Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 7291–7296

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Review paper

Syntheses of bismuth titanate templates obtained by the molten salt method

M.G.A. Ranieri[a,1], E.C. Aguiar[a,1], M. Cilense[a,1], A.Z. Simões[b,*], J.A Varela[a,1]

[a]São Paulo State University, UNESP, Chemistry Institute, 14800-900 Araraquara-SP, Brazil
[b]São Paulo State University, UNESP, Engineering Faculty, 12516-410 Guaratinguetá-SP, Brazil

Received 19 December 2012; received in revised form 26 February 2013; accepted 27 February 2013
Available online 15 March 2013

Abstract

Bismuth titanate templates ($Bi_4Ti_3O_{12}$) were synthesized by the molten salt method in Na_2SO_4 and K_2SO_4 fluxes, using an amorphous $Bi_4Ti_3O_{12}$ precursor and a mechanically mixed $Bi_2O_3+TiO_2$ mixture as the starting materials. The templates were characterized by means of X-Ray Diffraction, FT-IR, FT-Raman, FEG-SEM and TEM. The templates are free of secondary phases and present orthorhombic structure with orientation in the *c*-plane. FT-IR suggests no traces of sulfate groups revealing that the molten salt synthesis was beneficial for elimination of inorganic species and for the arrangement of individual nanocrystals into ordered lattices. FEG-SEM analyses of BIT templates revealed that most of the grains were homogeneous with a length of 3.1 μm and a width of 0.3 μm and had plate-like morphology. TEM investigations show that the *c*-axis of the perovskite units is parallel to the thickness direction of the grains and no liquid-phase was formed during BIT phase formation.

Keywords: A. Ceramics; B. Chemical syntheses; B. Powder metallurgy; C. X-ray diffraction.

Contents

1. Introduction

Bismuth titanate ($Bi_4Ti_3O_{12}$) is a well-known member of the bismuth oxide layer structure ferroelectrics. It is a candidate for high-temperature piezoelectric applications, memory storage, and optical displays because of its high Curie temperature of 675 °C [1–3] and electrooptic switching behavior [4–12,13]. Its structure is formed by Bi_2O_2 layers separated by $Bi_2Ti_3O_{12}$ layer with orthorhombic structure at room temperature. Due to the fact that it is a lead free structure, it has attracted much attention in recent years [1–4,14,15]. The pseudo-orthorhombic BIT unit possesses the lattice parameters of a=0.5450, b=0.54059, and c=3.2832 nm, and exhibits spontaneous polarizations P_s=50 and 4 μC/cm^2 along *a*- and *c*-axis, respectively [13–16]. During the sintering process, Bi_2O_3 can volatilize and then affect the ferroelectric properties of $Bi_4Ti_3O_{12}$ phase. As Bi_2O_3 is an ionic conductor, it is necessary to control its loss by adding excess of bismuth during thermal treatment due to the fact that its electrical

*Corresponding author. Tel.: +55 12 31232765; fax: +55 12 3123 2800.
E-mail addresses: gabi.ranieri@ig.com.br (M.G.A. Ranieri), alezipo@yahoo.com (A.Z. Simões).
[1]Tel.: +55 16 3301 6643; fax: +55 16 3301 6692.

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.02.091

properties such as remanent polarization, coercive field, dielectric permittivity and Curie temperature (T_c) are highly affected [1,2,16].

The unit cell of this compound is orthorhombic allowing both 180° domain switching (switching in sign of the *a* axis) and 90° domain switching (interchanging of the *a* and *b* axes). In typical bismuth titanate textures arising from hot pressing or tape casting, the possible polarization directions and ferroelastic distortions are aligned in a plane normal to the axis of fiber symmetry. The main objective of the orientation engineering is to obtain *a–b* plane oriented BIT ceramics. Highly *c*-plane orientated BIT-type ceramics are reported by mechanical force, but the texture degree of *a–b* plane is not mentioned [18]. It is also reported that the high electrical conductivity in the *a–b* plane makes poling difficult [19]. The main focus of this work is to prepare high-purity and anisotropic BIT crystals as growth templates by the molten salt method and evaluate its structure, morphology and purity [6].

