ELSEVIER

Ceramics International 30 (2004) 1917–1919

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Chemical synthesis of bismuth titanate microparticles

Pusit Pookmanee[a,*], Piyanan Boonphayak[a], Sukon Phanichphant[b]

[a] *Department of Chemistry, Faculty of Science, Maejo University, Chiang Mai 50290, Thailand*
[b] *Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand*

Received 29 November 2003; received in revised form 10 December 2003; accepted 22 December 2003

Abstract

Microparticles of bismuth titanate ($Bi_4Ti_3O_{12}$) powders were synthesized by a chemical coprecipitation route with the precursors containing bismuth nitrate and titanium isopropoxide. The precipitate was obtained at pH 9 after adding ammonium hydroxide into the mixed solution. The yellow precipitate powders were washed with deionized water, dried at 90 °C and calcined at the temperature ranging from 400 to 700 °C for 2 h. The phase formation was investigated by X-ray diffraction (XRD). A single phase of $Bi_4Ti_3O_{12}$ was obtained with the orthorhombic structure after calcining at 700 °C for 2 h. The microstructure and morphology were studied by the scanning electron microscopic (SEM) and energy dispersive spectroscopic (EDS) techniques. The powders were agglomerate, irregular in shape and the average grain sizes were increased from 0.20 to 0.70 μm with increasing calcining temperature. The elemental constituents of the powders were identified by the energy dispersive value.

Keywords: A. Powders: chemical preparation; Bismuth titanate

1. Introduction

Bismuth titanate ($Bi_4Ti_3O_{12}$) belongs to the Aurivillius compounds family that can be represented by the general formula $(Bi_2O_2)^{2-}$ $(A_{m-1}B_mO_{3m+1})^{2+}$ in which A can be a monovalent (Na^+, K^+, ...), divalent (Pb^{2+}, Ba^{2+}, ...) or trivalent (Bi^{3+}, ...) cation or a mixture of them, B represents Ti^{4+}, Nb^{5+}, Ta^{5+}, etc., and m can have values of 2, 3, 4, ... In the particular case of $Bi_4Ti_3O_{12}$, $m = 3$, and its crystal structure can be described as formed by two $BiTiO_3$ unit cells of hypothetical perovskite structure interleaved with $(Bi_2O_2)^{2+}$ layers [1]. The compound is monoclinic ($C_{1h} = m$) at room temperature, and then turns into tetragonal ($D_{4h} = 4\,mmm$) above the Curie temperature (675 °C). $Bi_4Ti_3O_{12}$ has been studied by various investigators for its ferroelectric, piezoelectrics and electrooptic switching behaviour [2,3]. It is used for various applications such as memory elements, optical displays, piezoelectric converters or pyroelectric devices in wide temperature range from 20 to 600 °C. $Bi_4Ti_3O_{12}$ is normally synthesized by conventional solid-state reaction, which often results in high agglomeration and compositional inhomogeneity of powders because of high calcinations temperature and repeated grinding [4]. The chemical synthesis routes have been performed as hydrolysis of metal organic salts [5], sol–gel [6,7] and coprecipitation methods [8,9]. The chemical methods improve the production of fine powders with compositional homogeneity. In this paper, $Bi_4Ti_3O_{12}$ powders were synthesized by a chemical coprecipitation route. The phase formation was investigated by X-ray diffraction (XRD). The microstructure and morphology were studied by the scanning electron microscopic (SEM) and energy dispersive spectroscopic (EDS) techniques.

2. Experimental procedures

The chemical coprecipitation route was modified from the oxalate coprecipitation method [8]. Bismuth nitrate [$Bi(NO_3)_3 \cdot 5H_2O$] and titanium isopropoxide [$Ti(OC_3H_7)_4$] (Aldrich Chemical Company) were used as the starting precursors with the mole ratio of bismuth:titanium = 4:3. Bismuth nitrate was dissolved in 6 M nitric acid (HNO_3) solution. Titanyl nitrate [$Ti(ONO_3)_2$] solution was obtained by adding ammonium hydroxide solution into the titanium isopropoxide in an ice bath at 10 °C. Titanyl hydroxide [$TiO(OH)_2$] was dissolved in nitric acid to form titanyl

---

[*] Corresponding author. Fax: +66-53-873544.
E-mail address: pusit@mju.ac.th (P. Pookmanee).

