Materials Chemistry and Physics 214 (2018) 464–471

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Influence of Nb_2O_5 substitution on the structural and electrical properties of Bi_3TaO_7 ceramics

K. Firman [a], K.B. Tan [a, *], C.C. Khaw [b], Z. Zainal [a], Y.P. Tan [a], S.K. Chen [c]

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

HIGHLIGHTS

- Novel Nb-substituted bismuth tantalates were synthesised.
- Influence of Nb_2O_5 substitution on the doping mechanisms was investigated.
- Qualitative structural and surface morphology studies were performed.
- AC impedance analyses of $Bi_3Ta_{1-x}Nb_xO_7$ subsolidus solution were conducted.

ARTICLE INFO

Article history:
Received 26 September 2017
Received in revised form
2 March 2018
Accepted 25 April 2018
Available online 27 April 2018

Keywords:
Solid-state method
Niobium-substituted bismuth tantalate
Solid solution
Conductivity

ABSTRACT

Herein we report the doping mechanism and impedance study of the Nb-substituted $Bi_3Ta_{1-x}Nb_xO_7$ ($0 \leq x \leq 0.5$) prepared via conventional solid-state method at 900 °C over 24 h. The substitutional solid solution crystallised in a cubic fluorite structure, space group Fm-3m and with lattice parameter, $a = b = c$, in the range 5.4477 (±0.0037)–5.4654 (±0.0011) Å. An insignificant unit cell expansion was observed with increasing Nb_2O_5 content and the linear correlation between lattice parameter and composition variable showed that the Vegard's Law was obeyed. Both TGA and DTA analyses confirmed that the $Bi_3Ta_{1-x}Nb_xO_7$ solid solution was thermally stable as neither phase transition nor weight loss was observed within the studied temperature range, ~28 °C–1000 °C. The electrical conductivities of these samples were found to increase with increasing Nb concentration; the $Bi_3Ta_{0.5}Nb_{0.5}O_7$ exhibited the highest conductivity, ~1.2×10^{-2} S cm^{-1} at 700 °C with a low activation energy of 1.03 eV.

1. Introduction

The application of δ-Bi_2O_3 in solid electrolyte has captured great attention owing to its high oxide ion conductivity, 1 Ω^{-1} cm^{-1} at 750 °C [1–5]. However, the δ-Bi_2O_3 is only stable in a limited temperature range, 725 °C–825 °C and such phase needs to be preserved to room temperature by appropriate methods or chemical dopings [3,5–8]. The structural instability of δ-Bi_2O_3 could be due to the high concentration of intrinsic oxygen vacancies, i.e. 25% of the anionic sites are vacant in this defective fluorite-type structure [4]. Previous studies showed that the δ-Bi_2O_3 can be quenched to room temperature by introducing a wide variety of pentavalent cations, such as V, Nb, and Ta, thus yielding many new phases that may able to retain comparable high oxide ionic conductivity [9]. Therefore, the replacement of Bi^{3+} cation by Nb^{5+} or Ta^{5+} cation has helped to replicate several structurally related binary phases [10].

The Bi_2O_3–M_2O_5 (M = Nb or Ta) binary systems have been of research subjects to many independent research groups [2–5,11–13]. Four distinct phases were reported in the Bi_2O_3–Nb_2O_5 phase diagram, which were recognised as type I, II, III, and IV, respectively [4,7]. The Bi_3NbO_7 exhibited a unique type-II and III phases; the type-II phase had a three-dimensional incommensurate modulated cubic fluorite superstructure that may form with Nb_2O_5 concentration ranging from 6.25% to 25% [13]. Such phase had an $8 \times 8 \times 8$ super unit cell based on the δ-Bi_2O_3 with a space group of either Fd3m or Fm3m [4,13]. Meanwhile, the model of type-II phase was proposed to have tetrahedral clusters of NbO_6

---

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

https://doi.org/10.1016/j.matchemphys.2018.04.095
0254-0584/

octahedra into the δ-Bi_2O_3-related matrix in order to create a fluorite-type superstructure [13]. In other words, it could be interpreted as strings of Nb atoms within a fluorite-type metal atom array that arranged along three of the six possible directions. The incommensurate variability in both the spacing and the continuity of these strings would allow a great flexibility of compositional variables [13]. Nevertheless, the type-II phase was only stable at temperatures below 800 °C and above 900 °C, but excluding the intermediate range. Between temperatures 800–900 °C, the type-II phase would undergo a polymorphic transition to the type-III tetragonal phase [14].

On the contrary, the type-III phase had a commensurate ordering relative to a tetragonal subcell, which was modelled as a tetragonal deficient fluorite-type structure with an *I*-centered $3 \times 3 \times 7$ supercell [10,13]. This superstructure consisted of independent rows and isolated tetrahedral units of corner-sharing NbO_6 octahedra imbedded in a Bi–O matrix [7,10]. The type-III phase could be treated as a derivative of the pyrochlore-type cluster motif, wherein the interaction of these clusters may create some perovskite-type regions [10,13,15]. A related study [7] claimed that the phase transition of Bi_3NbO_7 would occur at temperatures between 760 °C and 870 °C; the type-II cubic phase transformed to the type-III tetragonal phase as the type-III phase was only stable below 900 °C [7]. Such phenomenon was evidently shown by the presence of splitting diffraction plane, which was due to the formation of type-III superstructure. At 950 °C, the type-III phase would reversibly transform back to the type-II phase [7].

