

Characterization of lead-free bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) synthesized by a modified oxalate co-precipitation method

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Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) powders and ceramics were synthesized by a modified oxalate co-precipitation method, from the starting precursors of bismuth nitrate pentahydrate and titanium (IV) isopropoxide in the mole ratio of Bi : Ti of 4 : 3. The mill-precipitated powder was calcined at 500–800 °C for 2 h. The phase transition was studied by an X-ray diffractometer. An orthorhombic structure was obtained after calcination at 700 °C for 2 h. The morphology was characterized by a scanning electron microscope. The average particle size increased as the calcination temperature increased. Powder calcined at 700 °C for 2 h was pressed into pellets. The pellets were sintered at 900 and 1000 °C for 2 h. The phase and microstructure of the ceramic in the pellets were investigated by an X-ray diffractometer and a scanning electron microscope. A single phase orthorhombic structure of bismuth titanate was obtained. The average particle size increased as the sintering temperature increased. The chemical composition of the ceramics was analyzed by an energy dispersive X-ray spectrometer (EDXS). The elemental composition of bismuth, titanium and oxygen showed the characteristic X-ray energy values.

Key words: Bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, Modified oxalate co-precipitation method.

Introduction

Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) is a ferroelectric with wide applications in the electronic industry, as capacitors, sensors and memory devices [1]. It has a ferroelectric -to-paraelectric phase transition temperature of 675 °C, which gives it a potential applicability as a suitable candidate for a high temperature piezoelectric device. In addition, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is an interesting material that is lead-free and environmentally friendly [2]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is the simplest compound in the Aurivillius family of compounds that can be represented by the general formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ in which A can be a monovalent, divalent or trivalent cation or a combination of three in suitable proportions, B can be a tetravalent or pentavalent cation with m having values of 2, 3, 4, ...etc. Their structures comprise a stacking of n perovskite units of nominal composition $\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}$ interleaved with Bi_2O_3 layers along the pseudotetragonal c-axis. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is formed when A = Bi, B = Ti and m = 3 in the general formula [3]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics are normally synthesized by a conventional solid-state method from Bi_2O_3 and TiO_2 , with calcination at an intermediate temperature and finally sintering at a high temperature. This method requires a high calcination temperature and usually leads to an inevitable particle coarsening and aggregation of the

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders [4, 5]. The presence of hard particle agglomerates and compositional inhomogeneity will also result in a poor microstructure and properties of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics [6]. Basically, chemical synthesis methods have been used to avoid these problems by lowering the calcination temperature. The chemical syntheses used for the preparation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ include the urea method [7], the citrate method [8], the metalorganic decomposition method [9], the microemulsion method [10], a sol-gel method [11–13], a hydrothermal method [14, 15] and a co-precipitation method [16–18]. The advantages of chemical methods over other techniques are the controlled morphology, narrow particle size distribution, high purity, high degree of crystallinity and a possible reduction in sintering temperature. An oxalate co-precipitation method has been considered to be a promising way to synthesize powders for piezoelectric materials. In this research, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders were synthesized by a modified oxalate co-precipitation method. The phase formation was studied by an X-ray diffractometer (XRD). The morphology was characterized by a scanning electron microscope (SEM). The phase and microstructure of the ceramics were also investigated by XRD and SEM. The chemical composition of ceramics was analyzed by an energy dispersive X-ray spectrometer (EDXS).

Experimental Procedure

A modified oxalate co-precipitation method to synthesize $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders [17] and ceramics is shown in Fig. 1. The starting precursors used in this research included

