Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 36 (2010) 241–244

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

# Preparation of $Bi_4Ti_3O_{12}$ nanopower by azeotropic co-precipitation and dielectric properties of the sintered ceramic

Chen Zhi-hui [a,c,*], Qiu Jun-fu [b], Liu Cheng [a], Ding Jian-ning [a,c,d], Zhu Yuan-yuan [a,c]

[a] *Centre for Low Dimensional Materials, Micro-nano Devices and System, Faculty of Materials Science and Engineering, Jiangsu Polytechnic University, Changzhou, Jiangsu 213164, China*
[b] *Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100080, China*
[c] *Key Laboratory of New Energy Engineering, Jiangsu Polytechnic University, Changzhou, Jiangsu 213164, China*
[d] *Jiangsu University, Zhenjiang, Jiangsu 212013, China*

Received 12 September 2008; received in revised form 12 May 2009; accepted 24 July 2009
Available online 25 August 2009

## Abstract

$Bi_4Ti_3O_{12}$ nanopowders were prepared by an azeotropic co-precipitation method and the phase evolution process, microstructure and sintering behavior were investigated. The results indicate that well dispersed and agglomerate-free nanocrystalline $Bi_4Ti_3O_{12}$ with average particle size of 21 nm can be obtained by calcinating the precursor at 750 °C, which is 50 °C lower than traditional solid reaction. The relative density of the ceramic reaches 96% at 1000 °C and shows no evident decrease until 1100 °C. The broadened sintering temperature range and the lower loss tangent of the ceramic show good sintering activity of the nanopowders.

*Keywords:* A. Powders: chemical preparation; C. Dielectric properties; D. $BaTiO_3$ and titanates; Azeotropic process

## 1. Introduction

Bismuth titanate ($Bi_4Ti_3O_{12}$, BIT) with a typical layered perovskite structure is a promising candidate for ferroelectric device applications to nonvolatile random access memories (NVRAM), piezoelectric devices and optical displays [1,2] due to its high Curie temperature (675 °C), high dielectric constant and lead-free nature [3]. The conventional solid-state reaction for synthesizing BIT powders requiring high calcination temperature around 1373 K is inevitably associated with the occurrence of particle coarsening and hard aggregation of the BIT powder during calcination [4–6]. The presence of hard particle aggregation will lead to poor properties of the BIT ceramics. Many preparing methods have been researched to avoid the aggregation and to improve the sintering ability of the BIT powders such as mechanical alloying [7,8], self-propagation synthesis [9], crystallization from glass [10] soft chemical synthesis including precipitation synthesis [11–16] and sol–gel [17,18], hydrothermal [19,20]. The advantages of soft chemical routes over solid-state technique are the control of morphology, particle size and possible lower sintering temperature. However, the dispersion of the BIT powders and the high cost are still common challenges in wet chemical methods [11,21].

In a previous paper [22,23], we introduced an azeotropic co-precipitation method to prepare well dispersed and agglomerate-free nanopowders. n-Butanol is used as a low-cost and recyclable dehydration solvent. Water in precursors vaporizes prior to n-butanol at temperatures below 100 °C during the azeotropic distillation process, due to the far lower boiling point of water than the later. As a result, agglomerate-free nanopowders could be produced. The aim of the present work is to produce well dispersed BIT nanopowders by this method and investigate the dielectric properties of the sintered ceramics.

## 2. Experiment

Bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$, AR) and tetrabutyl titanate ($(C_4H_9O)_4Ti$, AR)were used as starting precursors. The precursor solutions of bismuth and titanium were prepared by adding the starting materials to ethanol and nitric acid

---

[*] Corresponding author at: Centre for Low Dimensional Materials, Micro-nano Devices and System, Faculty of Materials Science and Engineering, Jiangsu Polytechnic University, No.1 Dehu Road, Wujin District, Changzhou, Jiangsu 213164, China. Tel.: +86 519 86330100.
*E-mail address:* zhchen614@yahoo.com.cn (C. Zhi-hui).