Small proportions of templates are used (5–10 wt%) for making textured ceramics. In this process, the orientation of the texture ceramic is determined by aligning a small percentage of anisometric grains. A mixture of the larger "template" particles and fine powder is oriented by a shear process (e.g., tape casting or extrusion) and sintered to produce a dense ceramic. Subsequent grain growth increases the orientation of the ceramic by the preferential growth of the template particles to yield a highly textured ceramic [6].

Platelets-shaped particles of BIT, made by molten salt synthesis, can be oriented by tape casting. The platelets are apparently single crystals (monoclinic at room temperature) with the *c*-axis perpendicular to the major face. Appropriate processing orients the crystals along the *c*-axis, face to face [12,20]. Molten salt synthesis is a suitable method for synthesizing oxide powders with anisotropic particle morphologies [21]. Kimura et al. [21] conducted a study on the influence of the types of salts on the morphology and size of templates (BIT). For the molten salt synthesis, the templates were obtained using a mixture $NaCl+KCl+Na_2SO_4$ and also $Li_2SO_4 \cdot H_2O$. In the fused salt synthesis of $Bi_4Ti_3O_{12}$ and Bi_2WO_6 the shape of particles is determined by two processes, the formation of compound particles and their growth. In the former process, plate-like particles were formed in the chloride flux irrespective of the oxides but the particle shape depended on the oxide in the sulfate flux. In the latter process, however, the particles with well-developed (001) faces were formed regardless of the oxide and flux systems. The final morphologies characterized by plate like ($Bi_4Ti_3O_{12}$ from both fluxes and Bi_2WO_6 from chloride flux) or oblate (Bi_2WO_6 from sulfate flux) particles would indicate that both the chloride and sulfate fluxes have a (001)-stabilizing effect. The chloride flux appears to have a larger stabilizing effect than the sulfate flux, because plate-like primary particles were formed during the formation process. Kan et al. [1] reported that the mole ratio (*M*) of the sulfate flux to $Bi_4Ti_3O_{12}$ showed a remarkable influence on the growth rate of $Bi_4Ti_3O_{12}$ platelets. When *M* was increased from 7.9 to 15.8 and 23.7, the growth rate of $Bi_4Ti_3O_{12}$ particles declined. The main focus of this work is to prepare high-purity and anisotropic BIT crystal as growth templates by the molten salt methods and evaluate its structure, morphology and purity.

2. Experimental

$Bi_4Ti_3O_{12}$ powders (with 10 wt% of bismuth excess) were prepared by a solid state reaction. In this work, 10 wt% of bismuth excess was added to minimize bismuth loss during thermal treatment. Without this additional bismuth the pure phase could not be obtained, as was reported in the literature [22]. The following reagents were employed: Bi_2O_3 (98.0%, Vetec), TiO_2 (98.5%, Labsynth), Na_2SO_4 (99.0%, Labsynth) and K_2SO_4 (99.0%, Labsynth).

The precursor powder was obtained by milling ($Bi_2O_3+TiO_2$) for 2 h in a high energy mill followed by calcination at 500 °C/1 h. The resultant powder was amorphous bismuth titanate. $Bi_4Ti_3O_{12}$ templates were prepared by a molten-salt method [1]. Amorphous $Bi_4Ti_3O_{12}$ powder and Na_2SO_4/K_2SO_4 eutectic mixture were mixed in a sealed alumina crucible and heated at 1000 °C for 0.5 h in a ratio of $2BIT:1Na_2SO_4:1K_2SO_4$. After slowly cooling to room temperature, the reaction product was separated by centrifugation and washed several times with hot de-ionized water to remove the sulfate salts, and then dried at 100 °C.