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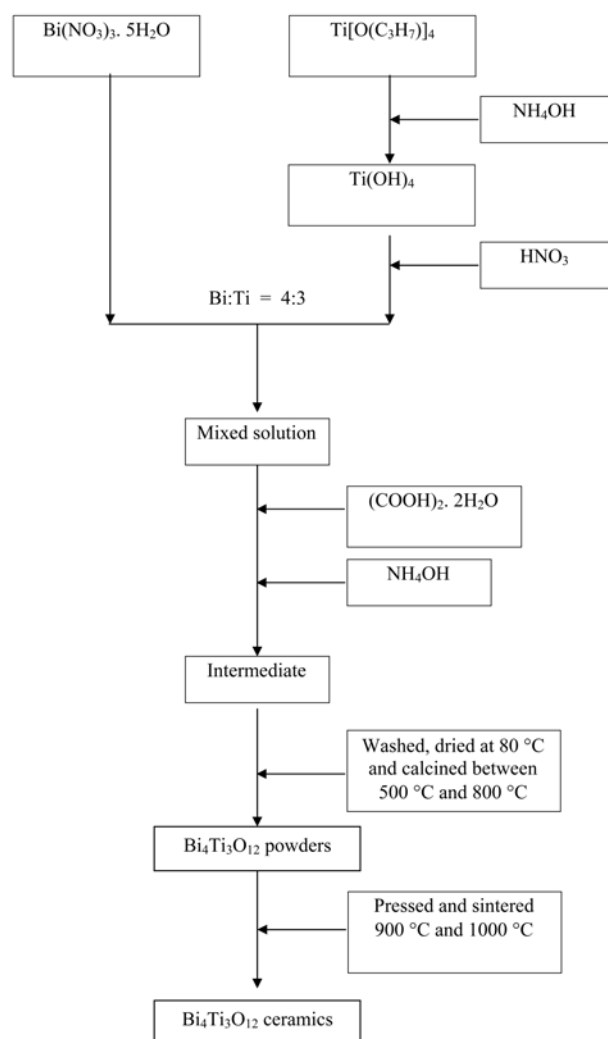


Fig. 1. Schematic diagram for the synthesis of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders and ceramics by a modified oxalate co-precipitation method.

bismuth nitrate pentahydrate [$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$] (99.0%, Fluka, Switzerland), titanium (IV) isopropoxide [$\text{Ti}(\text{OC}_3\text{H}_7)_4$] (97%, Fluka, Switzerland), nitric acid [HNO_3] (65%, Merck, Germany), ammonium hydroxide [NH_4OH] (30%, BDH, England) and oxalic acid dihydrate [$(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$] (99.5%, Fluka, Switzerland). Solution I: an aqueous solution of 0.048 M $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was prepared using 6 M HNO_3 as solvent. Solution II: an aqueous solution of 6 M NH_4OH was added to 0.036 M $\text{Ti}(\text{OC}_3\text{H}_7)_4$ in an ice bath at 10°C to form titanic acid [$\text{Ti}(\text{OH})_4$] and then dissolved with 6 M HNO_3 . The precursors with a mole ratio of $\text{Bi}:\text{Ti} = 4:3$ in 0.30 M $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ were mixed and the pH of the resultant mixture was adjusted to 9.0 by adding 6 M NH_4OH at room temperature. The precipitate was then filtered, washed and dried in an oven (Gallenkamp, England) at 80°C for 24 h. The powders were milled and sieved with a laboratory test sieve of 200 mesh (Endecotts, England). The fine powders were calcined in a muffle furnace (EFT2, Interkilns, Germany) in air at various temperatures from 500°C to 800°C for 2 h with a heating rate of $2\text{ K}\cdot\text{minute}^{-1}$.

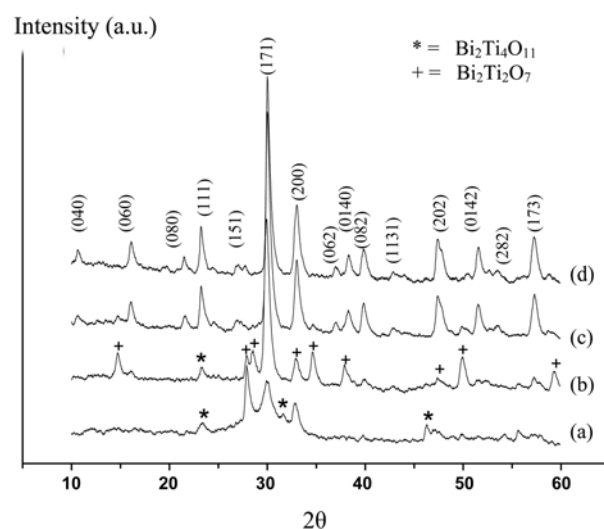


Fig. 2. X-ray diffraction patterns of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders calcined for 2 h at (a) 500°C , (b) 600°C , (c) 700°C and (d) 800°C .