0272-8842/$36.00 © 2009 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2009.07.022

solution ($HNO_3$). Bi was 4 wt% excess to compensate the bismuth loss during the thermal treatment. The precipitant consisting of ethanol (20 vol.%) and ammonia was 10% excess to get the required pH value during reaction by adjusting the flowing rate of the precipitant. The components of the precursor solutions and the precipitant were homogenized by stirring for 1 h separately, then injected into a reactor simultaneously at room temperature. White slurry was formed immediately at pH = 9.5 after the interaction of the reactants under vigorous stirring. Subsequently, the slurry was filtered and washed repeatedly with deionized water to remove the by-products, then was distilled with n-butanol under reduced pressure to remove the absorbed water and the hydrated water. The as-prepared precursors were dried in vacuum at 100 °C for 2 h, and were calcined at temperatures ranging from 600 °C to 900 °C. The BIT powders calcined at 750 °C were milled for 1 h in a deionized water medium and a binder solution of 1 wt% polyvinyl alcohol (PVA), fully dried and passed through a sieve of 80 mesh. Then the powders were dry-pressed into pellets at 20 MPa and sintered at temperatures ranging from 850 °C to 1100 °C for 2 h.

Thermal studies were performed in flowing air with the heating rate of 10 °C/min using a combined thermogravimetric analyser and differential thermal analyser (PerkinElmer, America). The bulk densities of the sintered pellets were determined by Archimedes' method. Phase identification of the calcined product was characterized by X-ray diffraction analysis using a diffractometer (DMax-RA Japan Rigaku). The morphology of the prepared powders and the ceramics was observed by transmission and scanning electron microscopy (TEM, Philips EM-420; SEM, HITACHI S-4300) respectively. Dielectric properties were measured using a computer-interfaced impedance analyzer in 100 Hz from room temperature to 800 °C.

## 3. Results and discussion

Fig. 1 shows the thermal behavior of the synthesized precursor. A sharp weight loss in TG curve occurring below 300 °C corresponds to the evaporation of water and the decomposition of the residual n-butanol. This process appears as one big exothermal peak at 270 °C in the corresponding DTA curve. The exothermic peak at 770 °C in DTA curve may be attributed to the crystallization of the precursor since no weight loss was observed above 750 °C in TG curve.

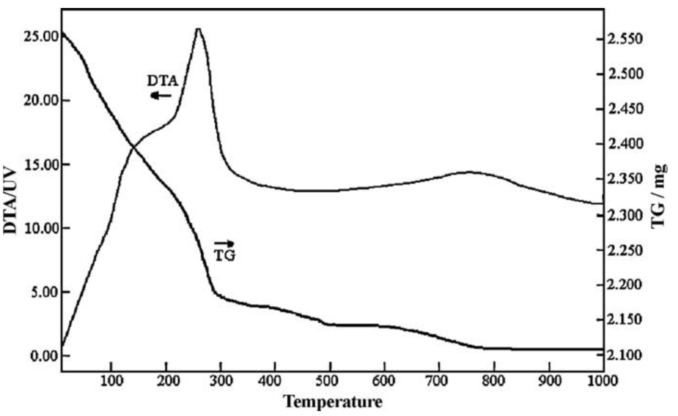

Fig. 1. TG-DTA curve of the as-prepared precursor.

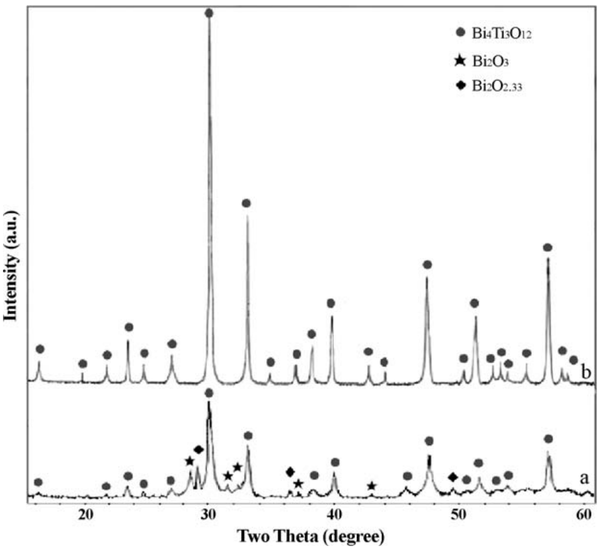

Fig. 2. XRD pattern of the powder calcined at 600 °C and 750 °C for 2 h.

The XRD patterns of the samples calcined at 600 °C and 750 °C for 2 h presented in Fig. 2 show that the BIT phase has appeared at 600 °C (Fig. 2a) accompanying with a small amount of $Bi_2O_3$ and $Bi_2O_{2.33}$ phases, while pure BIT phase was obtained at 750 °C (Fig. 2b) since all the patterns agreed well with the XRD data of a crystalline BIT (JCPDS card 35–0795). The crystallization temperature of BIT by this method is 50 °C lower than by solid-state method. The difference of the crystallization temperature between in DTA and in XRD can be attributed to the hysteresis of temperature in DTA.

