Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 38S (2012) S407–S410
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Dense $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramics prepared by spark plasma sintering

Juan Li *, Yi Sheng Cai, Yuan Yuan Che, Zhi Hui Chen, Zheng Zhou, Bin Fu, Jia Wei Sheng

College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 310014, China

Available online 12 May 2011

Abstract

$Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramics have attracted much attention due to its interesting dielectric and magnetic properties. However, the $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramics prepared by the conventional solid state reaction method have a maximum density of about 60% of the theoretical density. Decomposition at temperatures higher than 850 °C precluded the preparation of a more highly dense sample. In the present research, dense ferroelectric $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramics with a density of more than 97% of the theoretical one were prepared by spark plasma sintering. XRD data shows that $Bi_3Fe_{0.5}Nb_{1.5}O_9$ has an orthorhombic Aurivillius-type structure.

Keywords: A. Sintering; Aurivillius-type structure; $Bi_3Fe_{0.5}Nb_{1.5}O_9$; Dense ceramics

1. Introduction

Multiferroic materials which simultaneously exhibit at least two ferroic orders (ferroelectric, ferromagnetic, or ferroelastic) have attracted considerable attention due to their interesting physics and exciting potential for applications in multifunctional devices [1–3]. However, multiferroic single phase compounds are rare due to the mutual exclusive of the ferroelectric ordering and magnetic ordering [4–6]. In recent years, several Aurivillius-type layered phases such as $Bi_8Fe_4Ti_3O_{24}$, $Bi_5FeTi_3O_{15}$ and $Bi_6Fe_2Ti_3O_{18}$, which contain a regular stacking of $[Bi_2O_2]^{2+}$ slabs and perovskite-like $[A_{n-1}B_nO_{3n+1}]^{2-}$ blocks, $n[BO_6]$ octahedra in thickness [7], have been reported to display simultaneous electrical and magnetic ordering [8,9]. For example, dynamic magnetoelectric (ME) measurement of Aurivillius-type compound $Bi_8Fe_4Ti_3O_{24}$ at room temperature and at 77 K exhibited a nonlinear output signal [8].

In the system of Bi_2O_3–Fe_2O_3–Nb_2O_5, a new ternary phase $Bi_3Fe_{0.5}Nb_{1.5}O_9$ was observed [10,11]. This oxide adopted an Aurivillius-type structure with non-centrosymmetric space group symmetry $A2_1am$, where the [(Fe, Nb)O_6] octahedra exhibited tilting and distortion to accommodate the bonding requirement of the Bi cations located in the perovskite double layers [11]. So analogous to other Aurivillius-type compounds exhibit ferroelectricity, $Bi_3Fe_{0.5}Nb_{1.5}O_9$ has a ferroelectric phase transition near 250 °C. On the other hand, the magnetic measurement indicated it have non-Curie–Weiss-type behavior between 6 and 300 K.

However, $Bi_3Fe_{0.5}Nb_{1.5}O_9$ began to decompose at temperatures above 850 °C, which made it very difficult to prepare dense ceramics for electrical and magnetic measurements. Lufaso et al. [11] indicated that the pellet density of $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramic sintered at 850 °C for 550 h by solid state reaction method was only 60% of the theoretical density. So preparation of dense $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramic with single phase is of great important and interesting.

Recently, spark plasma sintering (SPS) has been used widely as a low temperature and rapid sintering method in the past decade [12,13]. SPS is a process that uses microscopic electrical discharge between particles under pressure. Ceramics can be sintered to high densities by SPS at relatively low temperatures (several hundreds of degrees Celsius lower than that of conventional sintering) for very short time (typically a few minutes). SPS has been widely investigated to prepare metastable phase ceramics, composites, nanostructure ceramics, transparent ceramics, and so on [14–16]. With the merit of low sintering temperature, SPS seems to be a promising process for the preparation of dense $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramic with single phase because a sintering temperature lower than the decomposition temperature can be expected for SPS.