Powder calcined at 700°C for 2 h was pressed into pellets. The pellets were sintered at 900°C and 1000°C for 2 h with a heating rate of $2\text{ K}\cdot\text{minute}^{-1}$. The density of all sintered $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics was measured and then compared with their theoretical density. The phase identification was performed at room temperature using a Ni-filtered monochromatic CuK_α radiation X-ray diffractometer (D500, SIEMENS, Germany). The detection range was $10\text{--}60^\circ$ with a step size of 0.10° ($2\theta/\text{s}$). The phase of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders and ceramics was confirmed using the Joint Committee on Powder Diffraction Standards (JCPDS) File Card No. 35-0795 [19]. The fine powders were dispersed with an ethanol [$\text{C}_2\text{H}_5\text{OH}$] (99.5%, Merck, Germany) medium in an ultrasonic bath (Model 5880, Cole-Parmer, USA) for 10 minutes. The dispersed fine powders and ceramics were coated with gold [Au] by a sputter coater (JSC-1200, JEOL, Japan) for 1 minute. The morphology and microstructure of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders and ceramics were characterized by a scanning electron microscope (JSM5410-LV, JEOL, Japan) with a tungsten (W) filament K type, an accelerating voltage of 20–25 kV, and a working distance of 18 mm. The chemical composition was analyzed by an energy dispersive X-ray spectrometer (ISIS300, Oxford, UK).

Results and Discussion

Part I: Powders

Figs. 2(a–d) show X-ray diffraction patterns of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders calcined at $500\text{--}800^\circ\text{C}$ for 2 h with a heating rate of $2\text{ K}\cdot\text{minute}^{-1}$. The powder calcined at a lower temperature was yellow in colour, which subsequently transformed to a white powder at a higher calcining temperature. The powders calcined at 500°C , Fig. 2 (a), show a mixture of multiphases of the impurity phases $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ and $\text{Bi}_2\text{Ti}_2\text{O}_7$, corresponding with Joint Committee on Powder Diffraction Standards (JCPDS) File Card No. and 15-0325 [20] and

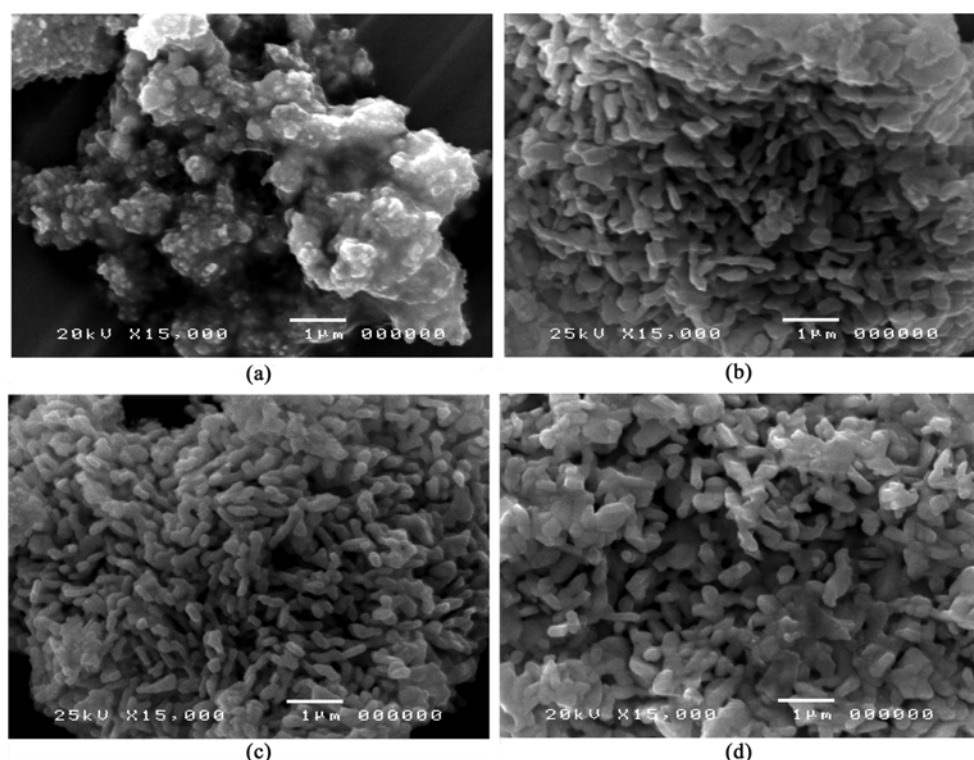


Fig. 3. SEM micrographs of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders calcined for 2h at (a) 500 °C, (b) 600 °C, (c) 700 °C and (d) 800 °C.

