Preparation and characterization of $BaTi_{0.89}Sn_{0.11}O_3$ and $Ba_{0.89}Sn_{0.11}TiO_3$

Mihaela Alexandrova, Lyuben Lakov, Vladimir Blaskov

Institute of Metal Science, Equipment and Technologies with Hydro- and Aerodynamics Centre "Acad. A. Balevski", Bulgarian Academy of Sciences, Shipchenski Prohod Blvd. 67, 1574 Sofia, Bulgaria, e-mail: mihaela.krasimirova@mail.bg

Abstract: *In recent years, interest in the application and use of materials for supercapacitors for electric vehicles has grown significantly. The advantage of capacitor ceramics over other dielectric materials for producing supercapacitors is its environmental friendliness and high economic efficiency. This paper presents the results of a study of capacitor ceramics doped with Sn at different locations of the modifier (tin) in $BaSnTiO_3$ and $BaTiSnO_3$ crystal lattice. The influence of modifiers in low-temperature sol-gel synthesis was studied. The samples were annealed at 1000°C. The resulting phases were identified by X-ray phase analysis. Microscopic analysis was also performed.*

Key words*: SOL-GEL, CONDENSER CERAMICS, $BaTiO_3$*

1. Introduction

At present, in the worldwide production of supercapacitors, porous carbon is most often used for both electrodes and a special electrolyte The .second well known method includes using of so-called carbon nanotubes. The possibility of a large area of the electrodes and a small distance between them is achieved and as a result acceptable dimensions for the supercapacitor [1].

Studies of compounds based on $BaTiO_3$ as a dielectric material have shown that it is possible to create a supercapacitor, both for the needs of electronics and for electric vehicles, where it is an important component device needed not to drive but to improve the dynamic driving qualities of the electric car and for absolutely trouble - free start in hybrid small and heavy cars [1-2].

$BaTiO_3$ is an electroceramics possessing good dielectric properties and does not emit harmful emissions into the environment. [3] The cubic phase of barium titanate shows a very high relative dielectric permittivity (1500-6000°C) (at room temperature) [4]. Meanwhile, tetragonal polymorphic forms possess ferroelectric, piezoelectric and thermoelectric properties. The most widely used application of barium titanate includes multilayer capacitors in electronic circuits, electro-optical devices, thermistors, piezoelectric drive, non-linear resistors, thermal switches, etc. [5-7].

Alkaline earth tin oxide compounds such as ($MSnO_3$, where M=Ca, Sr, Ba) are a series of materials that are widely used in industry in the manufacture of capacitors. Ostrik and colleagues report the results of measurements [6] at high temperatures, which clarify the presence of defects in the crystal lattice of the material, which in some cases favor the production of materials, such as sensors, transducers and others. [7-9]. Despite this technological significance, any information on the processing and evolution of the microstructure of these materials and their impact on electrical characteristics is missing in the literature. [10] Suggestions for $BaTiO_3$-$BaSnO_3$ solid solution interaction have been made. [11] Barium titanate obtained by appropriate doping with Sn is known to have a very high dielectric constant ε, which can reach values up to 5.104. This high value of ε is considered suitable for energy storage devices used as portable and wear-resistant electronics. [12] The high value of the dielectric constant of Sn doped $BaTiO_3$ materials is attributed to their nano and distorted structures. [13] There are insufficient literature data on electrical measurements of materials with similar structures.

2. Experimental part

$Ba(Ac)_2$ Alfa Aesar and $Ti(OBu)_4$ 99% Alfa Aesar are the main precursors used for the synthesis of $BaTi_{0.89}Sn_{0.11}O_3$ and Ba0.89Sn0.11TiO_3. $Sn(OOCCH3)_2$ and $Sn(OOCCH3)_4$ were used as modifiers.The solutions of above mentioned compounds are mixed in suitable stoichiometric ratios. and are homogenized on a Techno Kartel T22 magnetic stirrer for 30 minutes - the required time for each of the solutions.

2.1. Synthesis of $BaTi_{0.89}Sn_{0.11}O_3$

Barium acetate is dissolved in water and acetic acid CH_3COOH is added to the resulting solution - to make the acetate solution more resistant to moisture. The molar ratio of H_2O:CH_3COOH is 1:2 (Chernea 2006 [14]). Titanium butoxide is dissolved in a mixture of absolute alcohol and acetic acid, which acts as a catalyst and stabilizer of the synthesized titanium sol. Tin acetate - $Sn(CH_3COO)_4$ after dissolution in absolute alcochol is added to barium acetate. Clear, stable solution is formed and is added to the sol of $Ti(OBu)_4$. A new stable yellow sol is obtained. After heating to 60°C, the sol gelates and dried afterwards at 100°C. The resulting dried gel – xerogel - is annealed at 1000°C for 10 hours.