Fig. 3 shows the TEM morphologies of the BIT powders as a function of calcining temperature. The particle size of the precursor is less than 15 nm before calcination (Fig. 3a), then grows to 21 nm, 77 nm and 100 nm with the increase of the calcining temperature at 750 °C, 800 °C and 900 °C respectively. The particles remain well dispersed and free of agglomeration, meanwhile the schistose-like morphology became clearer in the samples with the temperature increasing. Generally speaking, the particle size prepared by traditional solid reaction is above 100 nm when calcined at 750 °C, and grows rapidly even to micrometer scaled at higher temperatures accompanying with the agglomeration of the particles. The improvement of the particles dispersion in this work can be attributed to the dehydration by n-butanol molecular during the azeotropic process. After water in precursors vaporizes prior to n-butanol during the azeotropic distillation process, the binding force among particles decreases due to the lower surface tension of the remained n-butanol, then well dispersed and agglomerate-free nanopowders are achieved.

The relative densities of the BIT ceramics as a function of sintering temperature were presented in Fig. 4, and the corresponding morphology of the ceramic sintered at 1000 °C for 1 h was shown in Fig. 5. The relative density of the samples

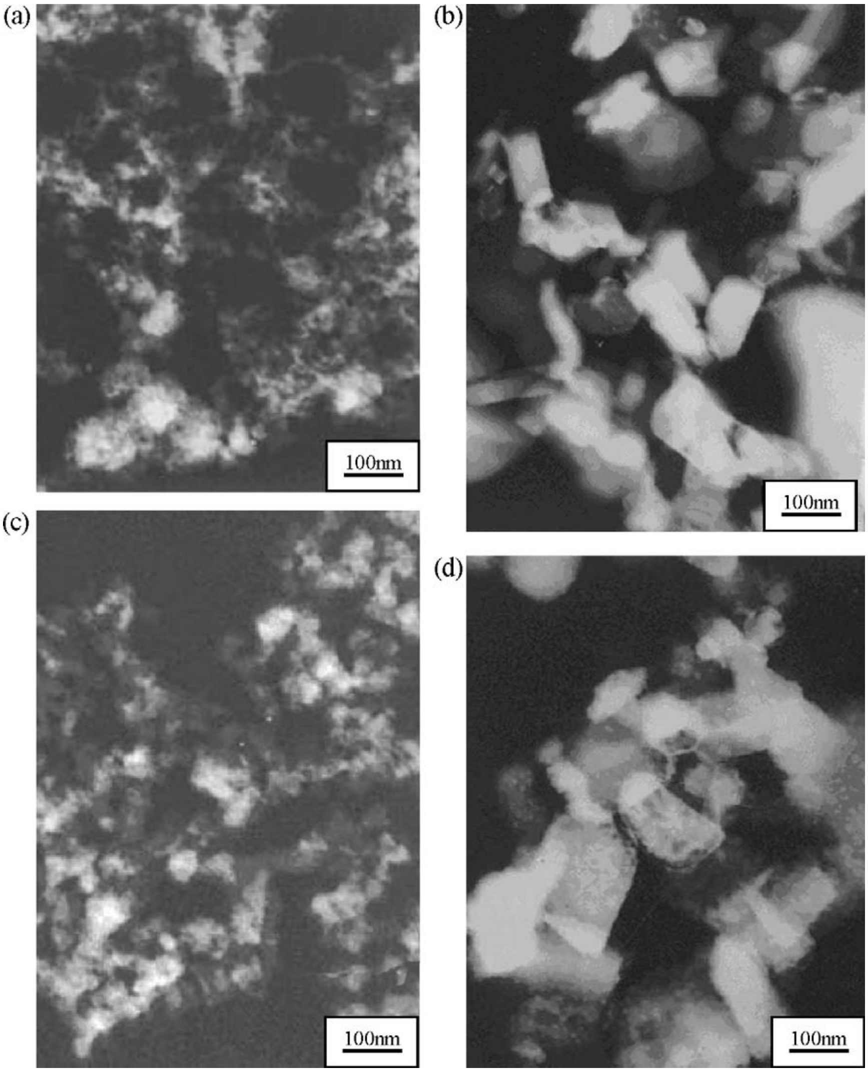

Fig. 3. TEM of as-prepared powders and the powders calcined at different temperatures: (a) as-prepared precursor, (b) 750 °C, (c) 800 °C and (d) 900 °C.

is 93.8% of theoretical density (TD = 8.04 g/cm$^3$) at 950 °C, and increases with the temperature until it reaches up to 96% at 1000 °C, then slightly decreases to 95.4% at 1050 °C and 93% at 1100 °C due to the evaporation of Bi under high temperature. The density decreasing much slower broadens the optimized sintering temperature range of the material (950–1050 °C).

