

Chemical synthesis and characterization of lead-free bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) from the oxalate method

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Bismuth titanate powders were synthesized by the oxalate method. Bismuth nitrate pentahydrate and titanium (IV) isopropoxide were used as the starting precursors with a mole ratio of Bi:Ti = 4 : 3 in 0.30M oxalic acid medium. The precipitate powders were calcined between 600 and 900°C for 2 h. The structure was studied by X-ray diffraction, the morphology by scanning electron microscopy, and the elemental composition by energy dispersive X-ray spectroscopy (EDXS). Orthorhombic $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders were obtained after calcination at 900°C for 2h. The particles were irregular in shape and highly agglomerated with a particle size ranging from 100-300 nm. The elemental composition of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders were identified by the EDXS data.

Key words: Bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and oxalate method

Introduction

Progress in the processing of ferroelectrics has opened a new era for applications such as memories, pyroelectric detectors, integrated optical modulators, actuators, infrared sensors, displays and switching devices [1]. Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) is a ferroelectric material with a layered perovskite structure and exhibits useful properties for optical memory, non-volatile memory, piezoelectric and electro-optic devices [2]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is potentially useful for device applications because of its relatively high dielectric constant, high Curie temperature of 675°C and high break down strength [3]. Moreover it is a suitable candidate for high temperature applications as a type of lead-free and environmental friendly material. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ belongs to 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 tetravalent or pentavalent cations and m has 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 [4]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders are normally synthesized by a conventional solid-state method from Bi_2O_3 and TiO_2 . The powders are often with high agglomeration and compositional inhomogeneity because of requiring a high calcination temperature and repeated grinding [5, 6].

Several alternative chemical synthesis methods have been proposed including hydrolysis of metal organic salts [7, 8], sol-gel [9-14], hydrothermal [15-19], citrate [20] and oxalate methods [21-25]. As a method for synthesizing high quality powders that have many advantages, such as, a high degree of crystallinity, a well-controlled morphology, high purity and narrow particle size distribution, the oxalate method is 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 have been synthesized by the oxalate method. The phase formation was investigated by X-ray diffraction (XRD). The morphology and elemental composition were studied by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDXS), respectively.

Experimental procedures

An oxalate method to prepare single phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders was modified as shown in Figure 1. The starting precursors used in this research included 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), oxalic acid ($(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, 99.5%, Fluka, Switzerland), ammonium hydroxide (NH_4OH , 30%, BDH, England) and ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.5%, Merck, Germany). An aqueous solution of 0.048 M $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was prepared using 6M HNO_3 as solvent. An ammonium hydroxide solution was added to 0.036 M $\text{Ti}(\text{OC}_3\text{H}_7)_4$ in an ice bath at 10°C to form titanate acid ($\text{Ti}(\text{OH})_4$) and then dissolved with nitric acid. The precursors with a mole ratio of Bi : Ti = 4 : 3 in 0.30M oxalic acid medium were mixed and the pH of the resultant mixture was adjusted to 9.0 by adding NH_4OH

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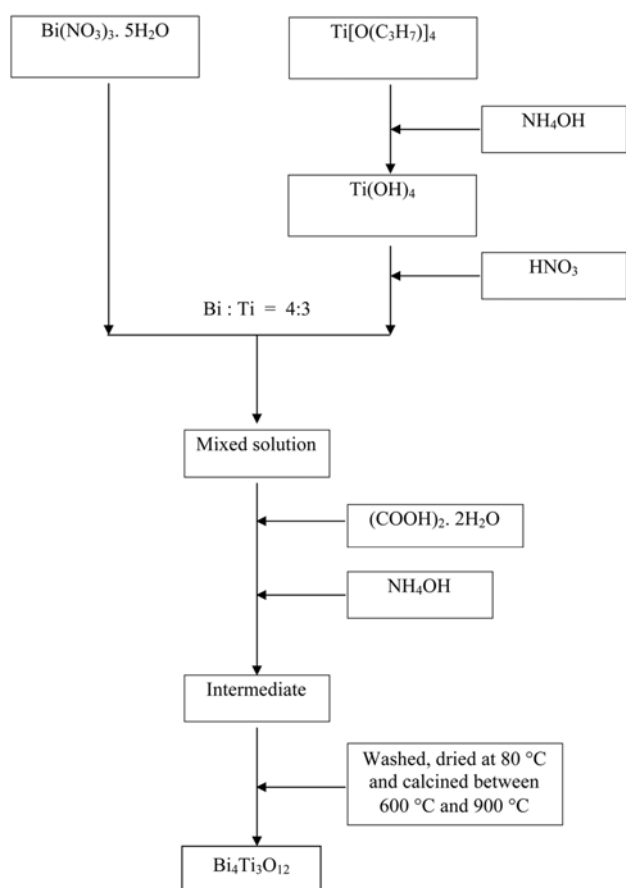


