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Sol-Gel Synthesis of Zr Doped $BaTiO_3$ and Influence of The Modification on The Obtained Phases

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Abstract
The present work relates to the synthesis of zirconium-doped BaTiO3. The synthesis was performed by a low temperature sol-gel method. The research is aimed at developing a target for magnetron sputtering of layers on an alloy steel substrate and others. The obtained phases were analyzed by XRD analysis, infrared spectroscopy was performed and the dielectric constant of the obtained sample was determined

Keywords: Ceramic, BaTiO3, Modifier, High Permittivity

1. Introduction

Ceramic capacitors are the most common type of capacitors with a significant share of total world production of electric capacitors due to the many advantages [1,2]: high values of ε, simple design, wide range of capacitance values (from parts of pF to hundreds of μF), relatively high stability in aggressive environments, structural compatibility with hybrid integrated circuits and other microelectronic elements. Capacitor ceramics with increased resistance to the values of dielectric constant in a wide temperature range and the presence of a zonal micro-heterogeneous structure obtained on the basis of $BaTiO_3$ (BTO) and solid solutions have been developed. The presence of phase transitions in accordance with the temperature values of the medium partially limits the possibilities for application of barium titanate [1-3].
The modification of barium titanate simultaneously by different modifying components allows the production of materials with high values of dielectric permittivity [3,4] and the presence of a structure composed of aggregates with semiconductor properties and intergranular dielectric layer. The introduction of ions with a tendency to replace Ba^{2+} or Ti^{4+} and the presence of higher valence values provokes the formation of semiconductor properties of ceramic grains, while the presence of modifiers (with valence values lower than 2 or 4) replacing Ba^{2+} or Ti^{4+}, favours the development of dielectric characteristics of the intergrain layers. [10,11,12,13]
The structure, grain size, synthesis methods and modification have a positive effect on the properties of WTO. Granting has been found to be an effective method for changing the properties of materials. [5]
When Zr is added to $BaTiO_3$, the obtained ferroelectric $BaZr_xTi_{1-x}O_3$ has a dielectric constant at room temperature of 10586 [6] Ba $(Ti_{0.7}Zr_{0.3})O_3$ for (Tc) equal to room temperature has a high dielectric permittivity of 5000. [7,8].
BTO thin films can be deposited by various known methods such as high frequency magnetron sputtering, laser deposition, dip-coating, spin-coating and the like.
In the present work, the research is focused on the synthesis of Zr donated $BaTiO_3$ and the development of a target for magnetron deposition of thin layers. The phase composition and the

relative dielectric constant were studied. Attention is paid to the influence of the modifier on the structure of the ceramic phase.

2. Experimental part

Barium acetate [Ba $(Ac)_2$] and titanium butoxide [$Ti(OBu)_4$] were used as precursors for the synthesis of sols. Solvents are absolute ethyl alcohol (C_2H_5OH), water and nitric acid (HNO_3); and acetic acid (CH_3COOH) complexes also used as solvent stabilizers, in some cases acetylacetone ($CH_3COCH_2COCH_3$) or diethanolamine [$NH(CH_2CH_2OH)_2$] were added. In the process of sol synthesis, it was found that in order to avoid undesired precipitation or gelling, the addition of the solutions or the mixing of the individual sol should be carried out very slowly with very good homogenization using a magnetic stirrer.
Depending on the type and amount of solution, the homogenization time can reach half an hour or even more. When obtaining ash, it is necessary to add a complexing agent (stabilizers). It was found that in some cases – for example in the preparation of Sm donated barium titanate ceramics, a non-traditional complex for titanate ceramics – diethanolamine – must be added. Less concentrated solutions are also used to obtain stable sols. Thus, for [$Ti(OBu)_4$] the sols obtained have molarities in the range 0.2 – 0.6 M.
The following approach was used to obtain sols containing modifying additives: the modifying additive in the form of an oxide or inorganic salt is dissolved. The resulting solution was added to the precursors barium acetate and titanium butoxide. This results in the final sol, which gels after proper air temperature treatment. In the preparation of sol, which contains a modifying additive Zr, the following synthesis is carried out: The precursor – zirconium oxychloride (1g) is dissolved in 31 ml of absolute alcohol and acetylacetone (complexing agent) and nitric acid (acid catalyst) in the ratio: HNO_3: $CH_3COCH_2COCH_3$ = 3:1:1 to give zirconium sol. 3.946г. barium acetate was dissolved in water to give sol. Titanium butoxide (4.2 ml) was added to a mixture of 25 ml of absolute alcohol and 25 ml of acetic acid to give a sol of [$Ti(OBu)_4$]. Mix the sol of [Ba $(Ac)_2$] with the sol of $ZrOCl_2.8H_2O$ – a new sol A is obtained, to which the sol of [Ti $(OBu)_4$] is added.
Thus, the final sol B is already synthesized. The final sol thus obtained gels at room temperature for 48 hours. If necessary, it is additionally dried in an oven at 100°C. The resulting powder sample is ground in an agate mortar and the following analyzes are performed to prove monophase and determine the relative dielectric constant.

