OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 5, No. 1, January 2011, p. 30 - 33

Spectroscopy study of $BaTiO_3$ obtained from mechanochemically activated oxides mixture

Z. Ž. LAZAREVIĆ*, N. Ž. ROMČEVIĆ, M. J. ROMČEVIĆ
Institute of Physics, University of Belgrade, P.O. Box 68, Belgrade, Serbia

$BaTiO_3$ was prepared by mechanochemical synthesis. A powder mixture of BaO and TiO_2 was treated in a planetary ball mill in an air atmosphere for up to 12 h, using zirconium oxide vial and zirconium oxide balls as the milling medium. After 60 minutes $BaTiO_3$ phase was formed. $BaTiO_3$ ceramic was sintered after 120 min on 1300 ºC without pre-calcinations step. The heating rate was 10 ºC min^{-1}. The formation of phase and crystal structure of $BaTiO_3$ was approved by XRD analysis and Raman spectroscopy. The morphology and microstructure of obtained ceramic powders were examined by SEM method. Sample $BaTiO_3$ obtained from mechanically activated oxides mixture sintered at 1300 ºC for 2 h exhibits a hysteresis loop, confirming that the synthesized material possesses ferroelectric properties.

(Received December 22, 2010; accepted January 26, 2011)

Keywords: $BaTiO_3$, Nanocrystalline materials, XRD, Raman spectroscopy, SEM

1. Introduction

Barium titanate, $BaTiO_3$ is the first ferroelectric ceramics, which is a good candidate for a variety of applications, such as piezoelectric actuators, multiplayer ceramic capacitors and positive temperature coefficient resistors, due to its excellent dielectric, ferroelectric and piezoelectric properties [1, 2]. Also, barium titanate is the first discovered ferroelectric perovskite. Its ferroelectric properties are connected with a series of three structural phase transitions. The Curie point T_c, of barium titanate is 120 ºC. Above 120 ºC the original cubic cell is stable up to 1460 ºC. Above this temperature a hexagonal structure is stable [3].

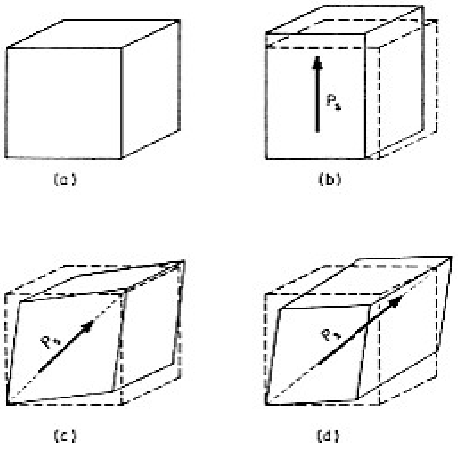


Fig. 1. Unit cells of the four phases of $BaTiO_3$: (a) Cubic, stable above 120 ºC, (b) Tetragonal, stable between 120 ºC and 5 ºC, (c) Orthorhombic, stable between 5 ºC and -90 ºC, (d) Rhombohedra, stable below -90 ºC.

When the temperature is below the Curie point, crystallographic changes in $BaTiO_3$ occur, first at about 120 ºC a ferroelectric transition between the cubic, paraelectric and ferroelectric phase of tetragonal structure takes place. At 5 ºC, the transition to a phase of the orthorhombic structure goes on and at -90 ºC to the low temperature phase having a trigonal structure [4, 5]. Fig. 1 illustrates crystallographic changes of $BaTiO_3$ [4].

$BaTiO_3$ powders were conventionally synthesized by solid-state reaction between $BaCO_3$ and TiO_2 at temperatures higher than 1200 ºC [6]. The high calcinations temperature required by solid-state reaction process leads to many disadvantages of the $BaTiO_3$ powders, such as large particle size, wide size distribution and high degree of particle agglomeration. In this regard, it is desired to lower preparing temperature in order to get $BaTiO_3$ powder with fine and homogenous microstructure. Various chemistry based methods have been developed to prepare $BaTiO_3$ at low temperatures. Examples include chemical co-precipitation, sol-gel process, hydrothermal, molten salt, microemulsion and auto-combustion [7-12].