Fig. 1. Schematic diagram for the synthesis of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders by the oxalate method.

at room temperature. Then the precipitate was 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 600°C to 900°C for 2 h with a heating rate of 3 K/minute. The phase identification was performed at room temperature using a Ni-filtered monochromatic $\text{Cu-K}\alpha$ radiation X-ray diffractometer (D500, SIEMENS, Germany). The detection range was 10 - 60° with a step size of 0.10° ($2\theta/\text{s}$). The phase structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders was confirmed using the Joint Committee on Powder Diffraction Standard (JCPDS) File Card No. 35-0795 [25]. The fine powders were dispersed with absolute $\text{C}_2\text{H}_5\text{OH}$ medium in an ultrasonic bath (Model 5880, Cole-Parmer, USA) for 10 minutes, and gold coated by a fine coater (JSC-1200, JEOL, Japan) for 1 minute. The morphological development and elemental composition of crystalline $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders were studied by a scanning electron microscope (JSM5410-LV, JEOL, Japan) and energy dispersive X-ray spectrophotometer (ISIS300, Oxford, England) with a tungsten (W) filament K type, accelerate voltage of 15 kV, and working distance of 18 mm.

Results and Discussion

To understand the fundamental issues of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ crystallization the precipitate powders were calcined in air at a temperature ranging from 600 - 900°C at 100°C intervals for 2 h with a heating rate of 3 K/minute. Figures 2 (a-d) show the XRD patterns of the milled precipitate powders and that heated at different temperatures. 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 600°C for 2 h show a mixed multi-phase of an impurity phase $\text{Bi}_2\text{Ti}_2\text{O}_7$ [26] and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (Fig. 2. (a)). A single phase of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ started to form at a calcination temperature of 700°C and 800°C for 2 h (Fig. 2. (b-c)). With an increase in the calcination temperature, the line width and intensity of diffraction line decreases and increases [22-24], respectively. A single phase of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with an orthorhombic structure was obtained after calcination at 900°C for 2 h (Fig. 2. (d)) corresponding to the JCPDS card No.35-0795 [27].

Figures 3 (a-d) show SEM micrographs of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders calcined at 600 - 800°C for 2 h. The particle size increased as the calcination temperature increased. The powders consisted of small and soft agglomerates. The SEM micrograph of powders calcined at 600°C (Fig. 3 (a)) showed the agglomeration and irregular particles 100 nm in diameter. At 700°C and 800°C , Fig. 3 (b-c), the particles were agglomerated and had become slightly larger in size ranging from 150 nm to 250 nm, respectively. At 900°C , Fig. 3 (d), the particles were agglomerated, fused together and some grain growth occurred with an average size of 300 nm. The particle sizes were smaller than previously reported from the oxalate method [21, 22].

Figure 4 shows the EDXS spectrum of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders calcined at 900°C for 2 h. This technique was used to investigate and indicate the composition of powders calcined with the energy dispersive X-ray values. The characteristic X-ray radiation of each element has

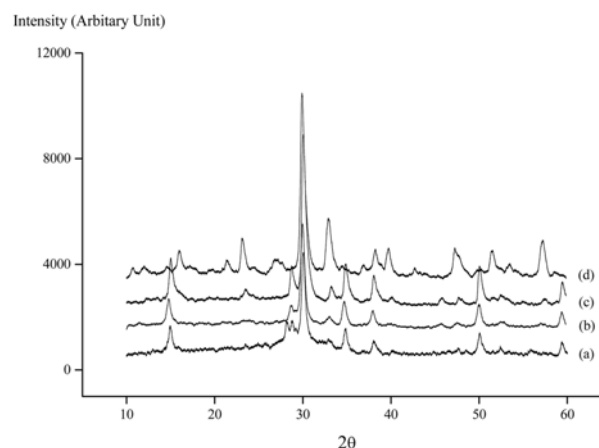


Fig. 2. X-ray diffraction patterns of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders calcined for 2 h at (a) 600°C , (b) 700°C , (c) 800°C and (d) 900°C .