0272-8842/$30.00
doi:10.1016/j.ceramint.2003.12.041

nitrate. Hydrogen peroxide was added to the above solution to form stable reddish brown titanium peroxo complex. The bismuth titanium peroxo complex solution was coprecipitated by adding ammonium hydroxide solution. The yellow coprecipitate powders were obtained after adjusting the final pH of solution to 9.0, filtered, washed with deionized water, and dried 90 °C for 3 h. The powders were calcined at 400–700 °C for 2 h with heating rate of 3 °C/min. X-ray diffraction analysis was performed on the calcined powders, using a modified D-500 Diffractometer, (Siemens, Germany), with radiation K_α, and Ni filter. The detection range was 10–60° with a step size 0.10 (2θ/s)/s. The powders were milled, sieved, dispersed with absolute ethanol medium in an ultrasonic bath, model 5880 (Cole-Parmer, USA) for 20 min and gold coated by finer coater, model JSC-1200 (JEOL, Japan) for 5 min. The microstructure and morphology were studied by using the scanning electron microscope, model JSM5410-LV (JEOL, Japan) and energy dispersive X-ray spectrometer, model ISIS 300 (Oxford, UK).

3. Results and discussion

Fig. 1a–d shows the X-ray diffraction patterns of $Bi_4Ti_3O_{12}$ powders calcined at 400, 500, 600 and 700 °C for 2 h. The powder calcined at lower temperature was yellow in colour, which subsequently transformed to white powder at higher calcining temperature. The powders calcined at 400 °C for 2 h (Fig. 1a) show a typical halo pattern, indicating that the sample was still in an amorphous state. Orthorhombic structure of $Bi_4Ti_3O_{12}$ was started to form at calcining temperature of 500 and 600 °C for 2 h (Fig. 1b and c). With the increasing calcining temperature, the line width and intensity of diffraction line decreases and increases, respectively. A single phase of $Bi_4Ti_3O_{12}$ with orthorhombic structure was obtained after calcining at 700 °C for 2 h (Fig. 1d) corresponding with the JCPDS Card No. 35-0795 [10].

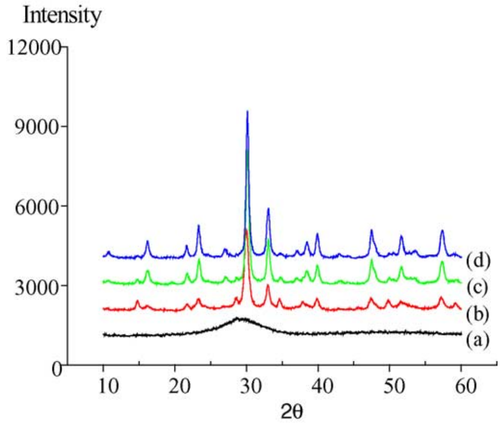

Fig. 1. X-ray diffraction patterns of $Bi_4Ti_3O_{12}$ powders calcined for 2 h at (a) 400 °C, (b) 500 °C, (c) 600 °C and (d) 700 °C.

Fig. 2a–d shows SEM micrographs of $Bi_4Ti_3O_{12}$ powders calcined at 400, 500, 600 and 700 °C for 2 h. The particle size was increased as the calcining temperature increased. The powders consisted of small and soft agglomerate. The SEM micrograph of powders calcined at 400 °C (Fig. 2a) showed