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].

The objective of this work is to study the feasibility of $BaTiO_3$ formation and ceramics properties obtained from powders prepared by mechanically activated the constituent oxides.

2. Experimental procedures

$BaTiO_3$ was prepared by mechanochemical synthesis starting from barium oxide (BaO) from (Alfa Aesar, 88 %) and titanium oxide TiO_2 in anatas crystal form (Reagelte Ruro Cardoerba, 99 %). An equimolar mixture of BaO and TiO_2 was treated in a Fritsch Pulverisette 2 planetary ball mill. The milling medium used was zirconium oxide balls around 10 mm diameters. Zirconium oxide vial of 500 cm^3 was used. Mass of the mixture was 25 g per a vial. The Mass ratio ball to powder was 20:1. The angular velocity of the supporting disk and vials was 38.04 rad s^{-1} (363 rpm). Milling time was 1 h.

The powder synthesized with this method was pressed at 98.1 MPa, into 8 × 2.5 mm^2 pallets, using a cold isostatic press. The sample was sintered at 1300 ºC for 2 h (in the tube furnace "Lenton", UK). The heating rate was 10 ºC min^{-1}, with nature cooling in air atmosphere.

The X-ray diffraction (XRD) data for barium titanate powders and for sintered samples were measured using CuKα radiation and a graphite monochromatic (Model Phillips PW1710 diffractometer) under the following experimental conditions: 40 kV, $10\,^{\circ} < 2\theta < 120\,^{\circ}$, 2θ = 0,020 º.

Room temperature Raman spectra in spectral range from 100 to 900 cm^{-1}, in back scattering geometry, was obtained by Micro Raman Chromex 2000 using 532 nm of a frequency doubled Nd : YaG laser. The spectral resolution was 1 cm^{-1}.

The grain sizes and morphology were examined using a scanning electron microscope (Model JEOL – JSM 5300). The microstructure of the sintered samples was obtained by polishing and chemical etching with the mixture of 10 % HCl with 5 % HF for 60 s. Some of the samples were observed on fracture surface.

The ferroelectric hysteresis loop was measured using a standard ferroelectric analyzer based on Sawyer-Tower circuit [15].

3. Results and discussion

The XRD result of powder (Fig. 2) indicates the formation of cubic phase of $BaTiO_3$. The appearance of X-ray reflections at 2θ =31.645; 38.955; 45.270 and 56.135 are in correlation with JCPDS standards, which approve that in this way of synthesis the formation of cubic phase is obtained. It can be observed that in the case of mechanochemistry process, significant amount of amorphous phase was detected.

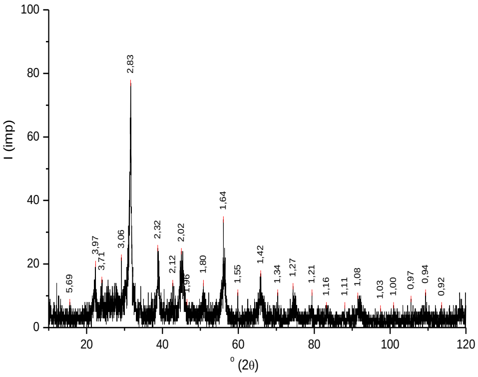


Fig. 2. X-ray data for $BaTiO_3$ powder prepared by mechanochemical synthesis.

The XRD results of sintered sample shows the formation of tetragonal phase of $BaTiO_3$, which is approved by the appearance of X-ray reflections at 2θ =31.530; 38.920; 44.860 and 56.310 (Fig. 3).

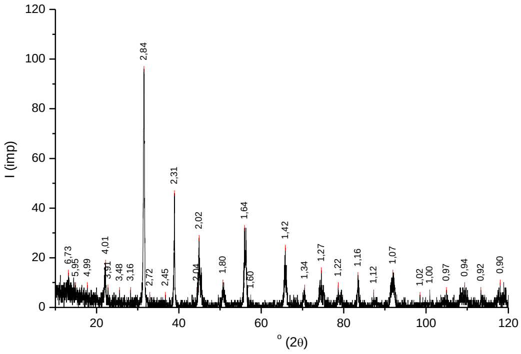


Fig. 3. X-ray data of sintered sample $BaTiO_3$ at 1300 ºC for 2 h.

