JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 7, July 2007, p. 2262 - 2265

Synthesis of $Bi_4Ti_3O_{12}$ nanoparticles by mechanochemical reaction

Z. Ž. LAZAREVIĆ[a, *], B. D. STOJANOVIĆ[b], N. Ž. ROMČEVIĆ[a]
[a]*Institute of Physics, P.O. Box 68, Belgrade, Serbia*
[b]*Center for Multidisciplinary Studies University of Belgrade, Belgrade, Serbia*

The influence of milling of a mixture of Bi_2O_3 and TiO_2 powders in planetary ball mill on the reaction synthesis of nanosized $Bi_4Ti_3O_{12}$ was studied. The mechanochemical reaction leading to formation of the $Bi_4Ti_3O_{12}$ phase was followed by X-ray diffraction. The $Bi_4Ti_3O_{12}$ phase was first observed after 1 h of milling and its formation was completed after 6 h in case of the Bi_2O_3-TiO_2 mixture. The synthesized $Bi_4Ti_3O_{12}$ has a nanocrystalline structure with a crystallite size of about 15 nm. The thermal treatment of the milled powder at 1000 °C for 12 h led to formation of the $Bi_4Ti_3O_{12}$ crystalline phase.

(Received February 19, 2007; accepted June 27, 2007)

Keywords: $Bi_4Ti_3O_{12}$, Nanocrystalline materials, Mechano-synthesis

1. Introduction

Developments in microelectronic devices have promoted the development of new methods for their preparation. An essential prerequisite for tailoring ferroelectric materials is the possibility of creating a broad range of microstructures, i.e. from amorphous to single crystals.

Beside chemical composition, microstructure has a significant influence on ferroelectric properties. Therefore nanostructured materials exhibit unusual physical and chemical properties, significantly different from those of conventional bulk materials, due to their extremely small grain size or large specific surface area.

$Bi_4Ti_3O_{12}$ is a ferroelectric material with wide applications in the electronic industry, as capacitors, memory devices and sensors [1-3]. Its ferroelectric-to-paraelectric phase transition temperature is near 675^{o}C [4], which give it a potential applicability as a suitable candidate for high temperature piezoelectric device. In addition, BIT is an interesting material that is lead-free and environmental friendly.

Bismuth titanate is the simplest compound in the Aurivillius family that can be presented by the general formula (Bi_2O_2) $[A_{m-1}(B)_mO_{3m+1}]$, which consists of $(Bi_2O_2)^{2+}$ sheets alternating with $(Bi_2Ti_3O_{10})^{2-}$ perovskite-like-layers [5].

$Bi_4Ti_3O_{12}$ ceramics were conventionally prepared by solid-state reaction process, where oxide mixture of Bi_2O_3 and TiO_2 was ball milled, calcined at an intermediate temperature and finally sintered at high temperature [6,7]. The conventional method requires a high calcinations temperature, usually leading to inevitable particle coarsening and aggregation of the $Bi_4Ti_3O_{12}$ powders. The presence of hard particle agglomerates will also result in poor microstructure and properties of the $Bi_4Ti_3O_{12}$ ceramics. Many efforts have been made to avoid this problem by lowering the calcination temperature [8]. The methods reported in the literature to prepare $Bi_4Ti_3O_{12}$ ceramics include chemistry-based preparations, such as precipitation [9], sol-gel [10], hydrothermal [11], and molten salt route [12] and recently mechanically assisted synthesis.

Mechanically activated processes have been recently employed by Benjamin and Gilman to prepare nano-sized oxides and compounds [13]. In many cases, the mechanical technique is superior to both the conventional solid-state reaction and the wet-chemistry-based processing routes for the ceramic powder preparation for several reasons. It uses low-cost and widely available oxides as starting materials and skips the calcinations step at an intermediate temperature, conducting to simplified process [14]. Although mechanical activation has been successful with Pb-based electroceramics of perovskite structure, it has not been much studied for the layered structured compounds, such as $Bi_3Ti_4O_{12}$ ceramics.

The objective of this work is to study the feasibility of $Bi_3Ti_4O_{12}$ formation and ceramics properties obtained from powders prepared by mechanically activating the constituent oxides.

2. Experimental procedures

The mixture of crystalline powders were used as starting material bismuth oxide (Bi_2O_3, Fluka, p.a. 99. 8%) and titanium oxide (TiO_2 anatase, Carlo Erba p.a 99%), commercially available. These oxyde powders exhibited a particle size distribution in the range 2-4 μm for TiO_2 and 1-5 μm for Bi_2O_3. To make a batch required for $Bi_3Ti_4O_{12}$ composition, corresponding amount of Bi_2O_3 and TiO_2 were weighed and loaded into zirconia jars together with zirconia milling balls ~10 mm in diameter. Mechanochemical tretment was performed in air atmosphere in a planetary ball mill (Fritsch Pulverisette 5).