2.1. Characterization

Powders were first analyzed by X-ray diffraction (XRD) for phase determination. X-ray diffraction data were collected with a Rigaku 20-2000 diffractometer under the following experimental conditions: 40 kV, 30 mA, $20° \leq 2\theta \leq 60°$, $\Delta 2\theta = 0.02°$, λCu k_α monochromatized by a graphite crystal, divergence slit = 2 mm, reception slit = 0.6 mm, and step time = 10 s. For comparison, a standard XRD pattern of BIT phase obtained from the Crystallographica Search-Match is presented. Infrared spectroscopy (FT-IR) was employed to investigate the composition of the templates. Measurements were made by diffuse reflectance (DRIFT) directly from the sample without dilution in KBr. The equipment is an FTIR Vertex 70 (Bruker), 4000–400 spectra. Raman spectroscopy is a widely used method for characterizing materials. This technique allows us to identify the types of links and provide information on the degree of disorder of the crystal lattice. In this work, measurements were performed on a Fourier transform spectrometer, RFS 100/S, excited by Nd-YAG laser. The morphology of as-prepared samples was observed using a high resolution field-emission gun scanning electron microscopy FEG-SEM (Supra 35-VP, Carl Zeiss, Germany). Specimens for TEM were obtained by drying droplets of as-prepared samples from an ethanolic dispersion which had been sonicated for 5 min onto 300 mesh Cu grids. TEM, HRTEM images and SAD patterns were then taken at an accelerating voltage of 200 kV on a Philips model CM 200 instrument. Three measurements were performed to determine the average size of templates in a field emission gun microscope. $Bi_4Ti_3O_{12}$ templates obtained were plate-like with a width of (0.3 ± 0.2) μm and a length of (3.1 ± 1.7) μm. All measurements were taken at room temperature.

3. Results and discussion

The crystallinity and phase formation of bismuth titanate templates calcined at 1000 °C—0.5 h was evaluated by X-ray diffraction (Fig. 1a). The templates are free of secondary phases and present orthorhombic structure. The peaks are indicative of a textured phase with orientation in the *c*-plane, mainly characterized by higher intense peak (*hkl*—00l). Our XRD results are in agreement with the data reported in the Crystallographic Search-Match program (Fig. 1b). We can infer that the molten salt synthesis allows to obtain BIT templates free of impurities and reduce synthesis time. The main differences can be related to the preparation method, synthesis conditions (heat treatment temperature, time), lattice distortion, residual stresses in the lattice and/or structural defects. The main peaks are *c*-axis oriented (008), (0010), (0012), (0014), (0016) e (0018) [1,2,23].

Fig. 2 shows the FT-IR spectrum of the bismuth titanate templates produced by the molten salt synthesis. The main band characteristic of the oxygen–metal bond was observed in the region 450–640 cm^{-1}. There was, however, a vibration band noted that is associated to the deformation of O–H bonds near 1680 and 3400 cm^{-1}. This is attributed to water adsorbed at the powders surface when the sample was in contact with the environment. No traces of sulfate groups are evidenced in the FT-IR spectra suggesting elimination of such groups during the cleaning of the particles being not chemically bonded to the surface of the BIT nanocrystals. This is probably the result of reactions forming chemical bonds between the nanocrystal surface and the inorganic molecules employed in the molten salt synthesis. This results in the unique reaction conditions of supercritical water which are essential for the perfect elimination of inorganic species and for the arrangement of individual nanocrystals into ordered superlattices.

Raman scattering has proven to be a valuable technique to obtain information about local structures within materials. To confirm the formation of BIT templates, FT-Raman spectrum was obtained (see Fig. 3). The main modes located at 95, 120, 191, 226, 268, 327, 354, 419, 455, 537, 562, 616, and 849 cm^{-1} are characteristics of $Bi_4Ti_3O_{12}$ single crystal [17,18] and are in agreement with those reported in the literature [19–27]. Usually, higher wavenumber phonon modes can be attributed to vibrations of Ti–O atoms inside the perovskite layer while lower wavenumber phonon modes to vibrations of Bi–O atoms within the Bi_2O_2 layer. The modes located at 262 and 268 cm^{-1} are relative to distortions in octahedral TiO_6 [28]. The modes located at 537 cm^{-1} and 849 cm^{-1} are correspond to stretching vibrations and *c*-axis symmetric stretching of TiO_6 octahedra, respectively. Yau et al. [29] observed that excess of bismuth leads to better stability of the Bi_2O_2 layer instead of perovskite phase being incorporated on it [30].