2.2. Synthesis of $Ba_{0.89}Sn_{0.11}TiO_3$

The preparation of $Ba_{0.89}Sn_{0.11}TiO_3$ is similar to the synthesis of $BaTi_{0.89}Sn_{0.11}O_3$, but differs in that the starting compound of the tin is $Sn(CH3COO)_2$, Sn^{2+} is used, and for $BaTi_{0.89}Sn_{0.11}O_3$ $Sn(CH3COO)_4$ - Sn^{4+} is used. In the process of synthesis it is noticeable that with $Sn(CH3COO)_2$ a suspension is obtained in a solution of absolute alcohol, while $Sn(CH3COO)_4$ dissolves very well in the absolute alcohol.

Characterization of the obtained samples is performed with Bruker 8 d advance \ automatic - X-ray diffractometer with CuKα radiation (Ni filer) and a Lynx Eye solid detector.

3. Results and Discussion

The performed X-ray phase analysis presented in Fig. 1 and Fig. 2 shows the patterns of diffraction of powders of tin-doped $BaTiO_3$ and products of a chemical reaction carried out at a temperature (1000°C). The data were taken with CuKα radiation (λ=0.56 Å) - Bragg angles 2θ up to 120 degrees, ie. vectors with approximately 2θ A -1phases $BaTi_{0.89}$ $Sn_{0.11}O_3$ and $Ba_{0.}89TiSn0_{.11}O_3$. The width of the peaks determine the size of the crystallites, which range from 89 up to 103 nm.

According to the X-ray phase analysis of the sample $BaTi_{0.89}Sn_{0.11}O_3$ only pure cubic $BaTiO_3$ phase with crystallite size of 103 nm is registered (fig.1), while concerning $Ba_{0.89}TiSn_{0.11}O_3$ a cubic $BaTiO_3$ is the main phase concomitant with small amount of SnO_2, as well as of traces of Ti_7O_{13} and TiO_2 (rutile) (Fig. 2)

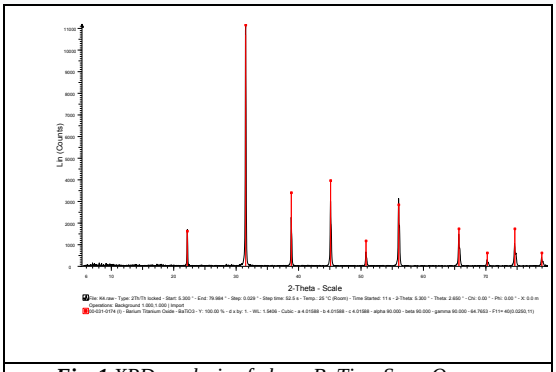

Fig .1 *XRD analysis of phase $BaTi_{0.89}$ $Sn_{0.11}$ O_3*

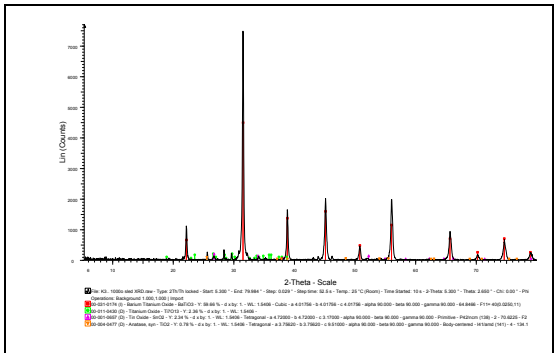

Fig. 2 *XRD analysis of phase* $Ba_{0.89}$ $TiSn_{0.11}O_3$

The difference in the two diffractograms is due to mode of Sn substitution in the crystal lattice of the two compounds ($BaTi_{0.89}Sn_{0.11}O_3$ and $Ba_{0.89}TiSn_{0.11}O_3$), the temperature treatment and the time of soaking. The better result of $BaTi_{0.89}Sn_{0.11}O_3$ is obvious, because in this case tin replaces titanium in the crystal lattice and shows more reliable properties according to data from the literature for further future development, namely the preparation of a target for magnetron sputtering. After high-frequency magnetron sputtering, layers were deposited on stainless steel substrates and with a mirror surface with thicknesses of the seeded layers in the range of 40, 50, 100, 200, 500, 800, 1000 nm. The layers showing the best results are shown in Table 1. The studies are supported by microprobe analysis Fig.3.

Sample	Thickness (nm)	Standard deviation (nm)
4 hours	1400	120
2 hours	610	60
1 hour	230	25

Table. 1*. Experimental results of the measured layer thicknesses*

In the photomicrograph, the three thicknesses of the layers are clearly distinguished. The places with the best indicators in nanometers are marked, respectively 1400 nm, 610 nm and 230 nm.

The thin layers deposited by magnetron sputtering were examined with an Amplival microscope. The micrographs of the individual layers were taken with a Carl Zeiss digital camera, Jenoptic CT3. Microscope magnifications with 6.3 X, 12.5X and 25X lenses were used in combination with a 12.5X eyepiece.