3. Results and discussion

The characterization of the synthesized powder ceramics was performed by X-ray diffraction (XRD, Bruker D8 Advanced). The results are presented in fig. 1. The presence of a single phase is clearly visible. The characteristic peaks are of the Zr subsidized $BaTiO_3$ cubic phase.
The size of the crystallites is 19μm.
Infrared spectroscopy proves the results of XRD. The band at 556 cm^{-1} and the arm at 664cm^{1} are attributed to valence oscillations of TiO_6 octahedra and valence oscillations associated with the Ba ion. Very weak bands at 1467 cm^{-1} and 1633 cm^{-1} are characteristic of the presence of COO-groups. The wide very weak band at 3450 cm^{-1} is attributed to valence fluctuations of OH groups [9,14,15].

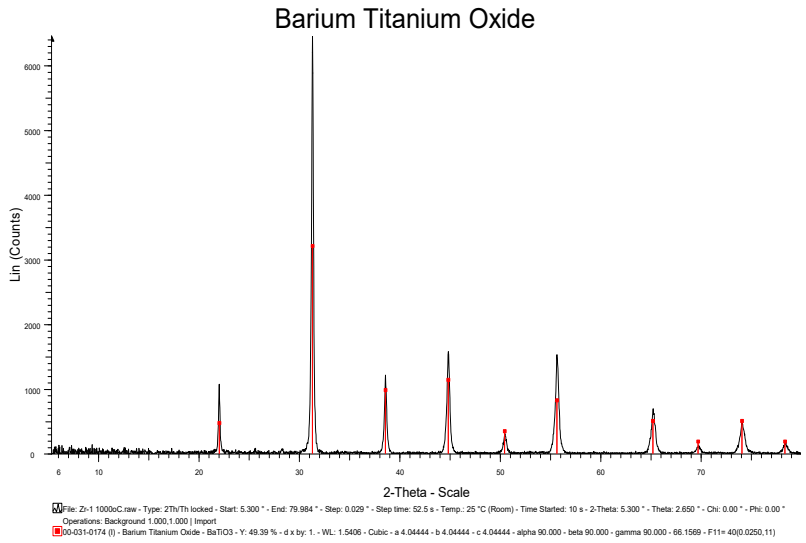

Fig. 1. XRD of cubic Zr doped $BaTiO_3$ phase prepared at 1000°C thermal treatment

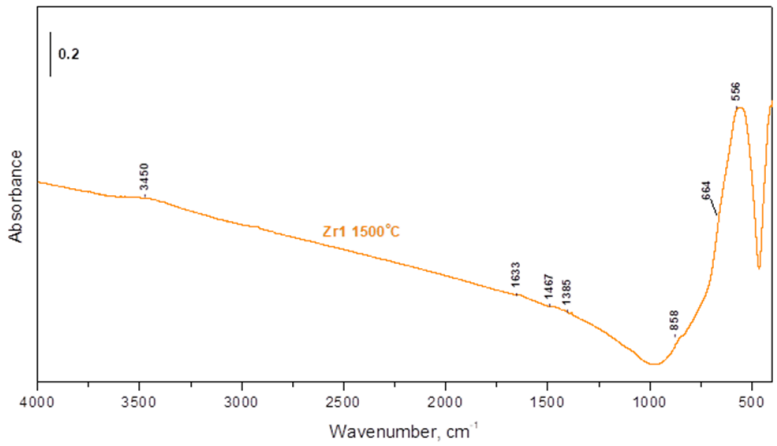

Fig. 2 Infrared spectroscopy of Zr doped barium tiatanate

The relative dielectric constant is also determined. Very high dielectric constant was recorded for $BaTiO_3$ donated with Zr ions, which significantly increased the dielectric constant of barium titanate itself at room temperature.

The inclusion of trivalent ions, in which an extremely high value of the dielectric constant of $BaTiO_3$ at room temperature, has been reported, thus improving the performance of the respective energy storage devices (capacitors and supercapacitors). It was found that the dielectric constant depends very strongly on the size of the crystallites and with decreasing their size it initially increases, but then decreases, i.e. a maximum is observed.

