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Structural and electrical properties of bismuth magnesium tantalate pyrochlores

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Abstract

The subsolidus cubic pyrochlore phases in the Bi_2O_3–MgO–Ta_2O_5 (BMT) system were prepared with the proposed formula, $Bi_{3+(5/2)x}Mg_{2-x}Ta_{3-(3/2)x}O_{14-x}$ ($0.12 \leq x \leq 0.22$). Replacement of smaller cations, Mg^{2+} and Ta^{5+} by larger Bi^{3+} cations with considerable oxygen non-stoichiometry within structure was proposed. The synthesised samples were confirmed phase pure by X-ray powder diffraction and their refined lattice parameters were in the range of 10.5532(4)–10.5672(9) Å. The grain sizes of the samples determined by SEM analysis were in the range of 0.6–10.60 μm and their average relative densities were more than 80%. Five infrared-active modes were also observed in their FTIR spectra due to their metal–oxygen bonds. The BMT pyrochlores were highly electrical resistive with high dielectric constants, ε' in the range of ~70–85; dielectric losses, tan δ in the order of 10^{-3} at frequency 1 MHz and a negative temperature coefficient of permittivities, TCε' of ~−158 to −328 ppm/°C.

Keywords: C. Dielectric properties; D. Tantalates; Pyrochlores; Ceramics

1. Introduction

Oxide pyrochlores with a general formula of $A_2B_2O_7$ have been studied carefully due to their interesting properties. In general, A and B represent cations at different crystallographic sites as A site is eight-coordinated and B site is six-coordinated with different anions. Due to the compositional variables and structural complexity of pyrochlore phases, two different types of pyrochlore, e.g. $A_2{}^{2+}B_2{}^{5+}O_7$ and $A_2{}^{3+}B_2{}^{4+}O_7$ or required average mixed valence type are reported. This includes a wide variety of pyrochlores, $Cd_2Nb_2O_7$, $Hg_2V_2O_7$ and $Pb_2Ta_2O_7$ in $A_2{}^{2+}B_2{}^{5+}O_7$ system and lanthanide based pyrochlores, $Ln_2Sn_2O_7$ and $Ln_2Pb_2O_7$ in $A_2{}^{3+}B_2{}^{4+}O_7$ system. Pyrochlore materials demonstrate a wide spectrum of electrical properties ranging from insulating to metallic of which few compounds exhibiting semiconductor-to-metal transition. The applications of these materials are found in capacitors, thermistors, resistors, switching elements and microwave communication [1].

Recently, Bi-based pyrochlores in the Bi_2O_3–ZnO–X_2O_5 (X = Sb, Ta and Nb) ternary systems have triggered great research interests owing to their relatively low sintering temperatures and excellent dielectric properties [2–4]. Two structurally related compositions, $Bi_3Zn_2Nb_3O_{14}$ (P-phase) and $Bi_4Zn_{4/3}Nb_{8/3}O_{14}$ (β-phase) have been reported in the Bi_2O_3–ZnO–Nb_2O_5 ternary system. The P-phase existed as cubic pyrochlore whereas the β-phase was found as monoclinic zirconolite-phase. $Bi_3Zn_2Nb_3O_{14}$ exhibited a high dielectric constant, $\varepsilon' = \sim 150$ and low dielectric loss, tan $\delta \approx 0.0005$ at 1 MHz, together with a negative temperature coefficient of capacitance, TCC ~−500 ppm/°C. On the other hand, $Bi_4Zn_{4/3}Nb_{8/3}O_{14}$ had slightly lower $\varepsilon' = 80$, tan $\delta = \sim 0.001$, and a positive TCC of +200 ppm/°C at 1 MHz [4–7]. Given the opposite signs of temperature coefficient of capacitance, this gave a strong indication to achieve dielectrics with NPO (negative positive zero) characteristic of 0 ppm/°C if careful composition and processing control were applied [7].

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In the case of Ta analogue, ideal nominal composition, $Bi_3Zn_2Ta_3O_{14}$ was reported in the Bi_2O_3–ZnO–Ta_2O_5 system as confirmed by detailed phase diagram study [7]. It existed as cubic pyrochlore with ε' of 58, tan δ of 0.0023 at 30 °C and 1 MHz; TCC of −156 ppm/°C in the range of 30–300 °C at 1 MHz [4]. On the other hand, Sb analogue showed extremely low electrical conductivity, $1.00 \times 10^{-20}\ \Omega^{-1}\ cm^{-1}$ at room temperature as determined using extrapolation method [8]. $Bi_3Zn_2Sb_3O_{14}$ showed lower ε' of ~32 with a tan δ of ~0.0001 at room temperature, 1 MHz [9]. Among pyrochlores in the Bi_2O_3–ZnO–M_2O_5 (M = Sb, Nb and Ta) ternary systems, lowest ε' in the Sb analogue was postulated to be resulted from the relatively lower polarisability of SbO_6 octahedra within the structure [9,10].

