [4–6,11–13]. $Bi_{2.48+y}Cu_{1.92-x}Ta_{3.6+x-y}O_{14.64+3x/2-y}$ solid solutions are crystallised in a cubic structure and their XRD diffraction peaks are fully indexed based on space group $Fd3m$, No. 277, Fig. 1, which is similar to the α-BZT analogue [6]. The varying stoichiometry of BCT pyrochlores with different cationic amounts could be proposed with two subsolidus series; the compositional variable x represents the cationic substitution of Cu^{2+} by Ta^{5+} whereas the variable y symbolises the replacement of Ta^{5+} by Bi^{3+}. These mechanisms, of course, require additional changes to preserve charge balance and it is presumed that the oxygen content adjusts so as to maintain electroneutrality. On the other hand, the presence of 442 forbidden diffraction plane, Fig. 1a and b, indicates that a possible cationic displacement off the ideal crystallographic sites. Such predilection is believed to achieve a reduced coordination number and/or a shorter chemical bond due to the incompatible Cu^{2+} at the large eight-coordinated A site. Similar observation were reported previously in the Bi_2O_3–MO–Nb_2O_5 (M = Zn, Ni, Co) systems [3,17,18].

The refined lattice parameters are plotted against x and y variables; these values are in the range 10.4838 (8)–10.5193 (8) Å, Fig. 2. Both series expand slightly in their lattices when the amount of relatively larger cation increases [23]. The effect of large Bi^{3+} is evidently clear, albeit a small deviation in cell expansion occurs. Such anomalies suggest that the structural parameters are also influenced by other factors, e.g. defect, internal strain and structural disorder. For a quantitative comparison, crystallite size and internal strain for the two series, Fig. 3, are calculated using the Williamson-Hall method:

$$\beta\cos\theta = k\lambda/D + 4\varepsilon\sin\theta \tag{3.1}$$

where β is the full width at half maximum (FWHM, in rad); θ is the scattering angle; $\lambda = 1.5418$ Å; k is the shape factor, 0.9; D is the coherent scattering length (crystallite size) and ε is the internal strain. The end-member of the two series, composition 155, $Bi_{2.48}Cu_{1.92}Ta_{3.6}O_{14.64}$ ($x = 0$, $y = 0$) exhibits the highest internal strain, ε, 0.058%. This indicates a high possibility of structural disorder has been developed within the pyrochlore structure. On the other hand, the strain and crystallite size could affect the XRD peak profile in several ways; these factors are highly correlated to the peak width, peak intensity and shift of 2θ position [24–26]. As a result, a broadened diffraction (222) plane is discernible in which a constant 2θ shifts towards lower angle occurs in the compositions