FEG-SEM micrographs of BIT templates at different magnifications are shown in Fig. 4a–c. According to the image, most of the grains are homogeneous with a length of 3.1 μm, a width of 0.3 μm and a plate-like morphology. Aggregation between the particles is not evident and monodispersed particles are

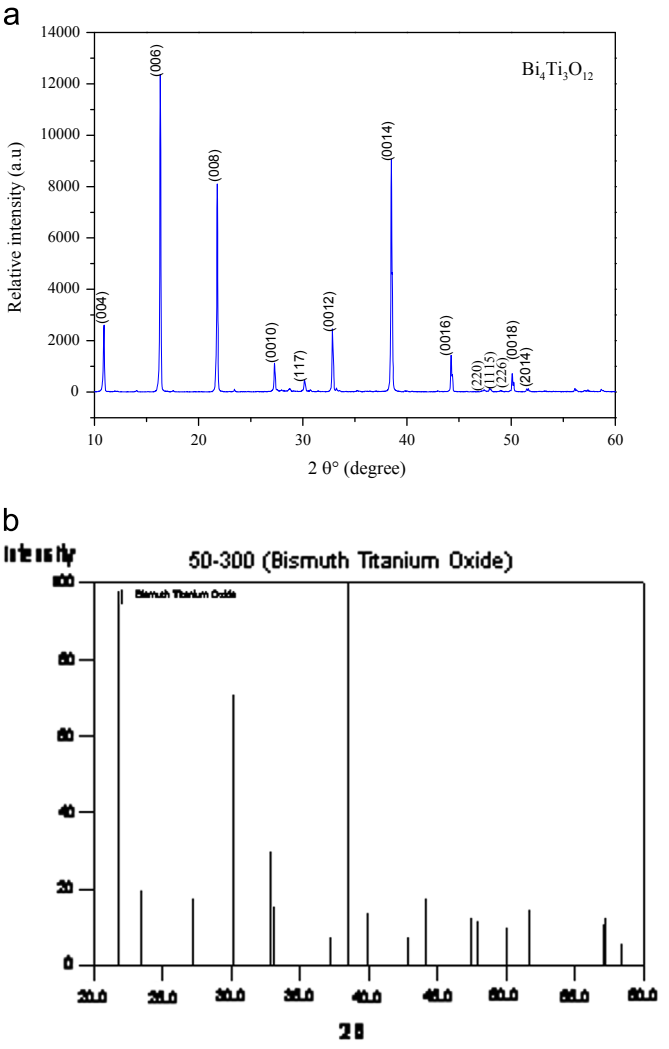

Fig. 1. (a) X-ray diffraction pattern of BIT templates obtained by the molten salt method at 1000 °C for 0.5 h and (b) X-ray diffraction pattern of BIT phase obtained in the Crystallographic Search-Match program.

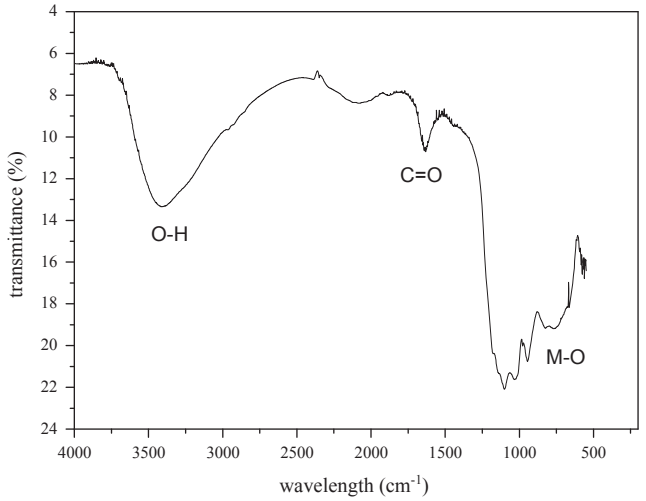

Fig. 2. FT-IR spectrum of BIT templates obtained by the molten salt method at 1000 °C for 0.5 h.