32-0118 [21]. With an increase in the calcination temperature, the impurities in the powders decrease. At 600 °C, Fig. 2(b), shows a dominant impurity phase with the $\text{Bi}_2\text{Ti}_2\text{O}_7$ structure by comparison with Joint Committee on Powder Diffraction Standards (JCPDS) File Card No. 32-0118 [21]. A single phase of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ started to form at a calcination temperature of 700 °C, Fig. 2(c). A single phase of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with an orthorhombic structure was obtained after calcination at 700 °C, Fig. 2(c), corresponding to the Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 35-0795 [19]. With an increase in the calcination temperature, the line width and intensity of diffraction line decreased and increased, respectively [22]. This is in good agreement with a previous report [17, 23].

Figs. 3(a-d) show SEM micrographs of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders calcined at 500–800 °C for 2 h with a heating rate of $2 \text{ K} \cdot \text{minute}^{-1}$. The particle size increased as the calcination temperature increased. The powders consisted of small soft agglomerates. The SEM micrograph of powders calcined at 500 °C, Fig. 3(a), showed an agglomeration and irregular particles 0.1 μm in diameter. At 600 °C, Fig. 3(b), the particles were agglomerated and had become slightly larger in average size to 0.3 μm . At 700 °C, Fig. 3(c), the particles were agglomerated, fused together and some particle growth occurred with an average size of 0.5 μm . At 800 °C, Fig. 3(d), the particles were agglomerated, fused together and some particle growth occurred with an average size of 0.7 μm . The particle sizes were smaller than previously reported from an oxalate co-precipitation method [22, 23].

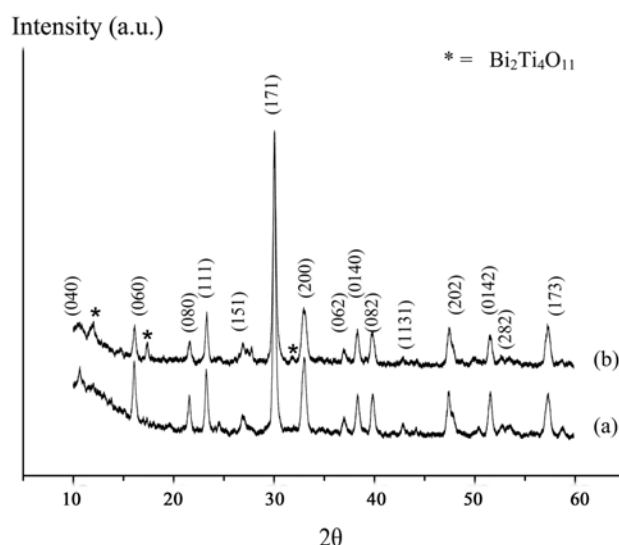
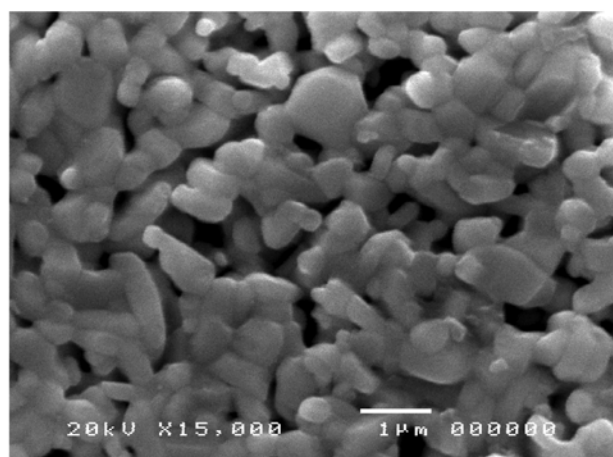


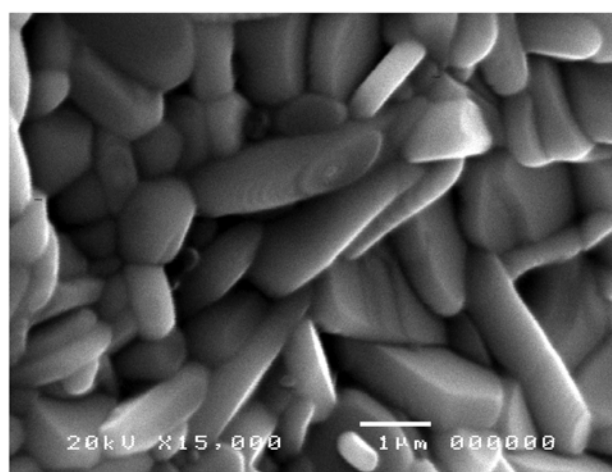
Fig. 4. X-ray diffraction patterns of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics sintered for 2 h at (a) 900 °C and (b) 1000 °C.