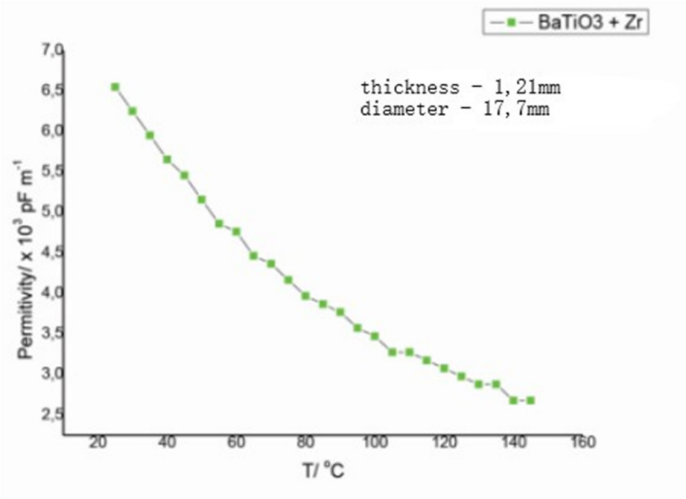

Fig. 3 Relationship between the RDP (relative dielectric permittivity) and measured temperature.

4. Conclusion

The effects of Zr^{4+} ions on the crystal structure, ferroelectric and dielectric behavior of the modified barium titanate ceramics were thoroughly studied. Emphasis was placed on the efficiency of Curie point displacement by Zr-doping in Ba (Zr,Ti)O_3 ceramics and the possibility of their application as capacitor dielectric materials.

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References

1. Panda P. K., Review: environmentally friendly lead-free piezoelectric materials, Journal Mater Sci, 44, 2009, pp. 5049–5062.
2. Coondoo I., N. Panwar A. Kholkin, Lead-free piezoelectrics: Current status and perspectives, Journal of Advanced Dielectrics, Vol. 3, No. 2, 2013, pp. 1330002-22.
3. Biscaglia M.T., V. Buscaglia, M. Viviani, P. Nanni, M. Hanuskova, Influence of foreign ions on the crystal structure of BaTiO3, Journal of European Ceramic Society, 20, 2000, pp.1997–2007.
4. Kim Y.J., J.W. Hyun, H.S. Kim. J.H. Lee, M.Y. Yun. S.J. Noh, Y.H. Ahn, Microstructural characterization and dielectric properties of barium titanate solid solution with donor dopants, Bulletin of Korean Chemical Society, Vol. 30, No. 6, 2009, pp. 1268-1273.
5. Vijatovic M.M., J.D. Bobic, B.D. Stojanovic, History and challenges of barium titanate: Part I, Sci. Sinter. 40, 2008, pp. 155–165.
6. Hanin S. D., A.I. Ader, V.N. Voroncov, O.V. Denisova, V.Y. Holkin, Passive radio components, Part I., Electric capacitors, UDC 621.37: 621.319.4., St. Petersburg, 1998.

7. Tewatia Kr., A. Sharma, M. Sharma, A. Kumar, Factors affecting morphological and electrical properties of Barium Titanate: A brief review. Materials Today: Proceedings, Vol. 44, Part 6, 2021, pp. 4548-4556, ISSN 2214-7853.
8. Yu Z., Ch. Ang, R. Guo, A.S. Bhalla, Ferroelectric-relaxor behavior of Ba (Ti0.7Zr0.3)O3 ceramics, J. Appl. Phys. 92, 2655 (2002); https://doi.org/10.1063/1.1495069.
9. Asaree Md.J., Sh. Upadhyay, Study of phase evolution and dielectric properties of Sn doped barium titanate, Emerging Materials, 6, 2017, pp.21-28.
10. Kashchieva E.P., V.D. Ivanova, B.Tzv. Jivov, P.K. Petkov, Y.B. Dimitriev, Structure-Property Correlation in Lead-Borate Composites with Participation of PbMoO4, Proceedings of the 13th Conference on Glass and Ceramics, 29.09-01.10.1999, Varna, Bulgaria, Vol. 1 (Glass), Eds B. Samuneva et al. (Science Invest, Sofia, 1999), pp. 159-164.
11. Ivanova V. D., E. P. Kashchieva, B. T. Jivov, Y. B. Dimitriev, Electron Microscopic Study of Lead-Borate Composites Containing PbMoO4 Nanocrystals, Nanostructured Materials Application and Innovation Transfer, Heron Press Science Series, Sofia, 2001, pp 30-32.
12. Yordanov St.I., A.D. Bachvarov-Nedelcheva, R.S. Iordanova, Influence of ethylene glycol on the hydrolysis-condensation behavior of Ti(IV) butoxide, Bulgarian Chemical Communications, Special Issue A, Volume 49, 2017, pp 265-270.
13. Bachvarova-Nedelcheva A., St. Yordanov, R. Iordanova, I. Stambolova, Comparative study of sol-gel derived pure and Nd-doped TiO2 nanopowders, J. Chem. Technol. Metall., 53 (6), 2018, pp. 1167-1172.
14. Ismail F. A., R.M.A. Osman, M.S. Idris, Review on dielectric properties of rare earth doped barium titanate, AIP conference proceedings, 1756, 09005 (2016).
15. Devi Ch.S., G.S. Kumar, G. Prasad, Spectroscopic and electrical studies on Nd3+, Zr3+ ions doped BaTiO3 ferroelectrics prepared by sol-gel method. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,136, Part B (2015), pp. 366-372.