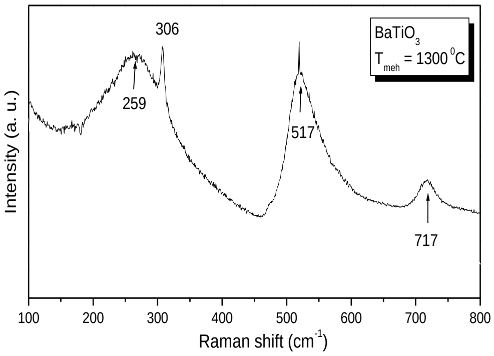
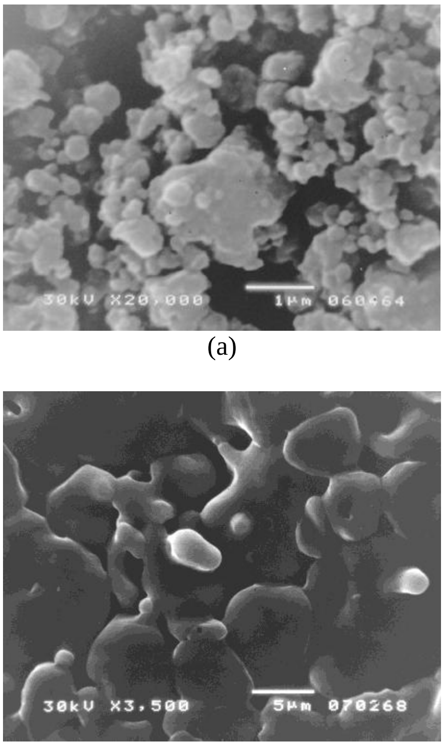


Fig. 4. Raman spectra at room temperature of $BaTiO_3$ sample obtained by mechanochemical synthesis and sintered at 1300 ºC for 2 h.

The Raman scattering spectrum of prepared $BaTiO_3$ was also measured. The Raman-active modes in tetragonal $4mm$ $BaTiO_3$ are $4E(TO + LO) + 3A_1(TO + LO) + B_1$ while there is no Raman-active mode in cubic $m3m$ $BaTiO_3$. The E and A_1 mode split into longitudinal (LO) and transverse (TO) components due to long range electrostatic forces associated with lattice ionicity. In the

Raman spectrum of $BaTiO_3$, the peaks around 259 and 517 cm^{-1} correspond to the TO modes of A_1, whereas the sharp peak at about 306 cm^{-1} is assigned to the B_1 mode. The weak peak around 717 cm^{-1} is related to the LO mode of A_1. These are typical peaks in the Raman spectrum for the tetragonal $BaTiO_3$ phase. Among them, the peaks around 305 and 715 cm^{-1} disappear at above the Curie temperature, which is the stable region of the cubic phase. This means that is it possible to discern between the cubic and tetragonal phases by the presence of the two peaks in Raman spectrum. Fig. 4 shows the Raman spectrum of $BaTiO_3$ with the average crystallite size of 100 nm. From the Raman spectrum, it could be found that our sample contains the Raman peaks corresponding to the cubic and tetragonal phase. Of them, the peak at 305 cm^{-1} was a typical one for the tetragonal $BaTiO_3$. Two broad peaks at about 280 and 516 cm^{-1} were characterized as ones of the cubic phase in $BaTiO_3$. The result of Raman spectrum supports that the $BaTiO_3$ ceramic powder in this study contains both cubic and tetragonal phases.

Fig. 5a) shows the SEM photographs of the $BaTiO_3$ synthesized by mechanochemically. The morphology of the powder consists of particles and its agglomerates. The agglomerates and particles depend on the synthesis method. The particles are big and with irregular shape. Average particle size of grains is about 250 nm. The average grains size of $BaTiO_3$ sintered sample at 1300 °C for 2 h and prepared from powder obtained by mechanochemical synthesis are around 0.75-4 μm with polygonal shape (Fig. 5b).