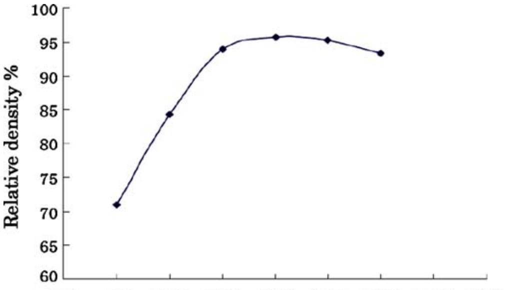

Fig. 4. The relative densities of the BIT ceramics changing with sintering temperature.

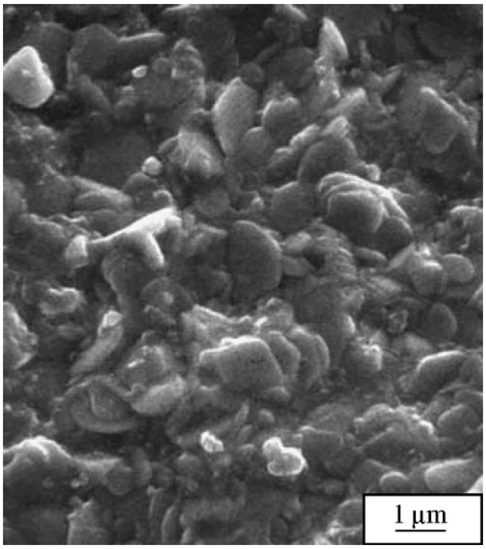

Fig. 5. The surface morphology of the BIT ceramic sintered at 1000 °C.

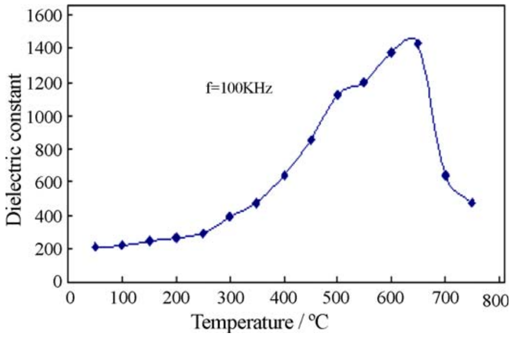

Fig. 6. Temperature dependent of dielectric permittivity in the BIT crystal.

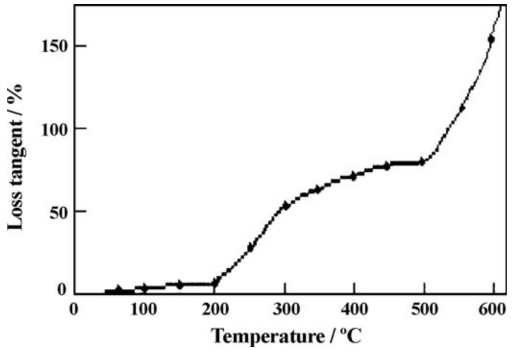

Fig. 7. Temperature dependent of dielectric loss in the BIT crystal.

This azeotropic process of powders is proved to be effective to improve the dispersion of powders, and have a significant influence on the sintering behavior. In contrast, the relative density of the BIT ceramics through solid-state reaction can only reach 92% at 1000 °C [24], whereas the density of the samples through normal wet chemical routes began to decrease at 900 °C due to the abnormal grain growth [22].

The Curie temperatures ($T_c$) of the BIT sample sintered at 1000 °C is 25 °C lower than the standard Curie temperature of 675 °C (Fig. 6), owing to smaller contribution of relaxing polarization to its dielectric properties deduced from the dimension effect of nanopowders [25]. The loss tangent of BIT ceramic is 70% (Fig. 7), lower than the data reported in the literature [26], which may be attributed to the high sintering ability of the prepared nanopowders.

