ELSEVIER

Ceramics International 30 (2004) 1913–1915

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Hydrothermal synthesis of fine bismuth titanate powders

Pusit Pookmanee[a,*], Phunthanee Uriwilast[b], Sukon Phanichpant[a]

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

Received 1 December 2003; received in revised form 8 December 2003; accepted 22 December 2003

Abstract

Bismuth titanate ($Bi_4Ti_3O_{12}$) fine powders were synthesized from a low temperature hydrothermal method. Bismuth nitrate and titanium isopropoxide were used as the starting materials with the mole ratio of Bi:Ti = 4:3. Sodium hydroxide was added to adjust the pH of the mixed final solution at 13. The temperature of reaction in the hydrothermal Teflon-lined vessel was 150 °C. The effect of reaction time at 5, 10, and 15 h was investigated. The phase structure was identified by X-ray diffraction (XRD) technique. Orthorhombic structure of $Bi_4Ti_3O_{12}$ fine powders was obtained without calcination step. The morphology and microstructure were investigated by scanning electron microscopic (SEM) technique. The powders were generally sphered in shapes and the average sizes were 0.50–1.20 μm.

Keywords: A. Powders; Hydrothermal; Bismuth titanate

1. Introduction

Bismuth titanate ($Bi_4Ti_3O_{12}$) has a layered perovskite structure built up by the regular intergrowth of $(Bi_2O_2)^{2+}$ layer and perovskite type layer $(Bi_2Ti_3O_{10})^{2-}$ where Bi ion occupy 12-coordinated sites [1]. At room temperature, $Bi_4Ti_3O_{12}$ presents a monoclinic ($C_{1h} = m$) symmetry, but above the Curie temperature, at about 675 °C, the symmetry becomes tetragonal ($D_{4h} = 4\,mmm$). The spontaneous polarization has a magnitude as high as $50\,\mu C/cm^2$ and lies in a direction tilted approximately 7° from the major crystal surface in a plane parallel to the monoclinic b_o–c_o plane. The polarization along the c_o direction, after applying an electric field on the major crystal surface, yields values of approximately $4\,\mu m/cm^2$. The piezoelectric coefficient is also relatively high in these directions. $Bi_4Ti_3O_{12}$ exhibits potential use in applications such as non-volatile memory, optical memory, piezoelectric, and electro-optic devices [2,3]. Several methods, including solid state reaction [4,5], coprecipitation method [6], sol–gel processes [7–9], and hydrothermal synthesis [10–12] were developed for the synthesis of $Bi_4Ti_3O_{12}$ fine powders. Calcining at high temperature and repeated grinding of the composition of oxides was necessary for the preparation of oxides by conventional solid state reaction, which often results in high agglomeration and compositional inhomogeneity of the powders. Although the improved methods such as coprecipitation and sol–gel can produce fine powders with compositional homogeneity, high calcined temperature is usually necessary for the crystallization of $Bi_4Ti_3O_{12}$ powders. Hydrothermal synthesis has several advantages including preparing crystalline oxides with narrow grain size distribution, producing highly $Bi_4Ti_3O_{12}$ fine powders without calcination at high temperature, and the resulted particles form low agglomeration [11]. In this research, we report a low temperature hydrothermal synthesis of $Bi_4Ti_3O_{12}$ fine powders and study the effect of reaction time on the phase formation by X-ray diffraction (XRD). Microstructure and morphology were investigated by the scanning electron microscope (SEM).

2. Experimental procedures

$Bi_4Ti_3O_{12}$ fine powders were synthesized by a low temperature hydrothermal method. Solution A was prepared by dissolving $Bi(NO_3)_3{\cdot}5H_2O$ in 6 M HNO_3. Solution B was prepared by adding concentrated NH_3 to $Ti(O(C_3H_7)_4)$ to form white precipitate $Ti(OH)_4$ which dissolved in 6 M

---

* Corresponding author. Fax: +66-53-873544.
E-mail address: pusit001@hotmail.com (P. Pookmanee).

0272-8842/$30.00 © 2004 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2003.12.043

HNO_3 and 30% H_2O_2 to produce $TiO(NO_3)_2$, a reddish brown solution. Solutions A and B were mixed well together by using the control temperature water bath with continuous stirring at 80 °C for 10 min in the mole ratio of Bi:Ti = 4:3. Aqueous solution of NaOH (12 M) was added to the mixed solution to form the yellow precipitate with the pH of the final solution of 13.0. After the hydrothermal treatment at 150 °C for 5, 10, and 15 h, the fine powders samples were filtered, washed with deionized water until the pH of the final solution was 7.0, and dried at 100 °C for 5 h. The phase structure of fine powders were identified by the X-ray diffractometer (D-500, Siemens) using the Ni-filtered monochromatic CuK_{α} radiation. The detection range was 10–60° with the step size of 0.10° (2θ/s/s). The phase structure of $Bi_4Ti_3O_{12}$ fine powders was confirmed by using the Joint Committee on Powder Diffraction Standard (JCPDS) File Card No. 35-0795 [13]. The fine powders were dispersed with absolute C_2H_5OH medium in an ultrasonic bath (model 5880, Cole-Parmer) for 10 min, and gold-coated by the fine coater (JSC1200, JEOL). The morphology and microstructure were investigated by scanning electron microscope (JSM5410-LV, JEOL) with the tungsten (W) filament K type, accelerate voltage 25 kV, and working distance of 18 mm.