Milling conditions were the following: the mass of the powder was 20 g and the balls-to-powder mass ratio was 20:1, basic disc rotation speed was 317 min^{-1}, rotation speed of disc with jars was 396 min^{-1}. At the expiration of the selected milling times (1, 3, 6 and 12 h) the mill was stopped and small amount of powder was removed from the vial for examination. X-ray diffraction analysis of the powders treated for various periods of the milling time was done by a Philips PH 1050 automatic diffractometer with CuK_α graphite-monochromatized radiation (λ=0.15418 Å).

Room temperature Raman spectra in spectral range from 100 to 900 cm^{-1}, in back scattering geometry, were obtained by Micro Raman Chromex 2000 using 532 nm of a frequency doubled Nd:YaG laser. The spectral resolution was 1 cm^{-1}. The average power density on the sample was about 2 mW mm^{-2}.

Specific surface areas were determined based on isotherms of nitrogen adsorption using the BET method (Micrometrics ASAP 2010). The samples were prepared by pressing at 210 MPa and sintered inside a box furnace with heating rate of 5°C/min from room temperature up to 1000°C for 4 hours using a closed system containing 3 wt % of Bi_2O_3, relative to the pellets' mass, to generate a bismuth atmosphere. The density of the pellets was determined by the water displacement method (Archimedes).

Scanning electron microscopy (SEM, Model JOEL-5300) was used to study particle size and powder morphology of activated powders and sintered samples. The pellets were prepared by pressing at 210 MPa and sintered at 1000 °C for 12 h. The average grain size of the mille powders was estimated using the Sherrer`s formula [15]. Sample milled for 12 h and subsequently sintered at 1000 °C for 24 h exhibit a hysteresis loop, confirming that the synthesized material possesses ferroelectric properties. All results showed that the structure $Bi_4Ti_3O_{12}$ were strongly dependent on the milling time.

3. Results and discussion

Mechanical milling of $3Bi_2O_3 + 8TiO_2 \rightarrow 2Bi_3Ti_4O_{12} + ½O_2$ was also carried out under air atmosphere. Fig. 1 shows the X-ray diffraction patterns of powder mechano-chemically milled for different milling times (1, 2 and 6 h). It was evident that before mechanical activation, sharp peaks of crystalline Bi_2O_3 and TiO_2 were observed (inset in Fig. 1), since the conventional ball milling used for homogenization did not trigger any reaction among mixed oxides. In the XRD patterns of milled powders the majority of these sharp peaks disappeared and after 60 min of milling broadened peaks at 2θ angles at around 32 and 39^0 were observed, which was reported previously [16, 17]. It indicates that upon grinding the solid-state reaction between initial oxides starts resulting in the mechano-chemical synthesis reaction. After 2 h of milling, the broadened peaks were separated in few main peaks indicating the formation orthorhombic perovskite $Bi_4Ti_3O_{12}$ phase. The crystalline phase $Bi_4Ti_3O_{12}$, formed after 2 h of milling time, possesses rather small amount of amorphous phase, which shows a small increase upon 6 h of milling.

The effect of mechanical treatment on the grain size is quite evident: as the milling time increases (1, 3, 6, and 12 h), the powder becomes more activated and grain size decrease (15.2, 7.3, 7.2, and 6.9 nm). When reducing the grain size, quantum effects at the Raman spectra, is reflected in the mode position change against balk crystal. And also, coagulation of each line appears, as well as a significant asymmetry of certain modes. The non-polarized Raman spectra of $Bi_4Ti_3O_{12}$ powders formed during different milling time (1-12 h), in the spectral range from 100 to 900 cm^{-1} at room temperature are shown in Fig. 2. Main difference in obtaining Raman spectra of nanocrystal powders $Bi_4Ti_3O_{12}$ from mechanically activated Bi_2O_3-TiO_2 mixture, in regard to obtaining Raman spectra of samples the same through other procedures of synthesis or bulk crystals to compete in simultaneous existence Raman lines which correspond to both orthorhombic and tetragonal structure. Reasons for such a trend can be different. Reduction of crystallite dimension leads to the fact that at the ambient temperature, below some characteristic dimensions, the crystallite surface behaves as if only tetragonal phase is present, while the interior behaves as if orthorhombic phase is present. With the reduction of the decreasing, the share of the surface at the expense of the volume increases, this is reflected on the Raman spectra in change of modes from intensity of determining.