observed. The low degree of agglomeration indicated that the amorphous phase obtained by the solid state reaction was transformed to BIT templates and that van der Waal's force is absent in this inorganic template. One can see that plate-like grains are piled up close to each other. The plate-like shapes of the grains are related to the layered perovskite structure of BIT. There is no evidence of liquid-phase indicating that the molten salt synthesis allows obtaining BIT templates distributed in a nanometric matrix. The abnormal/discontinuous grain particle, called exaggerated grain particle, comes from the fact that some particles grow faster than others with increasing sintering temperature in materials with high anisotropy in interfacial energy. The effective collision rates between particles by molten salt synthesis favors an anisotropic growth caused by the differences in the surface energies on the different crystallographic faces [1–2].

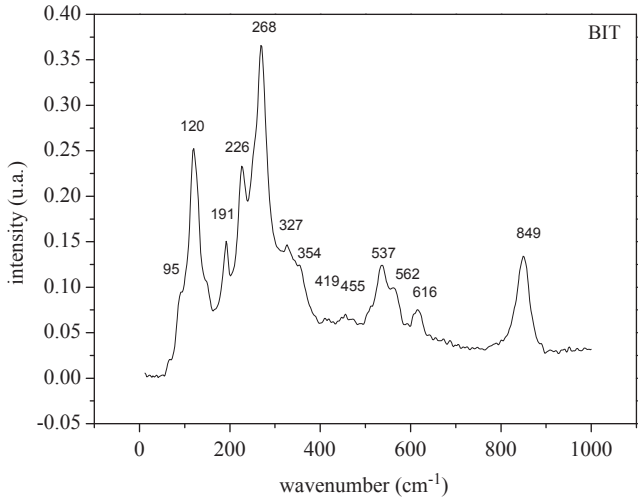

Fig. 3. FT-Raman spectrum of BIT templates obtained by the molten salt method at 1000 °C for 0.5 h.

TEM investigations show that the *c*-axis of the perovskite units is parallel to the thickness direction of the grains. BIT templates reveal particle size length in the range of (3.1±1.7) μm (Fig. 5a). The resultant particles have a plate-like shape with approximate width of (0.3±0.2) μm being originated from the high anisotropy of BIT crystal structure (Fig. 5b). These results indicate that when the particle size increases rapidly in the formation process the growth rate of each crystal face determines the outer shape of particles and furthermore, when the particle size increases slowly in the growth process the main surface consists of the facet with a minimum interfacial energy. Bismuth titanate templates showed weak agglomerates indicating no adsorption of deionized water molecules on the template surfaces, so that hydrogen bonds cannot be formed between approaching particles. The salts used during the synthesis were shown to be most effective in dehydrating the adsorbed water and decreasing the hydrogen bonding effect leaving weakly agglomerated BIT. Crystal defects (such as ferroelectric domains) are frequently observed in the BIT templates and will be studied by Piezoresponse Force Microscopy (PFM) briefly.