3. Results and discussion

Fig. 1(a)–(c) shows the XRD patterns of $Bi_4Ti_3O_{12}$ fine powders synthesized by hydrothermal process at 150 °C in 12 M NaOH with different reaction times without calcinations. $Bi_4Ti_3O_{12}$ began to crystallize at reaction time of 5 h (Fig. 1(a)), but the increased reaction time between 10 and 15 h (Fig. 1(b) and (c)) was necessary for the synthesis of well-crystallized $Bi_4Ti_3O_{12}$ fine powders. With increasing reaction time, the line width and intensity of diffraction line decreases and increases, respectively. The $Bi_4Ti_3O_{12}$ was shown to be in a good agreement with the orthorhombic structure reported in JCPDS File Card No. 35-0795 [13]. The single phase depended mainly on the reaction time which increased with the increasing of the reaction time. Fig. 2(a)–(c) shows the SEM micrographs of $Bi_4Ti_3O_{12}$ fine powders synthesized from hydrothermal at 150 °C of various reaction times. The $Bi_4Ti_3O_{12}$ fine powders without calcinations were agglomerated and irregular in shape. The average sizes of $Bi_4Ti_3O_{12}$ fine powders are about 0.50 μm (Fig. 1(a) and (b)) in diameter. As the reaction time

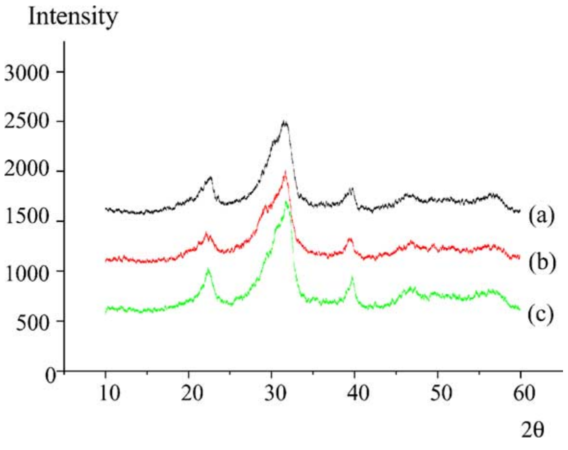

Fig. 1. X-ray diffraction patterns of $Bi_4Ti_3O_{12}$ powders synthesized by the hydrothermal process at 150 °C at different reaction times of (a) 5 h, (b) 10 h, and (c) 15 h.