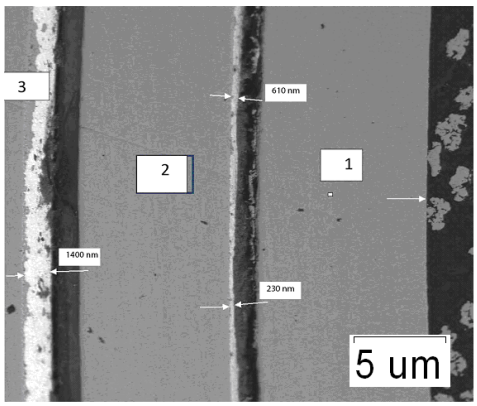

Fig.3*. Microscopic analysis of layer thicknesses marker 5nm*

4. Conclusions

In conclusion, it can be summarized that when Sn doped $BaTiO_3$ in the case when tin replaces titanium, a pure cubic phase of $BaTiO_3$ is obtained (concerning compound $BaTi_{0.89}Sn_{0.11}O_3$), while when barium is replaced with tin, in addition to cubic $BaTiO_3$, small amounts of other phases: SnO_2, TiO_2. (for compound $Ba_{0.89}TiSn_{0.11}O_3$). The size of the crystallites - in the range up to 103 nm- is determined from the performed XRD analysis. After high-frequency magnetron sputtering of a target on an stainless steel substrate, the layer thicknesses were determined, with the best result being the 1400 nm layer. The present study also aims at additional analyzes to confirm the necessary conditions for further research.

Acknowledgement

The authors wish to thank the National Science Fund at the Bulgarian Ministry of Education and Science for financing their research project, (Contract No. КП-06-Н 37/26) from 18.12.2019.

References

1. A. Mundy, G. L. Plette, Journ. of Energy Storage7,"Reduced-order physics-based modeling and experimental parameter identification for non-Faradaic electrical double-layer capacitor", (2016) 167-180.
2. A. Mazard, M. Hashim, S. Baptist, A. Badar, A. Haq, "Phase evolution and microstructural development in sol-gel derived $MSnO_3$ (M=Ca, Sr and Ba)", Journ. of Mat. Sci.,35 (2000), 5475-5483.
3. E. P. Kashchieva, V. D. Ivanova, B. T. Jivov and Y. B. Dimitriev, „Nanostructured borate glass ceramics containing $PbMoO_4$", Physics and Chemistry of Glasses, **41** (6), 2000, pp. 355-357.
4. Qingsong Zhang, Tahir Cagin, William A. Goddard III, "The ferroelectric and cubic phases in $BaTiO_3$ ferroelectrics are also antiferroelectric",PNAS October 3, 2006 103 (40) 14695-14700
5. E. P. Kashchieva, V. D. Ivanova, B. T. Jivov, P. K. Petkov and Y. B. Dimitriev, „Structure-property correlation in lead-borate composites with participation of $PbMoO_4$", In: Proceedings of the 13th Conference on Glass and Ceramics, 1999, Varna, Bulgaria, Vol. 1, Eds B. Samuneva et al., (Publishing House „Science Invest" Sofia, 1999), pp. 159-164.
6. R. Ostric, M. Fleisher and H. Meixner, J. Am.Cerm. Soc. **80** (1997), 2153.
7. P. T. Mousley, A. M. Stoneham and D. E. Williams, "Techniques and Mechanisms iin Gas Sensing", edited by P. T. Moseley, J.O.W. Norris and D. E. Williams, (Adam Hilder, Bristol,1991,ch.4).
8. P. Nanny, M. Viviani, V. Buscaglia, "Synthesis of dielectric ceramic Materials", Chapter 9, Handbook of Law and High Dielectric Materials and Their Applications, (1999)429-450.
9. O. Parkash, K. D. Mandal, C. C. Christopher, M. S. Sastray and D. Kumar, J. Mater. Sci. Lett. **13** (1994), 1616.
10. J. Cerda, J. arbiol, R. Diaz, G. Dezanneau, J. R. Morante, "Synthesis of perovskite-type $BaSnO_3$ particles obtained by a new simple wet chemical route based on a sol-gel process", Mater. Lett. **56** (2002) 131-136.
11. Bachvarova-Nedelcheva, R. Iordanova, K. L. Kostov, V. Ganev, St. Yordanov, Y. Dimitriev, "Synthesis and structural characterization of a glass in the Ag_2O-SeO_2-MoO_3 system", Journal of Non-Crystaline Solids, **481**, 2018, pp. 138-147.
12. J. Gao, Y.Wang, Y.Liu, X.Hu, X.Ke, L.Zhong, Y.He, X.Ren," Enhancing dielectric permittivity for energy- storage devices through tricritical phenomenon ", Scientific reports 7:40916/ DOI:10.1038/srep40916.
13. T. Shi, L.Hie,L. Gu and J. Zhu Why Sn doping significantly enhances the dielectric properties of Ba(Ti1-xSnxO3), Scientific Reports5 : 8606 (2015) DOI: 10.1038/srep08606
14. M. Cernea, O.Monnereau, Ph.Llewellin, L.Tortett, C.Callasi, "Sol-gel synthesis and characterization of Ce doped BaTiO3" Journal European Ceramic Society, **26** (2006) 3241-3246.