* Corresponding author. Tel.: +86 571 88320620; fax: +86 571 88320620.
E-mail address: juanli@zjut.edu.cn (J. Li).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.05.021

In this paper, the preparation of $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramics by SPS was investigated. The density and microstructures of $Bi_3Fe_{0.5}Nb_{1.5}O_9$ prepared by SPS were compared with that of the sample prepared by the conventional solid state reaction method.

2. Experimental procedures

High purity Fe_2O_3 (99%), Bi_2O_3 (99.9%) and Nb_2O_5 (99.9%) were used as raw materials. Stoichiometric mixture of the raw powders with nominal composition of $Bi_3Fe_{0.5}Nb_{1.5}O_9$ were grounded in distilled water for 24 h in a ball mill with ZrO_2 balls. The grounded powders were dried and calcined at 800 °C for 2 h. After re-grinding, the calcined powders were placed in a graphite die and spark plasma sintered at 700 °C and 800 °C for 5 min under in a vacuum of 6 Pa with an SPS apparatus (SPS-1050, SPS Systex Inc., Kanagawa, Japan), respectively. During the period of heating and soaking, a pressure of 30 MPa was applied to the sample. After sintered, the samples were heat treated at 700 °C for 2 h.

For comparison, $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramics were also prepared by solid state reaction method. The calcined powders were pressed into cylindrical compacts of 12 mm in diameter and 1–2 mm in thickness under a pressure of 98 MPa with the addition of 5 vol% polyvinyl alcohol as binders. These compacts were then sintered at the temperatures of 800–900 °C for 3 h.

Densities of the sintered samples were measured by the dimensional method for the polished samples. The crystalline phases were characterized by powder X-ray diffraction (RIGAKU D/max 2550 PC, Rigaku Co., Tokyo, Japan) with CuKα radiation. The microstructures of the samples were evaluated with scanning electron microscopy (JSM-5610LV, JEOL, Tokyo, Japan).

3. Results and discussion

The relative densities of the $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramics sintered by the conventional solid state reaction method and the spark plasma sintering process were shown as a function of sintering temperature in Fig. 1. For the samples prepared by the conventional solid state reaction method, the bulk density increased with increasing sintering temperature to 850 °C and then decreased. The relative density of samples sintered at 850 °C was about 97% (the theoretical density of $Bi_3Fe_{0.5}Nb_{1.5}O_9$ was 8.257×10^3 kg/m^3). This is different from the result reported by Lufaso et al. [11]. It may be because we applied a second grinding, longer grinding time (24 h) and a high forming pressure during solid state reaction preparation, which may make a contribution to higher density. On the other hand, the density of $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramics sintered by SPS at a low temperature of 700 °C for 5 min under a pressure of 30 MPa was 97% of the theoretical density, and increased to 98.2% when the sample was spark plasma sintered at 800 °C.

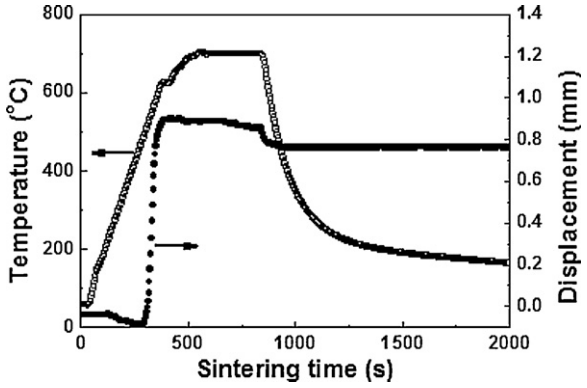

Fig. 2. Shrinkage curve and sample's temperature as a function of sintering time in spark plasma sintering of $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramics.