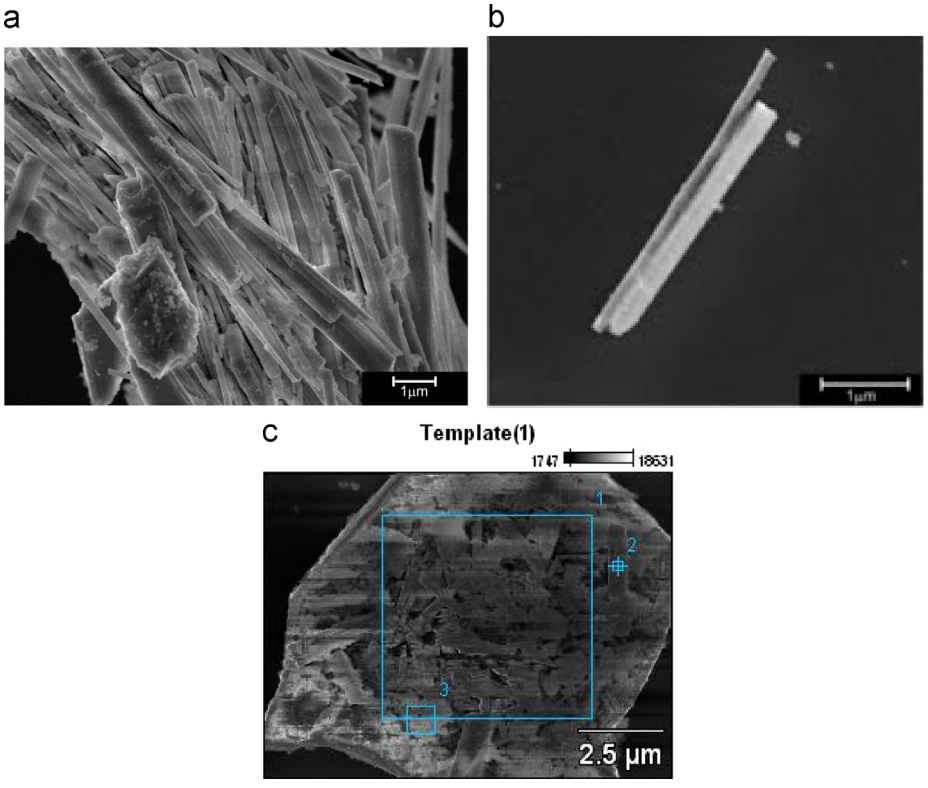

Fig. 4. FEG-SEM micrographs of BIT templates at different magnifications (a), (b) and (c) obtained by the molten salt method at 1000 °C for 0.5 h.

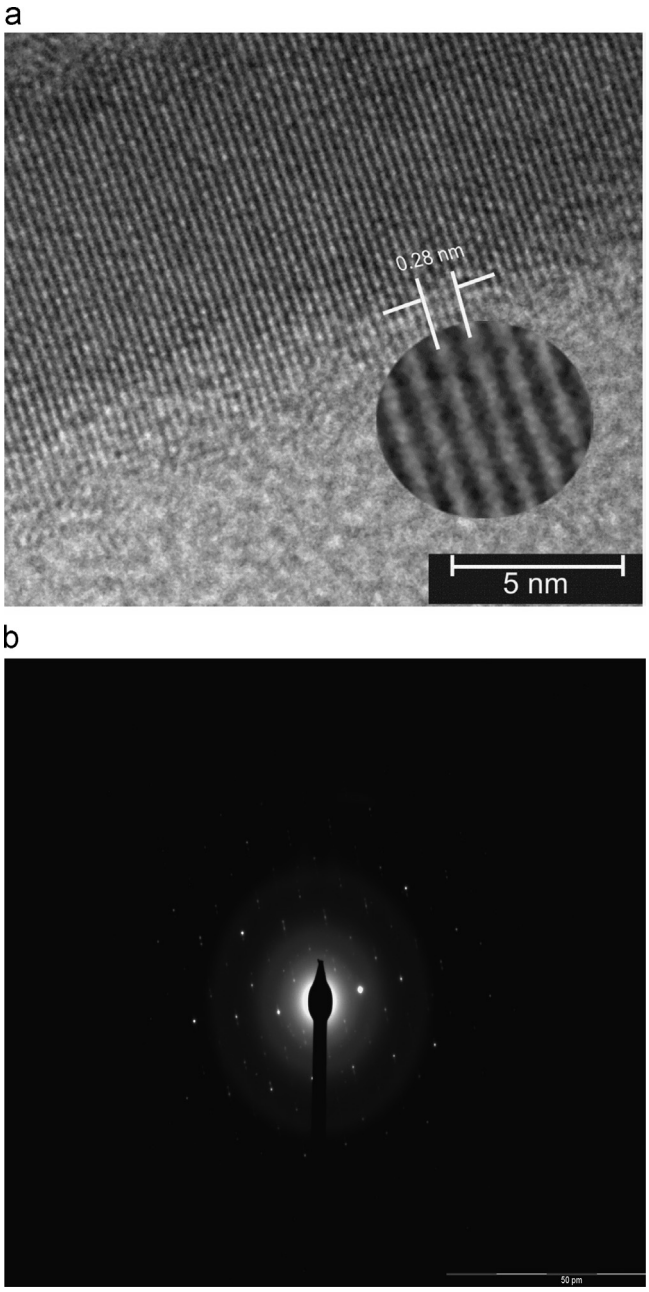

Fig. 5. (a) TEM images of BIT templates obtained by the molten salt method at 1000 °C for 0.5 h and (b) SAD micrograph of BIT templates obtained by the molten salt method at 1000 °C for 0.5 h.

