JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 10, October 2008, p. 2675 - 2677

Synthesis and characterization of barium strontium titanate powder

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

Barium strontium titanate, BST was prepared from polymeric precursors through Pechini process (soft chemistry) which was carried out as a three–stage process from oganometallic complex. The main objective of this study is to find experimental conditions, so that the polymeric precursor method is applicable for the BST powder synthesis without any formation of carbonates. BST powder was obtained after calcinations at 800 °C for 8 h and characterized by XRD, IR, BET and SEM analysis.

(Received March 29, 2008; accepted August 14, 2008)

Keywords: BST, Pechini process, XRD, IR, BET, SEM

1. Introduction

In recent years, ferroelectric thin films have been used in a wide range of applications owing to their promising dielectric, ferroelectric, piezoelectric, pyroelectric and electrostrictive properties [1, 2]. Hetero-structures based on these materials are used for high-density dynamic random access memories (DRAMS), especially for non-volatile random access memories (NVRAM) with low switching voltage exploiting their high dielectric properties and large values of switchable remnant polarization [3, 4]. Barium strontium titanate (BST) is a potential candidate for the DRAM and NVRAM because of its high dielectric constant, low leakage current and high breakdown strength at Curie temperature [5]. The Curie temperature of pure barium titanate is 130°C and with strontium doping the Curie temperature decreases to room temperature which is useful for specific device requirements. Thin films of BST have been fabricated by several techniques such as r.f. sputtering, laser ablation, metal organic chemical vapor deposition and sol-gel process. Among these techniques, the sol-gel technique involves the use of liquid solution mixtures as starting materials. Since the mixing is done with low viscosity liquids, the homogenization can be achieved at a molecular level within a short time. Fabrication of BST thin films on bare silicon and platinum coated silicon substrates by sol-gel technique using acetates and butoxide has already been reported. Calcinations temperature and time is one of the key parameters that would determined the characteristic of BST produced. The optimum calcinations temperature and time must be obtained to ensure the mixture completely formed BST through solid state reaction. If the calcinations temperature and time is set too low, the mixture will only be partially reacted [6, 7]. Chemical synthesis has grown up through techniques of sol – gel, coprecipitation, hydrothermal and polymeric precursor method [8, 9]. The advantage of chemical methods is the quasi – atomic dispersion of constituent components in liquid precursor, which facilitates synthesis of crystallized powder with submicron particles and high purity at low temperatures. The advantage of Pechini method (polymeric precursor method) is based on the fact of its simplicity and possibility to hold the initial stoichiometry.

Previously we have prepared nickel ferrites and bismuth titanate ultrafine powders [10, 11]. Now barium strontium titanate has been prepared by soft chemistry.

2. Experimental procedures

Powder preparation

BST was prepared by the polymeric organometalic precursors method (Pechini process). The procedure of synthesis, based on Pechini`s method is showed in Figure 1. Titanium (IV) isopropoxide (Ti $(O\text{-}C_3H_7)_4$, Alfa Aesar, 99,999% purity), barium carbonate ($BaCO_3$, Aldrich, 99,999% purity), strontium carbonate ($SrCO_3$, Aldrich, 99,9% purity), ethylene glycol ($C_2H_6O_2$, Labsynth, 99,5% purity) and citric acid ($C_6H_8O_7$, Tate&Lyle, technical grade) were used. The molar ratio titanium: citric acid: ethylene glycol is the same equal to the ratio of the barium and strontium solutions. The calculated quantities of Ba, Sr and Ti citrate solutions were mixed and under stirring successively heated at 90°C to evaporate the water content. Next, the temperature was increased to 130-140°C, yielding a dark and highly viscous polyester resin. In order to remove the main part of the organic material, the resin was pre-calcinated at 200°C for 24 hours, 300°C for 18 hours and 370°C for 10 hours. The obtained black powder was milled in an atritor with zirconia balls in acetone medium for 1 hour. After drying, the powder was calcinated at 800°C for 8 hours.