Fig. 2 shows the sintering behavior of the $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramic spark plasma sintered at 700 °C for 5 min. Small thermal expansion was observed with increasing the temperature from room temperature to about 500 °C. The shrinkage

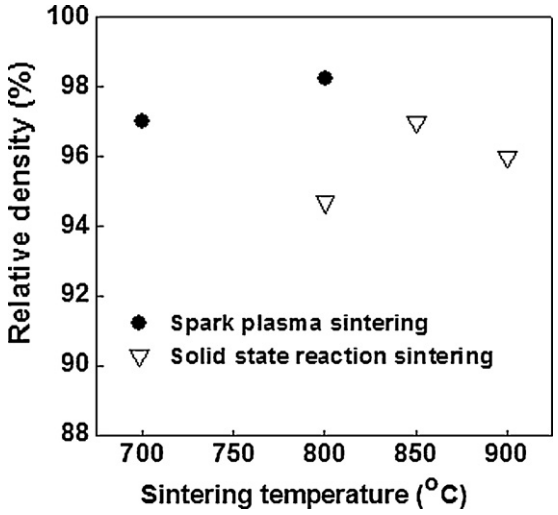

Fig. 1. Densities of $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramics prepared by conventional sold state reaction method and spark plasma sintering.

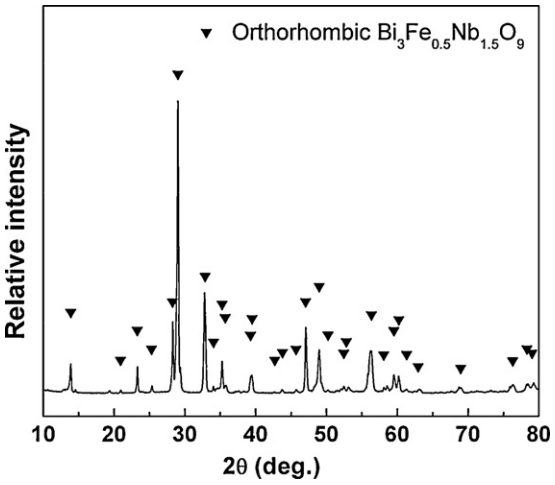

Fig. 3. X-ray diffraction pattern of $Bi_3Fe_{0.5}Nb_{1.5}O_9$ powders calcined at 800 °C for 2 h.

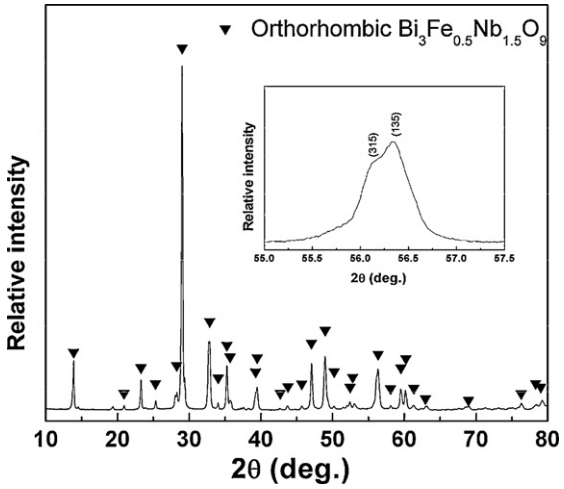

Fig. 4. X-ray diffraction pattern of the $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramic spark plasma sintered at 700 °C for 5 min and than heat treated at 700 °C for 2 h. The inset shows the splitting of the (3 1 5)/(1 3 5) reflections near 56° 2θ, which is indicative of orthorhombic symmetry.

initiated at about 480 °C, and increased rapidly as the temperature increased from 480 °C to 600 °C. The shrinkage stopped when the temperature increased over 650 °C, suggesting that the densification almost completed at temperatures below 700 °C. Compared with the density results of samples prepared by the conventional sintering method, the densification temperature of SPS was about 150 °C lower than that of the conventional sintering method. This can be attributed to the microscopic electric discharge between particles and the application of mechanical pressure during the SPS process.

Fig. 3 shows the powder X-ray diffraction pattern of the $Bi_3Fe_{0.5}Nb_{1.5}O_9$ powders calcined at 800 °C for 2 h. The JCPDS file No. 39-0233 reported for Bi_3TiNbO_9 [16] was used to index the structure of $Bi_3Fe_{0.5}Nb_{1.5}O_9$ because the ionic radii of Fe^{3+} and Nb^{5+} are similar and the crystal structure of these two compounds were very similar. All the peaks were indexed to be an orthorhombic Aurivillius-type structure and no secondary phase was observed. The powder X-ray diffraction pattern of the $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramics sintered at 700 °C for 5 min and heat treated at the same temperature for 2 h are shown in Fig. 4. The $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramics are well crystallized and were identified as a single phase with agreement of the JCPDS file No. 39-0233. The inset to Fig. 2 shows the splitting of the 3 1 5/1 3 5 reflections near 56° 2θ, indicative of orthorhombic symmetry. So, the dense $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramics in a single orthorhombic phase were obtained by SPS at 700 °C for 5 min and heat treated at 700 °C for 2 h.