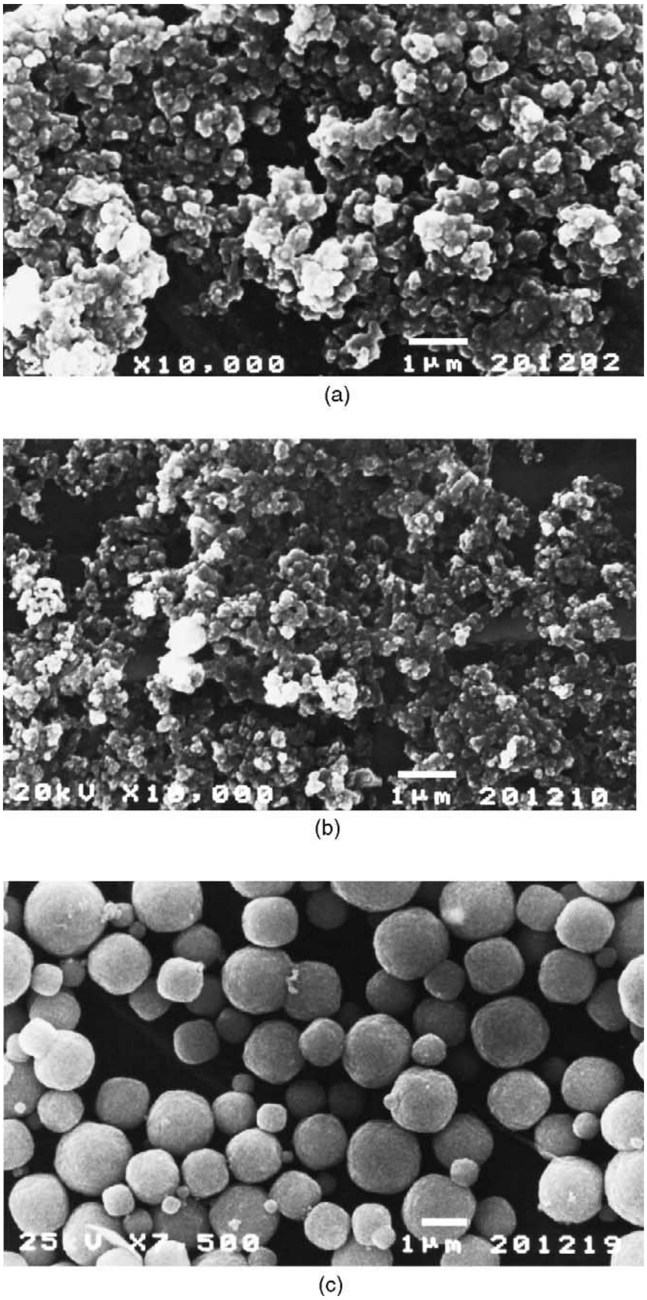

Fig. 2. SEM micrographs of $Bi_4Ti_3O_{12}$ powders synthesized by the hydrothermal process at 150 °C at different reaction times of (a) 5 h, (b) 10 h, and (c) 15 h.

increased (Fig. 2(c)), the powders were spherical in shape and well-dispersed with a range of 0.50–1.20 μm diameter. The effect of reaction time on the low temperature hydrothermal synthesized powders were investigated at 150 °C in 12 M NaOH ranging from 5 to 15 h. As the reaction time increased, the average grain size of particles also increased.

4. Conclusions

$Bi_4Ti_3O_{12}$ fine powders were hydrothermally synthesized at low temperature of 150 °C for 5–15 h from $Bi(NO_3)_3 \cdot 5H_2O$, $Ti(O(C_3H_7)_4)$, and 12 M NaOH aqueous solution. The single phase and the particles size of $Bi_4Ti_3O_{12}$ fine powders increased with increasing reaction time. The XRD results revealed that an orthorhombic structure of $Bi_4Ti_3O_{12}$ was obtained. The SEM showed that the $Bi_4Ti_3O_{12}$ are irregular in shape and agglomerate with average grain size of 0.50 μm at lower reaction time. At the longer reaction time, the particles are spherical and dispersed with the grain size ranging from 0.50 to 1.20 μm.

Acknowledgements

This research was partially supported by the Faculty of Science, Chiang Mai University, Chiang Mai, Thailand. The authors wish to express a sincere gratitude to Prof. Dr. R.B. Heimann for the hydrothermal vessel facilities, Mr. S. Chaisupan for evaluating the XRD results, and Ms. P. Luangphai for performing the SEM measurement.

References

[1] X.F. Du, I.W. Chen, Ferroelectric thin films of bismuth-containing layered perovskites. Part I. $Bi_4Ti_3O_{12}$, J. Am. Ceram. Soc. 81 (1998) 3253–3259.

[2] M. Billegas, C. Moure, J.F. Fernandez, P. Duran, Preparation and sintering behaviour of submicronic $Bi_4Ti_3O_{12}$ powders, J. Mater. Sci. 31 (1996) 949–959.

[3] 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.

[4] C.H. Lu, C.H. Wu, Preparation, sintering, and ferroelectric properties of layer-structure strontium bismuth titanium oxide ceramics, J. Eur. Ceram. Soc. 22 (2002) 707–714.

[5] L.B. Kong, J. Ma, W. Zhu, O.K. Tan, Preparation of $Bi_4Ti_3O_{12}$ ceramics via a high-energy ball milling process, Mater. Lett. 51 (2001) 108–114.

[6] A.M. Umabala, M. Suresh, A.V. Prasadarao, Bismuth titanate from coprecipitated stoichiometric hydroxide precursors, Mater. Lett. 44 (2000) 175–180.

[7] N.V. Giridharan, S. Madeswaran, R. Jayavel, Structural, morphology and electrical studies on ferroelectric bismuth titanate thin films prepared by sol–gel technique, J. Cryst. Growth 237–239 (2002) 468–472.

[8] A.V.P. Rao, A.I. Robin, S. Komarneni, Bismuth titanate from nanocomposite and sol–gel processes, Mater. Lett. 28 (1996) 469–473.

[9] H. Gu, C. Dong, P. Chen, D. Bao, A. Kuang, X. Li, Growth of layered perovskite $Bi_4Ti_3O_{12}$ thin films by sol–gel process, J. Cryst. Growth 186 (1998) 403–408.

[10] Y. Shi, C. Cao, S. Feng, Hydrothermal synthesis and characterization of $Bi_4Ti_3O_{12}$, Mater. Lett. 46 (2000) 270–273.

[11] D. Chen, X. Jiao, Hydrothermal synthesis and characterization of $Bi_4Ti_3O_{12}$ powders from different precursors, Mater. Res. Bull. 36 (2001) 355–363.

[12] Q. Yang, Y. Li, Q. Yin, P. Wang, Y.-B. Cheng, $Bi_4Ti_3O_{12}$ nanoparticles prepared by hydrothermal synthesis, J. Eur. Ceram. Soc. 23 (2003) 161–166.

[13] Joint Committee on Powder Diffraction Standards, Powder Diffraction File, Card No. 35-0795, Swarthmore, PA.