4. Conclusions

By adopting the molten salt method it is possible to obtain bismuth titanate templates with the *c*-axis orientation free of secondary phases. No traces of sulfate groups are evidenced in the FT-IR spectra suggesting elimination of inorganic species during BIT phase formations. FEG-SEM analysis has shown that most of the grains are homogeneous with a length of (3.1±1.7) μm. Aggregation between the particles is not evident indicating that van der Waals force is absent in this inorganic template. TEM analysis reveals that the resultant particles have a plate-like shape with approximately (0.3±0.2) μm width, being originated from the high anisotropy of BIT crystal structure, and that the main surface consists of the facet with a minimum interfacial energy. The molten salt method is a genuine technique to control the morphological and structural properties of templates with short treatment time and making them free of impurities.

Acknowledgments

The authors gratefully acknowledge the financial support of the CNPq.

References

[1] Y. Kan, P. Wang, Y. Li, Y. Cheng, D. Yan, Fabrication of textured bismuth titanate by templated by templated grain growth using aqueous tape casting, Journal of the European Ceramic Society 23 (2003) 2163–2169.
[2] Z.Z. Lazaveric, N.Z. Romcevic, M. Todoroviv, B.D. Stojanovic, Structural and ferroelectrical properties of bismuth titanate ceramic powders prepared by mechanically assisted synthesis, Science of Sintering 39 (2007) 177–184.
[3] M. Suzuki, Review on future ferroeletric nonvolatile memory: FeRAM, Journal of the Ceramic Society Japan 103 (1995) 1088.
[4] E.C. Aguiar, A.Z. Simões, C.R. Foschini, L.A. Perazolli, R.E. Mistler, E. Longo, J.A. Varela, Electrical properties of textured niobium-doped bismuth titanate ceramics, Journal of the American Ceramic Society (2012) 1–7.
[5] Y. Haixue, J. Reece, Effect of texture on dieletric properties and thermal depoling of $Bi_4Ti_3O_{12}$ ferroeletrics ceramics, Journal of Applied Physics 100 (2006) 76–103.
[6] J.A. Horn, S.C. Zhang, U. Selvaraj, G.L. Messing, S. Trolier-McKinstry, Templated grain growth of textured bismuth titanate, Journal of the American Ceramic Society 82 (4) (1999) 921–926.
[7] Q. Xiao Bao, L. Hui Zhu, Q. Wei Huang, J. XV, Preparation of texture $Ba_2NaNb_5O_{15}$ ceramics by templated grain growth, Ceramics International 32 (2006) 745–749.
[8] S. Su kim, J. Ki chung, I. Sung-Kim, J. Sung Song, C.J. Kim, W. Jeong Kim, Dielectric properties of ferroelectric $(Ba_{0.6}Sr_{0.4})TiO_3$ thick films prepared by tape casting, Journal of Electroceramics 17 (2006) 451–454.
[9] A. Sanson, R.W. Whatmore, Properties of $Bi_4Ti_3O_{12}$–(Na1/2Bi1/2)TiO_3 piezoelectric ceramics, Japanese Journal of Applied Physics 41 (11) (2002) 7127.
[10] L.B. Kong, J. Ma, W. Zhu, O.K. Tan, Preparation of $Bi_4Ti_3O_{12}$ ceramics via a high-energy ball milling process, Materials Letters 51 (2001) 108–114.
[11] B.D. Stojanovic, C.O. Paiva-Santos, C. Jovalekic, A.Z. Simões, J. A. Varela, Mechanically activating formation of layered structured bismuth titanate, Materials Chemistry and Physics 96 (2006) 471–476.
[12] V.K. Seth, W.A. Schulze, Grain-oriented fabrication of bismuth titanate ceramics and its electrical properties, IEEE Transactions on Ultrasonics, Ferroelectrics and Frequency Control 36 (1989) 1.
[13] Y. Kinemuchi, P.H. Xiang, H. Kaga, K. Watari, Preferred orientation of $Bi_4Ti_3O_{12}$ thick film, Journal of the American Ceramic Society 90 (9) (2007) 2753–2758.
[14] Z.S. Macedo, C.R. Ferrari, A.C. Hernandes, Impedance spectroscopy of $Bi_4Ti_3O_{12}$ ceramic produced by self-propagating high-temperature synthesis technique, Journal of the European Ceramic Society 24 (2004) 2567–2574.
[15] W. Chen, Y. Hotta, T. Tamura, K. Miwa, K. Watari, Effect of section force and starting powders on microstructure of $Bi_4Ti_3O_{12}$ ceramics prepared by magnetic alignment via slip casting, Scripta Materialia 54 (2006) 2063–2068.