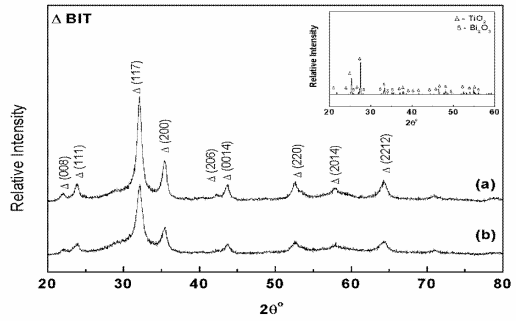

Fig. 1. X-ray data for $Bi_4Ti_3O_{12}$ powders prepared by mechanically assisted synthesis (a) 2 h of milling ,(b) 6 h of milling, and on onset: mixture of Bi_2O_3 and TiO_2 homogenized powders.

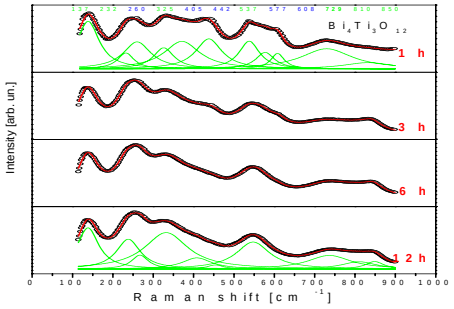

Fig. 2. Raman spectra of the $Bi_4Ti_3O_{12}$ samples prepared mechano-chemical activation for 1, 3, 6 and 12 h at room temperature.

The specific surface area of $Bi_4Ti_3O_{12}$, powders prepared by milling process has been changing depending on whether the breaking process of particles or the secondary agglomeration process dominates or mechanically assisted synthesis occurred. When $Bi_4Ti_3O_{12}$ becomes the dominant phase in the milling sample form, mechanically assisted process is dominant to the secondary agglomeration process. This corresponds to the increase of the value of specific surface area, from 5.2 m^2 g^{-1} at the beginning of milling to 7.2 m^2 $^{-1}$g after 2 h. On the contrary, the decrease trend of specific surface area to 6.6 m^2 g^{-1} can be seen after milling for 6 h as a result of secondary agglomeration processes. The strong powder agglomeration of $Bi_4Ti_3O_{12}$ prepared by mechanically assisted synthesis was confirmed by SEM analysis [17]. The individual crystallite size of approximately 15 nm of $Bi_4Ti_3O_{12}$ powders was observed.

The density of $Bi_4Ti_3O_{12}$ sample obtained by mechano-chemical process was at least 90 % of theoretical density (TD = 8.04 g/cm^3). The green density value was ~60 % T_D for mechanically assisted synthesis and the noted observation is assumed to be caused by strong agglomeration of milled powders [17].

The microstructure of the $Bi_4Ti_3O_{12}$ ceramics prepared from $Bi_4Ti_3O_{12}$ powders by mechanical activation (3 h milling time) and sintered at 1020 ^oC for 12 were presented in Fig. 3. There is tendency for the plate-like morphology for samples prepared by mechanochemically assisted synthesis.

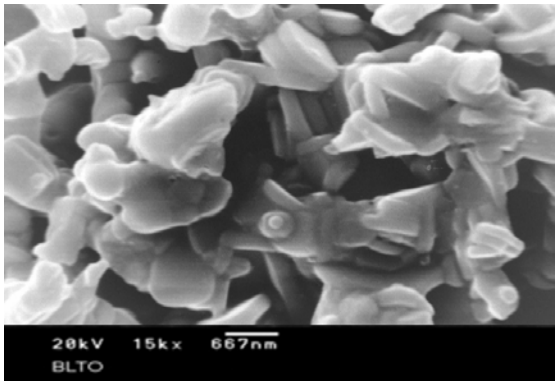

Fig. 3. SEM micrographics for sintered $Bi_4Ti_3O_{12}$ sample obtained from mechanochemically synthesized powders milled 3 h.

Due to the special structure of $Bi_4Ti_3O_{12}$, single crystal is strongly anisotropic in all its ferroelectric properties, including saturated polarization (P_s), remnant polarization (P_r) and coercitive field (E_c). The polarization direction of $Bi_4Ti_3O_{12}$ is 4.5^o off the base plane of its cell structure, thus giving rise to a much larger in-plane polarization (P_s=50 μC cm^{-2}) and E_c value for in-plane polarization is 50 kV cm^{-1} and E_c value for c-orientation is less than 5 kV cm^{-1} [17]. For randomly oriented $Bi_4Ti_3O_{12}$ ceramics or thin films, both remnant polarization and coercitive field have values different than those as above presented. Ferroelectricity in the $Bi_4Ti_3O_{12}$ ceramics was performed with a standardized ferroelectric tester and the results are presented in Fig. 4. Representative *P-E* hysteresis loop of $Bi_4Ti_3O_{12}$ ceramics prepared from powders obtained by mechano-chemical synthesis are almost fully saturated with a remnant polarization of 0.65 μC cm^{-2} and coercitive field of 1050 kV cm^{-1}. The grain morphology may be the factor causing rather large coercive field.