Part II: Ceramics

Figs. 4(a-b) show X-ray diffraction patterns of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics sintered at 900–1000 °C for 2 h with a heating rate of $2 \text{ K} \cdot \text{minute}^{-1}$. At a calcination temperature of 900 °C, a single phase of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was obtained with an orthorhombic structure as shown in Fig. 4(a), corresponding to the Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 35-0795 [19]. At a higher temperature, 1000 °C, the phase of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with an orthorhombic



(a)



(b)

Fig. 5. SEM micrographs of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics sintered for 2 h at (a) 900 °C and (b) 1000 °C.

structure and an impurity of the $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ structure are shown in Fig. 4(b), corresponding to the Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 35-0795 [19] and 15-0325 [20], respectively.

The measured densities of sintered $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics were found to be approximately 90.4–95.2% of the theoretical density when sintered at 800–1000 °C for 2 h [14]. In this research, the densities of sintered $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics at 900 and 1000 °C for 2 h, were found to be 83.7 and 96.5% of their theoretical density, respectively. This indicates that a sintering temperature of 1000 °C for 2 h yielded the highest density of the sintered ceramics. However, the sintering temperature has an influence on the morphology and microstructure of sintered $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics. The average grain size of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics obtained with different sintering condition have been report earlier [24]. It was found that the average grain size of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics sintered at 850 °C for 1 h were approximately 2.0 µm in width and 10 µm in length, respectively.

Figs. 5(a-b) show SEM micrographs of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics

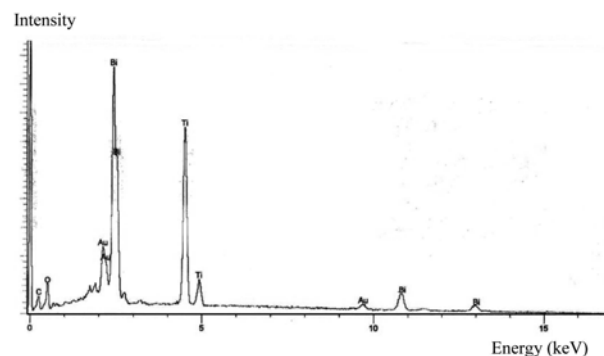


Fig. 6. EDXS spectra of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics sintered at 1000 °C for 2 h.

sintered at 900–1000 °C for 2 h with a heating rate of 2 K·minute⁻¹. At 900 °C, Fig. 5(a), the particles were agglomerated with an irregular shape and an average particle size of 0.6 µm in width and 1.5 µm in length. At 1000 °C, Fig. 5(b), the morphology was plate-like in shape [24] and the average grain size was 1.0 µm in width and 2.5 µm in length. The microstructure of sintered $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics was varied by altering the sintering temperature. As the sintering temperature was increased, the grain size also increased. The average grain sizes were smaller than previously reported from an oxalate co-precipitation method [22, 24].

Fig. 6 shows EDXS spectra of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics sintered at 1000 °C for 2 h with a heating rate of 2 K·minute⁻¹. Energy dispersive spectrometry was employed to investigate and indicate the composition of the sintered ceramics. The characteristic X-ray radiation of each element has different energy values; bismuth $M_a = 2.42$ keV, $L_a = 10.84$ keV and $L_b = 13.02$ keV, titanium $K_a = 4.51$ keV and $K_b = 4.93$ keV and oxygen $K_a = 0.52$ keV, respectively.

Conclusions

Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) powders and ceramics were successfully synthesized by a modified oxalate co-precipitation method with bismuth nitrate pentahydrate and titanium (IV) isopropoxide as precursors in an oxalic acid medium. A single phase orthorhombic structure of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders was obtained after calcination at 700 °C for 2 h with a heating rate of 2 K·minute⁻¹. The average particle size at a higher temperature was greater than at lower temperature. The powders were highly agglomerated, irregular in shape with an average particle size in the range of 0.1–0.7 µm which increased with an increase in the calcination temperature. An orthorhombic structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with an impurity of $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ was obtained after calcination at 1000 °C for 2 h with a heating rate of 2 K·minute⁻¹. The morphology was plate-like in shape with an average grain size of 1.0 µm in width and 2.5 µm in length. The elemental constituents of ceramics were identified by their energy dispersive values.

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