Both tantalum and niobium-containing compounds are usually isomorphous; their structures are expected to have same crystal symmetry and similar unit cell dimension [4]. Despite the facts of Nb and Ta having similar crystallochemical characteristics, such as same charge and identical ionic radii, only the Bi_3NbO_7 is known to have an unusual commensurate type-III polymorphism. The Bi_3NbO_7 tetragonal phase was reported to have a relatively higher electrical conductivity than that of its cubic phase. These phases had ionic conductivities of 12.2×10^{-5} S cm^{-1} and 7.2×10^{-5} S cm^{-1}; low activation energies of 0.8 eV and 1.06 eV at temperature 500 °C, respectively [7]. On the contrary, the Bi_3TaO_7analogue is less understood and has only limited information about its crystal structure and electrical properties. Our earlier impedance study indicated that the $Bi_{3+x}Ta_{1-x}O_{7-x}$ ($0 \leq x \leq 0.184$) solid solution had modest oxide ion conductivities, ~10^{-6}–10^{-3} S cm^{-1} with its activation energies in the range 0.98–1.08 eV [16]. Hence, the present work is undertaken to synthesise and characterise the Nb-substituted Bi_3TaO_7 fluorites, specifically to investigate the effect of Nb dopant in terms of the subsolidus formation and electrical properties.

2. Experimental

The Nb-substituted Bi_3TaO_7 solid solution was prepared by conventional solid-state reaction using high purity reactants, Bi_2O_3 (99.9%, Aldrich), Ta_2O_5 (99.9%, Aldrich) and Nb_2O_5 (99.9%, Aldrich). Bi_2O_3 was preheated at 300 °C and both Ta_2O_5 and Nb_2O_5 were preheated at 600 °C for 2 h, respectively. All the oxides were weighed, mixed and ground homogeneously in a stoichiometric amount with sufficient acetone using an agate mortar and pestle. The oxides mixture was transferred into an alumina boat and fired at 600 °C for 2 h, followed by sintering at 900 °C for 24–48 h in a furnace with intermediate regrinding. The weight loss checking was performed and the prepared powder was kept for further characterisation.

The phase purity of the prepare samples were examined by an automated Shimadzu X-ray Powder Diffractometer (XRD) 6000, which was equipped with a diffracted beam graphite monochromator, CuKα radiation, 1.5406 Å at scan rate 0.2°/min over 2θ range 10–70°. The data collected at slow scan rate 0.1°/min was used for the lattice refinement by *Chekcell* software. The pellets of the phase-pure samples were prepared in ~8 mm diameter and ~2 mm thick by a uniaxial hydraulic press before sintering at 900 °C to improve their mechanical strength and density. The pellets with density ≥85% were coated with gold electrodes and characterised by a Solartron impedance analyser over the frequency range 0.1 Hz–1 MHz. The measurements were conducted in the temperature range 25–850 °C by incremental steps of 50 °C in a heat–cool cycle. The electrical data were normalised by the geometric factor and corrected for the stray capacitance of the open jig. Further impedance analysis was performed by *Zview* software. The gold sputtered pellets were used for the surface morphology study by variable pressure scanning electron microscopy (VPSEM). The VPSEM images were further analysed by *ImageJ* software for the calculation of average particle sizes of the samples. The thermal stability of the phase pure samples was studied by a thermogravimetric analyser and differential thermal analyser (Perkin Elmer, STA 6000). The elemental analyses were performed in sample triplicates by inductively coupled plasma–optical emission spectroscopy (Perkin Elmer, Optima 2000DV).

3. Results and discussions

3.1. Phase formation of niobium-substituted Bi_3TaO_7 solid solution

The Nb-substituted $Bi_3Ta_{1-x}Nb_xO_7$ ($0 \leq x \leq 0.5$) solid solution is phase-pure by XRD after firing at 900 °C over a duration of 24–48 h. The XRD diffraction planes are fully indexed (Fig. 1) in accordance with the International Crystal Diffraction Data (ICDD), 44-0202. These materials are isostructural to the fluorite-type Bi_3TaO_7, which crystallised in a face-centered cubic structure with a space group of Fm-3m, Z = 1. The subsolidus solution mechanism is proposed to be a one-to-one replacement of Ta by Nb, wherein a proportion amount of Ta^{5+} is substituted by Nb^{5+}. In order to form an extensive substitutional solid solution range, two important requirements should be met: (i) the replacing ion

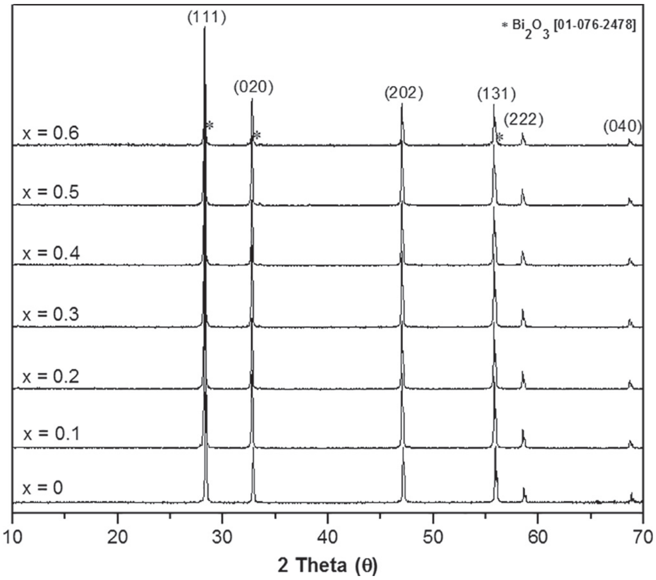

Fig. 1. XRD patterns of the phases in the $Bi_3Ta_{1-x}Nb_xO_7$ system.