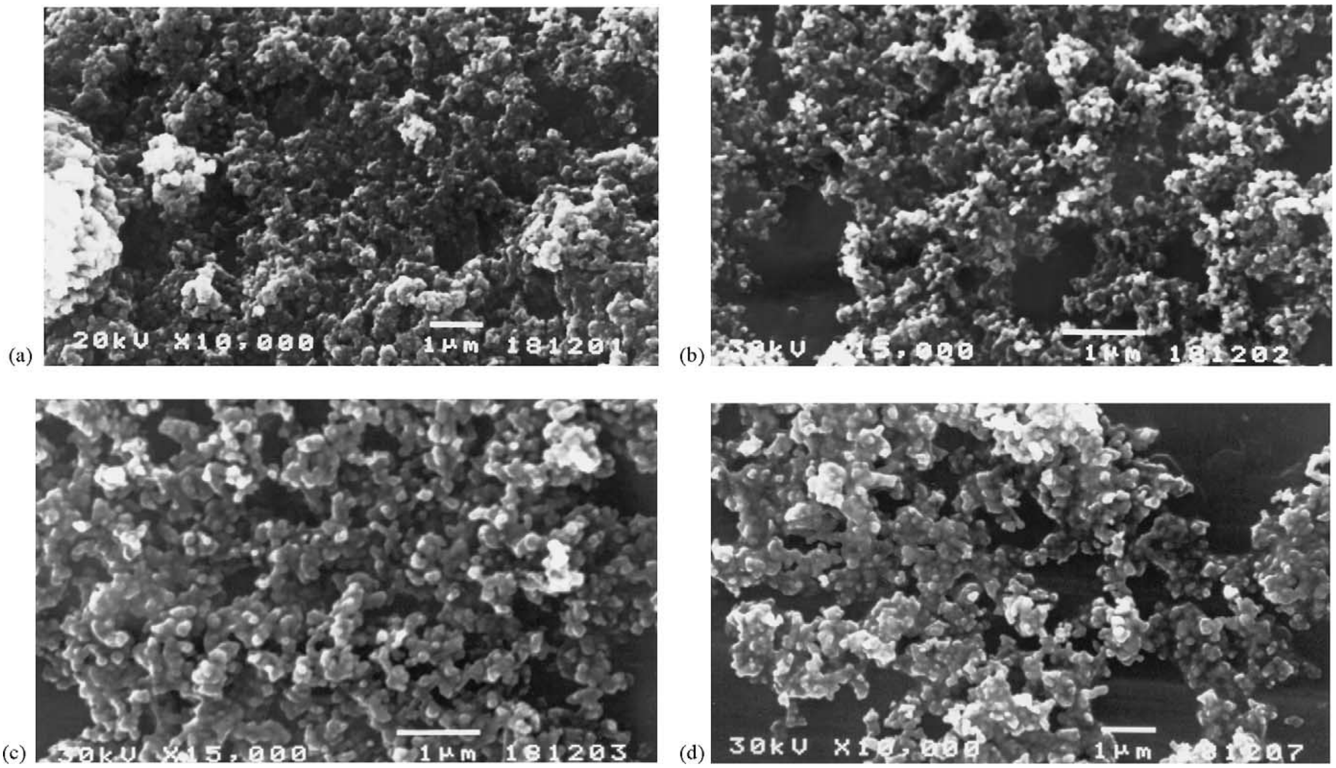

Fig. 2. SEM micrographs of $Bi_4Ti_3O_{12}$ powders calcined for 2 h at (a) 400 °C, (b) 500 °C, (c) 600 °C and (d) 700 °C.

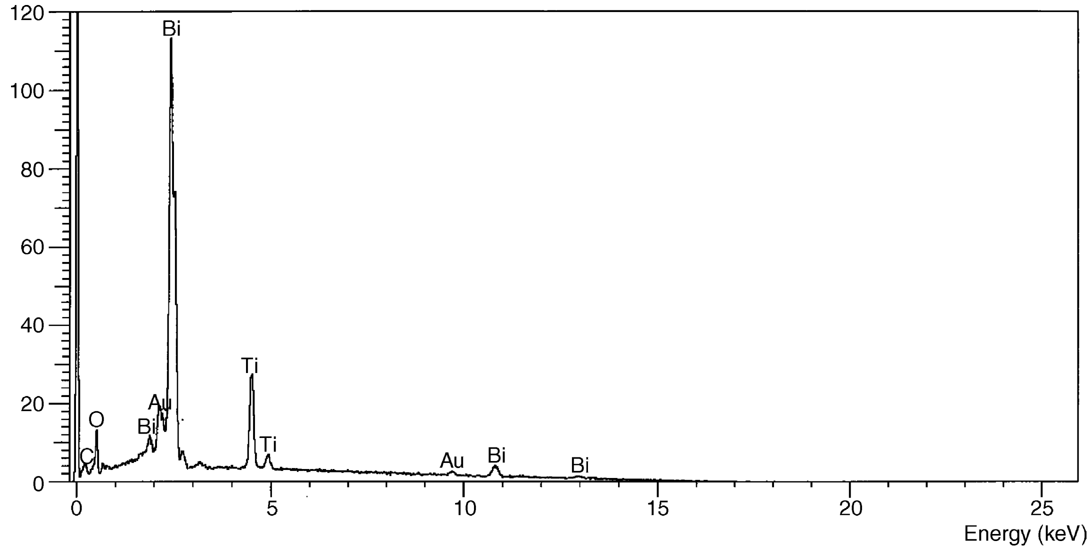

Fig. 3. EDS spectrum of $Bi_4Ti_3O_{12}$ powders calcined at 700 °C for 2 h.