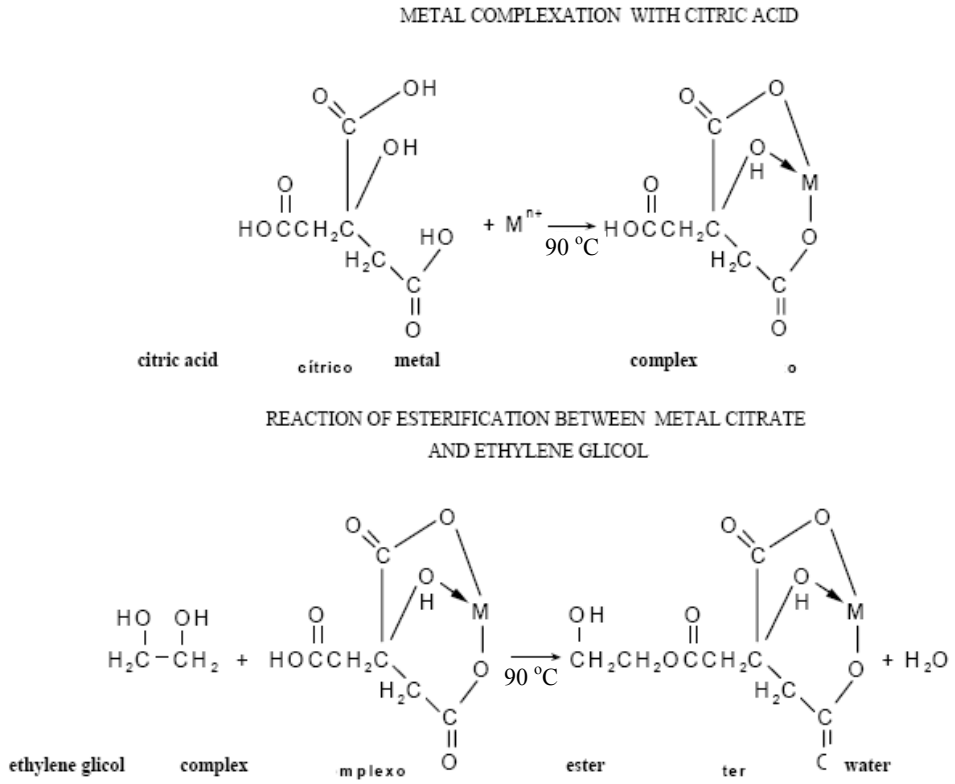

Fig. 1. The flow chart for the Pechini process.

Characterization

Thermogravimetry was performed using a NETZSCH STA 409 unit with a heating rate of 5°C/min. XRD-data were collected with a Siemens D5000 diffractometer under the following experimental conditions: copper anode, 50 kV, 150 mA, CuK_α radiation monocromatized by a graphite crystal. Infrared spectra were recorded on an IMPACT 400-IR-FT spectrometer. The samples were mixed with KBr and pressed into pellets. Scanning Electron Microscopy (SEM) was performed on a TOPCON SM-300 unit. Surface area of the material was carried out by standard nitrogen absorption and desorption experiments using a MICROMERITICS ASAP 2010 surface area and pore analyzer.

3. Results and discussion

In order to determine the best condition of annealing, a thermal analysis was performed. The existence of three stages of weight loss can be observed. The first stage (25 to 290°C) is related to elimination of water produced during the process of esterification and the excess of ethylene glycol. The second one (290 to 580°C) corresponds to a break away of the polymeric chains formed by a polyesterification reaction. The last one between 580-660°C is due to the decomposition of organic compounds.

To evaluate the influence of temperature on the formation of carbonate, the polyester resin was directly heated to 400°C for pyrolyzation of the organic material and then calcinated at 600°C, 700°C or 800°C for 2 hours. X-ray diffraction data depending on the calcinations temperature are shown in Fig. 2.

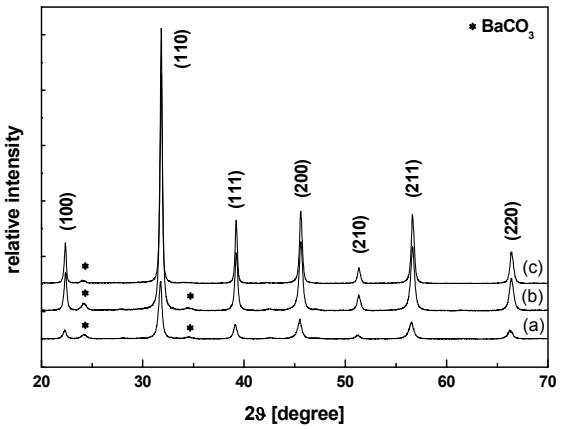

Fig. 2. XRD pattern of BST powder obtained under the following conditions: pre-calcinations at 400°C for 10 hours; calcinated at (a) 600°C, (b) 700°C or (c) 800°C for 2 h.

It can be seen, that with an increase in temperature the amount of formed carbonate decreases. However, high calcinations temperatures cause particle growth and surface area decrease. The powder is less reactive for sintering. Therefore, the elimination of carbonate at high temperatures is not recommended.