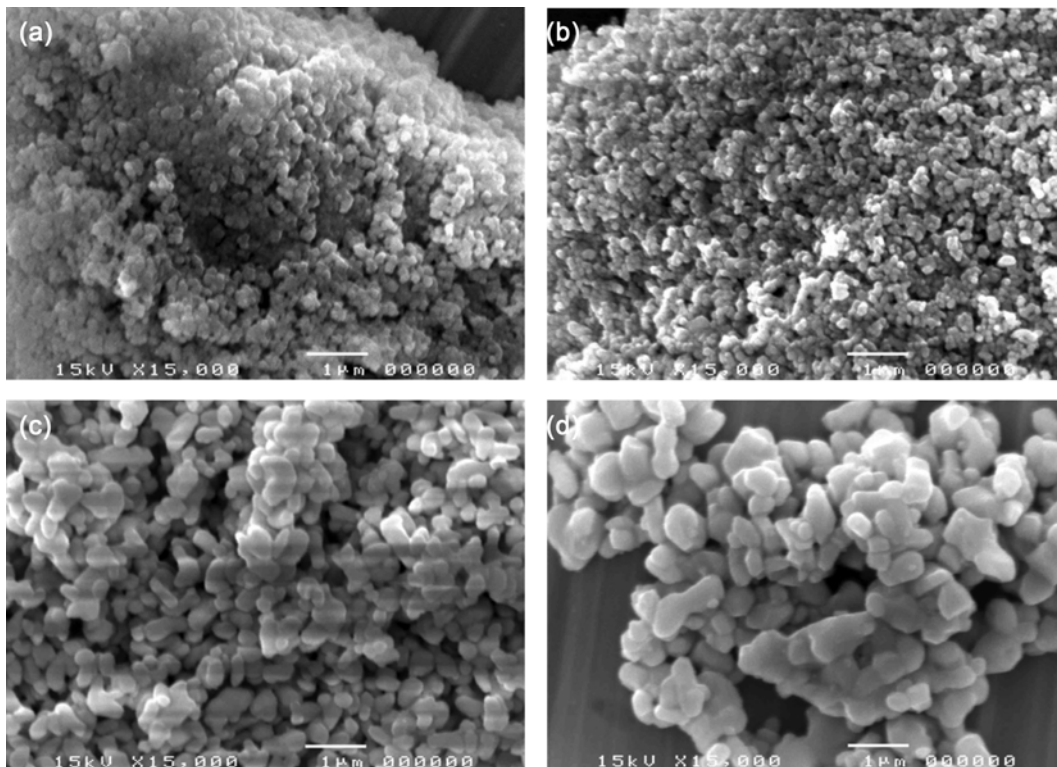


Fig. 3. SEM micrographs of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders calcined for 2 h at (a) 600°C, (b) 700°C, (c) 800°C and (d) 900°C.

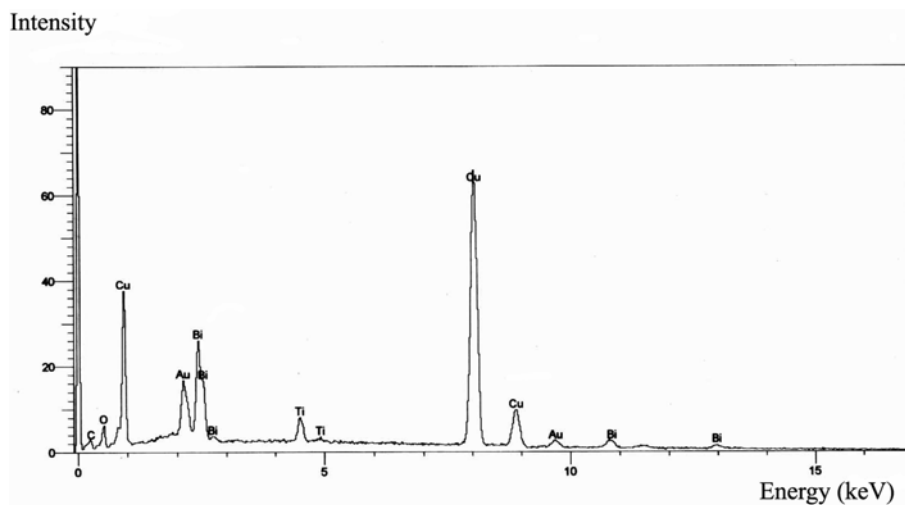


Fig. 4. EDXS spectrum of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders calcined at 900°C for 2 h.

different energy values as follows: bismuth of $M_{\alpha} = 2.42$ keV, titanium of $K_{\alpha} = 4.51$ keV and $K_{\text{ab}} = 4.96$ keV and oxygen of $K_{\alpha} = 0.52$ keV, respectively.

Conclusions

Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) powders were successfully synthesized by the oxalate method with bismuth nitrate pentahydrate and titanium (IV) isopropoxide as precursors in an oxalic acid medium. A single phase orthorhombic structure of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powder was obtained after calcination at 900°C for 2h. The average particle size at

a higher temperature is greater than at lower temperature. The powders were highly agglomerated, irregular in shape with an average particle size in the range of 100-300 nm with increasing calcination temperature. The elemental composition of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders were identified by the energy dispersive X-ray values.

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