Enormous attempts are made to reduce the dielectric loss and to fine-tune the dielectric constant of dielectric materials, making them suitable candidates for various electrical applications. The low dielectric loss of MgO and comparable ionic radii between Mg^{2+}, 0.72 Å and Zn^{2+}, 0.74 Å have shed new idea to study the Mg-substituted pyrochlore phases [11,12]. There appears limited literature available on pyrochlores in the Bi_2O_3–MgO–Ta_2O_5 (BMT) ternary system and the actual stoichiometry of different phases is still remained unclear. Inconsistencies and controversial descriptions on the pyrochlore phases are found in the two reported different compositions, $Bi_3Mg_2Ta_3O_{14}$ and a bismuth-rich, $Bi_4Mg_{4/3}Ta_{8/3}O_{14}$. Cann et al. [13] reported $Bi_4Mg_{4/3}X_{8/3}O_7$ (X = Ta and Nb) as cubic pyrochlores whereas Sirotinkin and Bush [14] reported Nb analogue, $Bi_3Mg_2Nb_3O_{14}$ existed as single cubic pyrochlore phase. On the other hand, $Bi_3Mg_2Nb_3O_{14}$ was also claimed by Nguyen et al. [15] to contain a trace amount of secondary phase. In this paper, we confirm that none of these compositions exist as phase pure but rather a Bi-rich pyrochlores, $Bi_{3+(5/2)x}Mg_{2-x}Ta_{3-(3/2)x}O_{14-x}$ $(0.12 \le x \le 0.22)$ are successfully prepared after firing at the temperature 1025 °C over a duration of 48 h. We also discuss on the structural and electrical properties of BMT pyrochlores using various spectroscopy techniques.

2. Experimental

Samples of nominal compositions, $Bi_3Mg_2Ta_3O_{14}$, $Bi_4Mg_{4/3}Ta_{8/3}O_{14}$ and $Bi_{3+(5/2)x}Mg_{2-x}Ta_{3-(3/2)x}O_{14-x}$ (x = 0.12, 0.14, 0.16, 0.18, 0.20, 0.22) were prepared by conventional solid state method. The starting materials were reagent grade oxide powders, Bi_2O_3 (Alfa Aesar, 99.99%), MgO (Aldrich, 99%) and Ta_2O_5 (Alfa Aesar, 99.9%). Stoichiometric amount of oxides were weighed and mixed homogeneously with acetone in an agate mortar. The mixed powders were then transferred into the platinum boat for calcinations. The samples were pre-treated at 300 °C for 1 h and further heated at 600 °C for 1 h to ensure the Bi_2O_3 reacted to form less-volatile compounds; this allowed firing at higher temperatures without significant losses of bismuth. The pre-treated powders were heated at 800 °C overnight and further synthesised at 1025 °C for 48 h with intermediate regrinding to reach equilibrium. The powders were pressed into pellets of 8 mm in diameter and ~1.5 mm in thickness prior to sintering at 1075 °C for 24 h.

The phase purity of the samples were characterised by X-ray powder diffraction using an automated Shimadzu diffractometer XRD 6000, Cu Kα radiation in 2θ range of 10–70° at the scan speed of 2°/min. Data for lattice parameter determination were collected at a scan rate of 0.1°/min and the refinement was performed by *Chekcell* software. The relative densities were also calculated from comparisons of densities which determined by both geometrically and theoretically. The surface morphologies of the samples were examined by scanning electron microscopy (SEM, JOEL JSM-6400). The elemental analysis was conducted by ICP-OES, Perkin Elmer Optima 2000DV using triplicate samples.

The electrical behaviours of the samples were measured using HP4192A ac impedance analyser in the frequency range of 5 Hz–13 MHz. Gold coated pellet was attached to conductivity jig prior to electrical measurement in temperature controlled horizontal tube furnace. The electrical data were collected in heat–cool cycle in the temperature range of 30–850 °C after 25 min equilibration time.

3. Results and discussion

3.1. XRD and elemental analysis

Fig. 1a and b shows the XRD patterns for the nominal compositions $Bi_3Mg_2Ta_3O_{14}$, P (x = 0) and $Bi_4Mg_{4/3}Ta_{8/3}O_{14}$ which synthesised at 1025 °C. In Fig. 1a, additional diffraction planes observed at 2θ, 19.8800° and 32.4059° are attributed to $Mg_4Ta_2O_9$ (ICDD 38-1458). Meanwhile, the reported $Bi_4Mg_{4/3}Ta_{8/3}O_{14}$ is found to be mixed phases of monoclinic and cubic phases. Our observation disagrees to those results in literature [13–15]. The phase pure cubic pyrochlore phases in Bi_2O_3–MgO–Ta_2O_5 system are formed with the proposed formula, $Bi_{3+(5/2)x}Mg_{2-x}Ta_{3-(3/2)x}O_{14-x}$ $(0.12 \le x \le 0.22)$ as evidently shown in Fig. 1c. All characteristic peaks belonging to cubic pyrochlore are fully indexed based on space group, *Fd*3*m*. On the other hand, Fig. 2 shows the partial subsolidus phase diagram of Bi_2O_3–MgO–Ta_2O_5 system, which includes the ideal P and solid solution series. The phase pure samples are deviated away from ideal P, composition, having richer bismuth in content, e.g. 41 mol% above. The three different types of metal ions in the samples vary with x for which increase of Bi is compensated by a decrease of Mg and Ta cations together with a variation of oxygen within the structure. The locus of the solid solution behaves towards direction of Bi_2O_3 as denoted in the cations ratio, Bi: Mg: Ta is 5/2: 1: 3/2.

Fig. 3 shows the variation of lattice parameters as a function of composition. The lattice parameters for the samples are in the range of 10.5532 (4)–10.5672 (9) Å. A linear graph with positive gradient is obtained for which the Vegard's law is obeyed. The lattice parameters of a continuous substitutional solid solution should vary linearly with concentration at constant temperature if the chemical bondings of constituent