Fig. 5(a) and (b) shows the SEM micrographs on the fracture surfaces of the $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramics prepared by the SPS process, while Fig. 5(c) and (d) shows the micrographs of samples prepared by the conventional sintering method. Compared with the spark plasma-sintered sample, the sample prepared by the conventional method showed considerable pores and larger but inhomogeneous grains. In addition, some needle-like grains were observed in the micrographs, indicating small amount of the secondary phase in the sample prepared by the conventional sintering method.

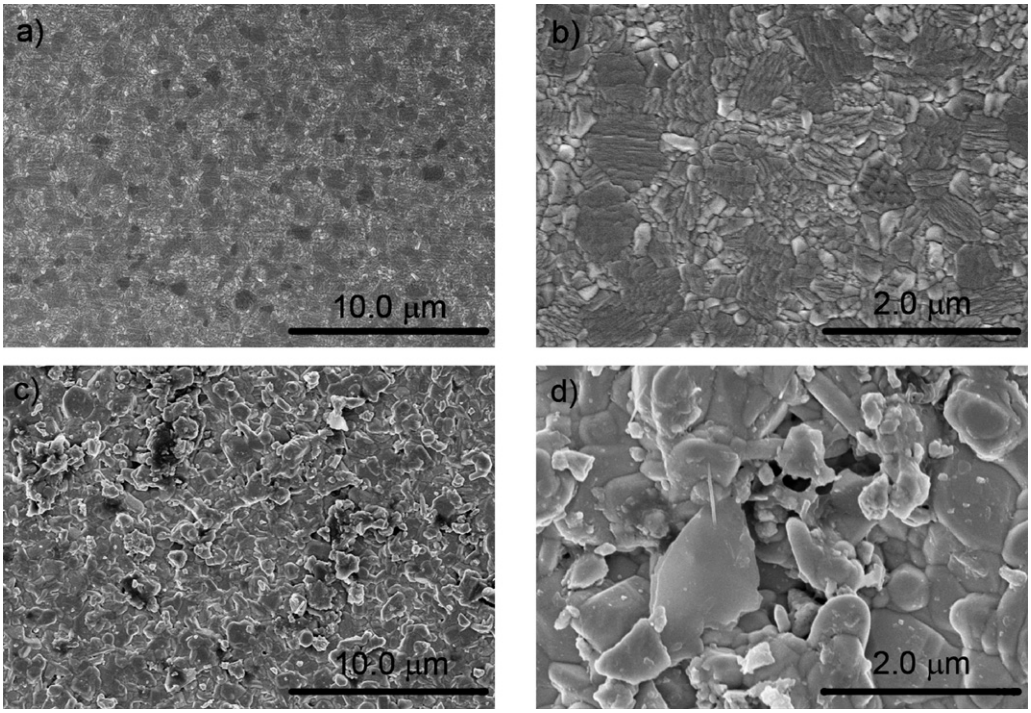

Fig. 5. SEM micrographs of the fracture surfaces of $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramic (a), (b) spark plasma sintered at 700 °C for 5 min and heat treated at 700 °C for 2 h; (c) and (d) conventional sintered at 800 °C for 3 h.

4. Conclusions

Synthesis of $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramics in a single orthorhombic phase by spark plasma sintering was investigated. Dense $Bi_3Fe_{0.5}Nb_{1.5}O_9$ ceramics with a relative density of over 97% have been spark plasma sintered at 700 °C for 5 min and then heat treated at 700 °C for 2 h. Compared with the ceramics prepared by solid state reaction method, the ceramics prepared by SPS at lower temperatures have a more homogeneous and denser microstructure, which indicates SPS is a promising process for preparing hard-to-sinter ceramics.