the agglomerate and irregular particles with 0.20 μm in diameter. At 500 and 600 °C (Fig. 2b and c), the particles were agglomerate and become larger the sizes ranged from 0.30 to 0.40 μm, respectively. At 700 °C (Fig. 2d), the particles were agglomerated, fused together and some grain growth occurred with the sizes ranging from 0.50 to about 0.70 μm.

Fig. 3 shows the EDS spectrum of $Bi_4Ti_3O_{12}$ powders calcined at 700 °C for 2 h. It was used to investigate and indicate composition of powders calcined with the energy dispersive value. The characteristic X-ray radiation of each element has different energy value; bismuth of M_α 2.419 keV, L_α 10.837 keV and L_β 13.021 keV, titanium of K_α 4.508 and K_{ab} 4.964 keV and oxygen of K_α 0.525 keV, respectively.

4. Conclusions

A single phase of $Bi_4Ti_3O_{12}$ microparticle powders was successfully synthesized by a chemical coprecipitation route. $Bi_4Ti_3O_{12}$ powders were crystallized between calcined at 500 and 700 °C for 2 h and showed an orthorhombic structure corresponding with JCPDS Card No. 35-0795. The average grain size at higher temperature is greater than at low temperature. The powders were agglomerate, irregular in shape and the average grain sizes were increased from 0.20 to 0.70 μm with increasing calcining temperature. The elemental constituents of the powders were identified by the energy dispersive value.

Acknowledgements

This experiment was partially supported by the Department of Chemistry, and the Faculty of Science, Maejo University, Thailand. The authors would like to thank Mr. S. Chaisupan from Department of Physics, Chiang Mai University, Thailand for the XRD analysis, and Ms. P. Luangphai from Biotechnology Center, Maejo University, Thailand for the SEM/EDS facilities.

References

[1] B. Aurivillius, Mixed bismuth oxides with layer lattices, Arkiv. Kemi. 1 (1949) 499–512.
[2] J.F. Dorrian, R.E. Newnham, D.K. Smith, M.I. Kay, Crystal structure of $Bi_4Ti_3O_{12}$, Ferroelectrics 3 (1971) 17–27.
[3] M. Billegas, C. Moure, J.F. Fernandez, P. Duran, Preparation and sintering behavoiur of submicronic $Bi_4Ti_3O_{12}$ powders, J. Mater. Sci. 31 (1996) 949–959.
[4] S. Kojima, A. Hushur, F. Jiang, S. Hamazaki, M. Takashige, M.-S. Jang, S. Shimada, Crystallization of amorphous bismuth titanate, J. Non-Cryst. Solids 293–295 (2001) 250–254.
[5] Y. Osamu, M. Noboru, H. Ken, The formation and characterization of alkoxy-derived $Bi_4Ti_3O_{12}$, Br. Ceram. Trans. J. 90 (1991) 111–113.
[6] A.V.P. Rao, A.I. Robin, S. Komarneni, Bismuth titanate from nanocomposite and sol–gel processes, Mater. Lett. 28 (1996) 469–473.
[7] N.V. Giridharan, S. Madeswaran, R. Jayavel, Structural, morphological and electrical studies on ferroelectric bismuth titanate thin films prepared by sol–gel technique, J. Cryst. Growth 237-239 (2002) 468–472.
[8] M. Villegas, C. Moure, J.F. Fernandez, P. Duran, Low-temperature sintering of submicronic randomly oriented $Bi_4Ti_3O_{12}$ materials, Ceram. Int. 22 (1996) 15–22.
[9] A.M. Umabala, M. Suresh, A.V. Prasadarao, Bismuth titanate from coprecipitated stoichiometric hydroxide precursors, Mater. Lett. 44 (2000) 175–180.
[10] Joint Committee on Powder Diffraction Standards, Powder Diffraction File, Card No. 35-0795, Swarthmore, PA.