[16] P.H. Xiang, Y. Kinemuchi, K. Watari, Preparation of axis-*c*-oriented $Bi_4Ti_3O_{12}$ thick films by template grain growth, Journal of the European Ceramic Society 27 (2007) 663–667.
[17] H. Idink, V. Srikanth, W.B. White, Raman study of low temperature phase transitions in bismuth titanate, $Bi_4Ti_3O_{12}$, Journal of Applied Physics 76 (1994) 1819.
[18] D. Fu, T. Ogawa, T. Suzuki, K. Ishikawa, Thickness dependence of stress in lead titanate thin films deposited on Pt-coated Si, Applied Physics Letters 77 (2000) 1532.
[19] S. Kojima, R. Imaizumi, S. Hamazaki, M. Takashige, Raman scattering study of bismuth layer-structure ferroelectrics, Japanese Journal of Applied Physics 33 (1995) 5559.
[20] T. Takenaka, K. Sakata, Electrical properties of grain-oriented ferroelectric ceramics in some lanthanum modified layer-structure oxides, Ferroelectrics 38 (1981) 769.
[21] T. Kimura, T. Yamaguchi, Advances in ceramics, in: G. Messing, K.S. Mazdiyashi, J.W. McCauley, R.A. Haber (Eds.), Ceramic Powder Science, vol. 21, American Ceramic Society, Westerville, OH, 1987, p. p. 169.
[22] R.M. Silverstein, et al., Identificação espectrométrica de compostos orgânicos, 5 ed., Guanabara Koogan, Rio de Janeiro, 1994.
[23] E.C. Aguiar, Desenvolvimento de cerâmicas texturizadas de titanato de bismuto puro e dopado com nióbio,126, Tese de doutorado, Universidade Estadual Paulista, Instituto de Química, Araraquara, 2009.
[24] R. Zallen, M. Slade, Rigid-layer modes in chalcogenide crystals, Physical Review 9 (1974) 1627.
[25] R. Nicklow, N. Wakabayashi, H.G. Smith, Lattice dynamics of pyrolytic graphite, Physical Review B 5 (1972) 4951–4962.
[26] P.J. Klar, T. Rentschler, Variation of the soft modes with composition in the Raman spectra of charge-compensated series of $n=2$ and 3 Aurivillius phases, Solid State Communications 103 (1997) 341.
[27] U. Balachandran, N.G. Eror, Laser-induced Raman scattering in calcium titanate, Solid State Communications 44 (1982) 815–818.
[28] U. Chon, K.B. Kim, H.M. Jang, G.C. Yi, Fatigue-free samarium-modified bismuth titanate film capacitors having large spontaneous polarizations, Applied Physics Letters 79 (2001) 3137–3139.
[29] C.Y. Yau, R. Palan, K. Tran, R.C. Buchanan, Raman study of Bi site—occupancy effect on orientation and polarization in $Bi_4Ti_3O_{12}$ thin films, Applied Physics Letters 85 (20) (2004) 4714–4716.
[30] C.J. Brinker, G.W. Scherrer, in: Sol–Gel Science, Academic Press, San Diego, 1990 908.