Acknowledgement

The present work was supported by Qianjiang Project of Zhejiang Province under Grant No. 2009R10038.

References

[1] W. Eerenstein, N.D. Mathur, J.F. Scott, Multiferroic and magnetoelectric materials, Nature 442 (2006) 759–765.
[2] J. Wang, J.B. Neaton, H. Zheng, V. Nagarajan, S.B. Ogate, B. Liu, D. Viehland, V. Vaithyanathan, D.G. Schlon, U.V. Waghmare, N.A. Spaldin, K.M. Rade, M. Wuttig, R. Ramesh, Epitaxial $BiFeO_3$ multiferroic thin film heterostructures, Science 299 (2003) 1719–1722.
[3] N. Hur, S. Park, P.A. Sharma, J.S. Ahn, S. Guha, S.-W. Cheong, Electric polarization reversal and memory in multiferroic materials induced by magnetic fields, Nature 429 (2004) 392–395.
[4] N.A. Hill, Why are there so few magnetic ferroelectrics, The Journal of Physical Chemistry B 104 (29) (2000) 6694–6709.
[5] S.-W. Cheong, M. Mostovoy, Multiferroics: a magnetic twist for ferroelectricity, Nature Materials 6 (2007) 13–20.
[6] K.F. Wang, J.M. Liu, Z.F. Ren, Multiferroicity: the coupling between magnetic and polarization orders, Advances in Physics 58 (4) (2009) 321–448.
[7] B. Aurivillius, Mixed bismuth oxides with layer lattices, Arkiv for Kemi 1 (1949) 463–480.
[8] A. Srinivas, D.W. Kim, K.S. Hong, S.V. Suryanarayana, Study of magnetic and magnetoelectric measurements in bismuth iron titanate ceramic–$Bi_8Fe_4Ti_3O_{24}$, Materials Research Bulletin 39 (2004) 55–61.
[9] A. Srinivas, S.V. Suryanarayana, G.S. Kumar, M.M. Kumar, Magnetoelectric Measurements on $Bi_5FeTi_3O_{15}$ and $Bi_6Fe_2Ti_3O_{18}$, Journal of Physics-Condensed Matter 11 (1999) 3335–3340.
[10] M.W. Lufaso, T.A. Vanderah, I.M. Pazos, I. Levin, R.S. Roth, J.C. Nino, V. Provenzano, P.K. Schenck, Phase formation, crystal chemistry, and properties in the system Bi_2O_3–Fe_2O_3–Nb_2O_5, Journal of Solid State Chemistry 179 (2006) 3900–3910.
[11] M.W Lufaso, W.A. Schulze, S.T. Misture, T.A. Vanderah, Crystal structure, magnetic, and dielectric properties of Aurivillius-type $Bi_3Fe_{0.5}Nb_{1.5}O_9$, Journal of Solid State Chemistry 180 (2007) 2655–2660.
[12] M. Nygren, Z. Shen, On the preparation of bio-, nano- and structural ceramics and composites by spark plasma sintering, Solid State Sciences 5 (2003) 125–131.
[13] Y. Gao, Y.J. Wu, X.M. Chen, J.P. Cheng, Y.Q. Lin, Y. Ma, Dense YMn_2O_5 ceramics prepared by spark plasma sintering, Journal of the American Ceramic Society 91 (2008) 3728–3730.
[14] T. Takeuhi, M. Tabuchi, H. Kageyama, Y. Suyama, Preparation of dense $BaTiO_3$ ceramics with submicrometer grains by spark plasma sintering, Journal of the American Ceramic Society 82 (1999) 939–943.
[15] C.L. Song, Y.J. Wu, X.Q. Liu, X.M. Chen, K. Kakegawa, Dielectric properties of $La_{1.75}Ba_{0.25}NiO_4$ ceramics prepared by spark plasma sintering, Journal of Alloys and Compounds 490 (2010) 1–2.
[16] J.G. Thompson, A.D. Rae, R.L. Withers, D.C. Craig, Revised structure of Bi_3TiNbO_9, Acta Crystallographica B 47 (1991) 174–181.