The difference in the properties of $Bi_4Ti_3O_{12}$ ceramics obtained by both processes can be attributed to the variation in microstructure and grain size. The increase of grain size reduces the coupling between grain boundaries and the decrease of domain wall can appeared as a result of more difficult reorientation and the domain wall motion. This then translates to an increase in the domain alignment, corresponding to an increase in the values of remnant polarization and in domain wall mobility [17].

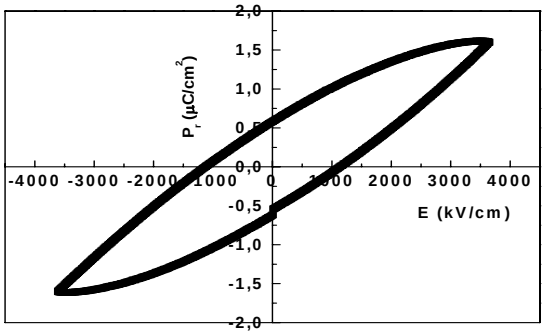

Fig 4. Hysterezis loop for $Bi_4Ti_3O_{12}$ obtained from powders synthesized from mechanochemically synthesized powders milled 3 h.

4. Conclusions

$Bi_4Ti_3O_{12}$ ceramic has been successfully prepared from nano-sized powders obtained by mechano-chemical synthesis via a high-energy ball milling process. The obtained values specific surface area and density data for $Bi_4Ti_3O_{12}$ prepared by this method is caused by several reasons. The most important ones are the closer packages of atoms in $Bi_4Ti_3O_{12}$ crystal lattice and less powders agglomeration of powders prepared by mechanically assisted synthesis. $Bi_4Ti_3O_{12}$ ceramics obtained from powders prepared by milling process presents a plate-like structure. $Bi_4Ti_3O_{12}$ ceramics obtained by this process possess ferroelectric properties. The mechano-chemical process has an advantage over other methods of synthesis because of using low-cost and widely available oxides as starting materials and skips the calcinations step at an intermediate temperature, leading to simplified process.

Acknowledgements

The authors gratefully acknowledge to the financial support of the Ministry of Science and Environmental Protection of the Republic of Serbia.

References

[1] M. Sedlar, M. Sayer, Ceram. Inter. **22**, 241 (1996).
[2] S. H. Ng, J. Xue, J. Wang, J. Am. Ceram. Soc. **85**, 2660 (2002).
[3] A. Megriche, L. Lebrun, M. Troccaz, Senzors and Actuators, **78**, 88 (1999).
[4] A. M. Umabala, M. Suresh, A. V. Prasadarao, Mater. Lett. **44**, 175 (2000).
[5] S. R. Dhage, Y. B. Khollam, S. B. Dhespande, H. S. Potdar, V. Ravi, **39**, 1993 (2004).
[6] S. E. Cummings, L. E. Cross, J. Appl. Phys. **39**, 2268 (1968).
[7] S. Kojima, A. Hushur, F. Jiang, S. Hamazaki, T. Takashige, M. S. Jang, S. Shimada, J. Non-Cryst. Solidas, **293-295**, 250 (2001).
[8] M. Villegas, A. C.Caballero, C. Moure, P. Duran, J. F. Fernandez, J. Am.Ceram. Soc. **82,** 2411 (1999).
[9] T. Thongtem, S. Thongtem, Ceram. Int. (2004), article in press.
[10] V. P. Rao, A. I. Robin, S. Kommarneni, J. Cryst. Growth **237-239**, 469 (2002).
[11] H. Xu, K. J. Bowman, E. B. Slamovich, J. Am. Ceram. Soc. **86** 1815 (2003).
[12] S. Goplan, K. Mehta,V. Virkar, J. Mater. Re. **11,** 1863 (1996).
[13] J. S. Benjamin, Mechanical alloying, Sci. Am. **234**, 40 (1976).
[14] J. Wang, J. M. Xue, D. M. Wan, B. K. Gan, J. Sol. State Chem. **154**, 321 (2000).
[15] Sherrer and warren equations (B. E. Warren, X-ray Diffraction, Addison Wesley: Reading MA), (1969).
[16] L. B. Kong, J. Ma, W. Zhu, O. K. Tan, Mat. Lett., **51**, 108 (2001).
[17] B. D. Stojanovic, C. O. Paiva-Santos, C. Jovalekic, A. Z. Simoes, Z. Lazarevic, M. H. Filho, J. Varela, Mat. Chem. Phys**. 96**, 471 (2006).

*Corresponding author: lzorica@yahoo.com