The IR spectrum of the BST phase powder is plotted in Figure 3. The very small absorption band at 1441cm^{-1} can be interpreted as C=O vibration arisen from extremely small unavoidable traces of carbonate. IR spectrum is according to XRD data.

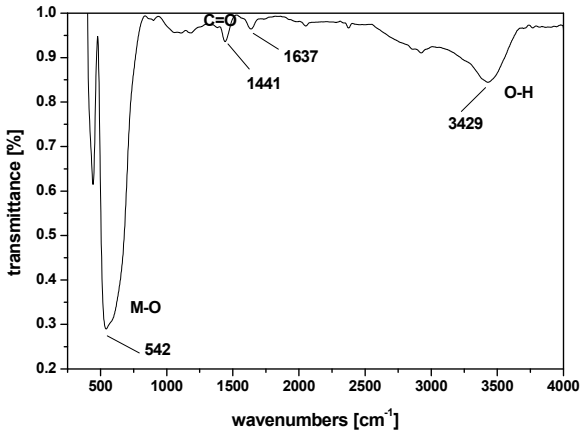

Fig. 3. IR spectrum of pure BST.

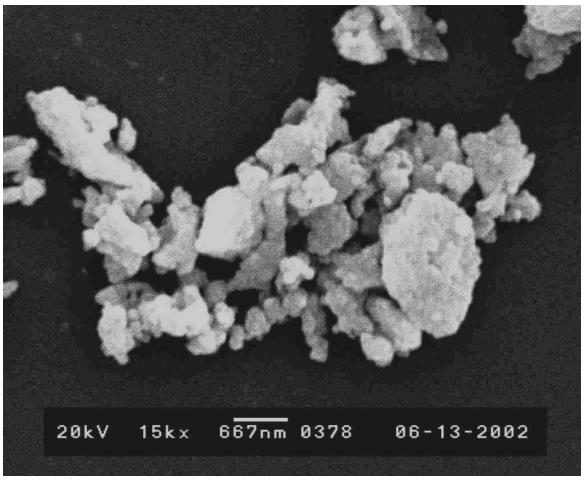

Fig. 4. SEM image of BST powder under 15 Kx magnification.

SEM images were taken to collect information about grain size, shape and agglomeration degree of the powder. Fig. 4 shows the microstructure of the powder. The grains are in micrometer range, irregularly formed and the powder is highly agglomerated. Under higher resolution can be seen that the larger grains are composed by numerous small particles. This leads to the conclusion that the applied calcinations conditions (800^{o}C for 8 hours) affect a pre-sinterization process with grain growth. Surface area was determined using BET method (5.13 m^2 g^{-1}). A large grain size is in agreement with the SEM images.

4. Conclusions

BST as prepared by polymeric organometallic precursors process. It is concluded that is possible to prepare carbonate-free BST by polymeric precursor method. In order to avoid the formation of carbonates, the organic material must be decomposed at low temperatures over a long time. The obtained powder is highly agglomerated and exhibits grains size in micrometer range.

Acknowledgements

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

References

[1] O. Auciello, R. Ramesh, Materials Research Bulletin, **21**, 29 (1996).
[2] O. Auciello, A. I. Kingon, S. B. Krupanidhi, Materials Research Bulletin **21**, 25 (1996).
[3] A. B. Catalan, J. V. Mantese, A. L. Micheli, N. W. Schubring, R. J. Poisson, Journal Apllied Physics, **76**, 2541 (1994).
[4] R. J. Cava, W. F. Peck, J. J. Krajewski, D. A. Fleming, Apllied Physics Letter, **67**, 3813 (1995).
[5] S. G. Yoon, A. Safari, Thin solid films, **254**, 211 (1995).
[6] A W Hilton, and B W Ricketts, J. Phys. D: Appl. Phys., **29,** 1321 (1996).
[7] T. M. Shaw, Z. Suo, M. Huang, E.Liniger, R. B. Laibowitz, J. D. Baniecki, Apllied Physics Letter, **75**, 2129 (1999).
[8] Pechini, M. P. US Patent 3 330 697 (1967).
[9] C. F. Kao, W. D. Yang, Appl. Organometal. Chem., **13**, 383 (1999).
[10] Z. Z. Lazarević, B. D. Stojanović, N. Z. Romcevic, J. Optoelectron. Adv. Mater. **9**(7), 2262 (2007).
[11] A. S. Nikolić, J. M. Puzović, M. B. Pavlović, P. Osmocrović, Z. Lazarović, J. Optoelectron. Adv. Mater. **9**(9), 2731 (2007).

*Corresponding author: lzorica@yahoo.com