(a)

(b)

Fig. 5. a) The microstructure of $BaTiO_3$ powders synthesized by mechanochemicly and b) SEM image of the sample $BaTiO_3$ sintered at 1300 °C for 2 h.

It could be notice that loop is very well performed with regular shape typical for ferroelectric materials. The remnant polarization was 2 μC cm^{-2} and the coercitive field was 1060 kV cm^{-2} (Fig. 6). The obtained values pointed to the regular microstructure of sintered specimens with small nanosized grains.

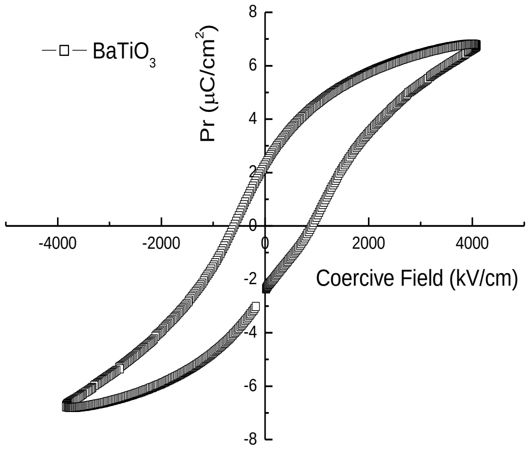


Fig. 6. The hysteresis loop of the sample $BaTiO_3$ sintered at 1300 °C.

4. Conclusions

Our paper reports on work carried out on fine $BaTiO_3$ powders synthesized via the mechanical activation of BaO and TiO_2 directly during high-energy milling. The resulting $BaTiO_3$ powders have been evaluated for powder characteristic. The XRD measurements indicated formation of tetragonal structure $BaTiO_3$. However, the Raman spectrum suggested that cubic ↔ tetragonal structure was achieved for sample $BaTiO_3$ prepared by mechanochemical synthesis ↔ tetragonal structure and sintered at 1300 °C. The particles are big and with irregular shape. Average particle size of grains is about 250 nm. $BaTiO_3$ sintered at 1300 °C exhibit a hysteresis loop, confirming that the synthesized material possesses ferroelectric properties.

Acknowledgements

This research was financially supported by Serbian Ministry of Science through project No.141028B.

References

[1] G. Alrt, D. Hennings, G. de With, J. Appl. Phys., **58**, 1619 (1985).
[2] A. K. Maurice, R. C. Buchanan, Ferroelectrics, **74**, 61 (1987).
[3] W. S. Cho, J. Phys. Chem. Solids, **59**, 659 (1998).
[4] F. Jona, G. Shirane, Ferroelectric Crystals, Dover Publications, INC., New York, 1993.

[5] A. Kolzynski, K. Tkacz-Smiech, Ferroelectrics, **314**, 123 (2005).

[6] L. B. Kong, J. Ma, H. Huang, R. F. Zhang, W. X. Que, J. Alloy. Compo., **337**, 226 (2002).

[7] T. T. Fang, H. B. Lin, J. B. Hwang, J. Am. Ceram. Soc., **73**, 3363 (1990).

[8] M. H. Frey, D. A. Payne, Chem. Mater., **7**, 123 (1995).

[9] R. K. Dutta, R. Asiaie, S. A. Akbar, W. Zhu, Chem. Mater., **6**, 1542 (1994).

[10] Y. Ito, S. Shimada, J. Takahashi, M. Inagaki, J. Mater. Chem., **7**, 781 (1997).

[11] J. Wang, J. Fang, S. Ng, L. Gan, C. Chew, X. Wang, Z. Shen, J. Am. Ceram. Soc., **82**, 873 (1999).

[12] H. Hsiang, F. Yen, J. Am. Ceram. Soc., **79**, 1053 (1996).

[13] P. S. Gilman, J. S. Benjamin, Annu. Rev. Mater. Sci., **13**, 279 (1983).

[14] J. Wang, J. M. Xue, D. M. Wan, B. K. Gan, J. Sol. State Chem., **154**, 321 (2000).

[15] C. B. Sawyer, C. H. Tower, Phys. Rev., **35**, 269 (1930).

---

[*] Corresponding author: lzorica@yahoo.com