## 4. Conclusion

Well dispersed $Bi_4Ti_3O_{12}$ nanopowders were prepared by azeotropic co-precipitation method. Nanocrystalline $Bi_4Ti_3O_{12}$ with average particle size of 21 nm can be obtained by calcining the precursor at 750 °C, and remains well dispersed and free of agglomerate with the increase of temperature. A relative density up to 96% of theoretical density was obtained at 1000 °C with no evident decrease until 1100 °C. The density decreasing much slower broadens the sintering temperature range of the material. This azeotropic process of powders is proved to be effective to improve the dispersion of powders, and have a significant influence on the sintering behavior.

## Acknowledgements

This work was supported by Key Programs for Science and Technology Development of Jiangsu China (BE20080030), Jiangsu Provincial Natural Science Foundation (SBK200930272), Qing Lan Project (2008-04), Changzhou Science and Technology Platform (CM2008301), Programs for Industrial Science and Technology Development of Changzhou (CE2008014).

## References

[1] P. Araujo, C.A. McMillan, L.D. Melnick, et al., Ferroelectric memories, Ferroelectrics 104 (1990) 241–256.
[2] B.H. Park, B.S. Kang, S.D. Bu, et al. Nature 401 (1999) 682–684.
[3] C.A. Araujo, J.D. Cuhair, L.D. McMillan, et al. Nature (London) 374 (1995) 627.
[4] L. Zhang, R. Chu, S. Zhao, et al. Short Communication Materials Science and Engineering B 116 (2005) 99–103.
[5] Q.Y. Tang, Y.M. Kan, Y.G. Li, et al. Solid State Communications 142 (2007) 1–5.
[6] Q.Y. Tang, Y.M. Kan, Y.G. Li, Scripta Materialia 54 (2006) 2075–2080.
[7] K. Han, T. Ko, J. Oh, Scripta Materialia 59 (2) (2008) 143–146.
[8] B.D. Stojanovic, A.Z. Simoes, C.O. Paiva-Santos, et al. Ceramics International 32 (2006) 707–712.
[9] Z.S. Macedo, C.R. Ferrari, A.C. Hernandes, Powder Technology 139 (2004) 175–179.
[10] K. Sunahara, J. Yano, K. Kakegawa, et al. Journal of the European Ceramic Society 26 (2006) 623–626.
[11] M. Anilkumar, S.R. Dhage, V. Ravi, Materials Letters 59 (2005) 514–516.
[12] T. Thongtem, S. Thongtem, Ceramics International 30 (2004) 1463–1470.
[13] M.E. Mendoza, F.J.L. Donado, Journal of Physics and Chemistry of Solids 64 (2003) 2157–2161.
[14] S.H. Ng, J. Xue, J. Wang, Journal of American Ceramic Society 85 (11) (2002) 2660–2665.
[15] Y. Du, J. Fang, M. Zhang, et al. Materials Letters 57 (2002) 802–806.
[16] Y. Kan, P. Wang, Y. Li, et al. Materials Letters 56 (2002) 910–914.
[17] A.V.P. Rao, A.I. Robin, S. Komarneni, Materials Letters 28 (1996) 469–473.
[18] S.R. Dhage, Y.B. Khollam, S.B. Dhespande, et al. Materials Research Bulletin 39 (2004) 1993–1998.
[19] Y.M. Kan, G.J. Zhang, P.L. Wang, Journal of the European Ceramic Society 28 (2008) 1641–1647.
[20] P. Pookmanee, P. Uriwilast, S. Phanichpant, Ceramics International 30 (2004) 1913–1915.
[21] P. Pookmanee, P. Boonphayak, Ceramics International 30 (2004) 1917–1919.
[22] Z.H. Chen, Y. Yang, J.T. Li, et al. Journal of Alloys and Compounds 433 (1–2) (2007) 328–331.
[23] Z.H. Chen, J.T. Li, J.J. Xu, et al. Ceramics International 34 (2008) 1709–1712.
[24] Q.Y. Tang, Y.G. Li, Y.M. Kan, et al. Journal of Inorganic Materials 22 (2007) 595–598.
[25] X.Q. Chen, H.Y. Qi, Y.J. Qi, et al. Physics Letters A 346 (2005) 204–208.
[26] Y.M. Kan, X.H. Jin, G.J. Zhang, et al. Journal of Materials Chemistry 14 (2004) 3566–3570.