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Synthesis of La Doped Barium Titanate Ceramics with Application in Electronics

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Abstract
The $BaLaTiO_3$ ceramics doped with 0,05 mol% La were prepared by sol-gel method. The obtained phases were characterized by X-ray gas analysis and IR spectroscopy confirming these results. A tablet is formed at a baking temperature of 1240 ° C. The value of the relative dielectric constant 21000 was determined. As the increasing La content, the transitions from tetragonal to cubic phase and grain growth was realized. The dielectric permittivity enhanced with increasing La content and the maximum value 21000 was attained with 0,05 mol% La doped.

Keywords: Barium titanate, La-doped ceramics, Sol-Gel

1. Introduction

With the intensive development of modern electronics significantly increases the need for the use of new materials [1,2] and electronic components with increased technical characteristics, allowing their operation under increasing operating loads and adverse environmental conditions (elevated temperature, electromagnetic interference, high humidity and others).). The main technological possibilities for solving the existing problems are the development of new unconventional products with appropriate indicators or the modification of traditional materials to innovative products.

For decades, barium titanate [3-5] has been essential for a number of technical fields and is used in the manufacture of resonators, emitters, posistors, thermistors, transducers, actuators, hydrophones, single-layer and multilayer ceramic capacitors and others. At the same time, the research of binary and multicomponent systems [1, 7-12] with the participation of BaTiO3 and of modified barium-titanate materials [3,4,13-16] obtained by applying different technological methods for synthesis continues.

The donation of barium titanate [17-28] with donor or acceptor ions with appropriate crystal chemical parameters (localized at A- or B-structural positions) and low concentration, provoking changes in the electrophysical parameters of the materials, finds significant application. Barium-titanate phases with semiconductor properties donated with donor trivalent ions (Y^{3+}, Sb3+, La^{3+}) positioned on the Ba-site or pentavalent ions (Ta^{5+}, Nb^{5+}) separated on the Ti-site were synthesized [3,18, 25]. In this technological approach, the ionic radius is a basic parameter determining the specific structural position of substitution in the modified phase. Hypothetical models have been developed analyzing the presumed structural changes and their mechanism when barium titanate is donated with La^{3+} and other components [17]. Due to structural incompatibility with the parameters of Ti^{4+} (0.68 Å), the introduced La3+ (1.15 Å) is localized only at positions characteristic of Ba^{2+} (1.35 Å) and provides the presence of an additional positive charge (replacement of Ba2 + with La^{3+} ion). [21,25,29]. In case of heterovalent replacement of Ba^{2+} (position A-site) by La^{3+} there is a need to compensate for the additional positive charge (until the formation of an electroneutral system) by cation vacations (A- or B-sites), free electrons or change of the valence state of Ti ions (from Ti^{4+} to Ti^{3+}). On the other hand, the joint presence of Ti^{4+} and Ti^{3+} in the structure creates conditions for the transfer of charge carriers between titanium cations with different valence values and increasing the conductivity of the material to levels typical of semiconductors [6]. The specificity of the charge compensation mechanism has a significant effect on the properties of the final reaction products and is significantly influenced by the raw materials used, their quantitative ratio and the method of synthesis [29].

It was found that the presence of low concentrations of La^{3+} in barium-titanate phases is accompanied by increased grain growth and lowering of the temperature of the phase transitions [19,20, 25]. When introducing La3 + in relatively insignificant amounts (<0.5 at%) in the role of donor ions, ceramic samples with semiconductor properties were synthesized (at room temperature conditions), and when the content of La^{3+} increased, insulating characteristics were found [3, 18-21, 25].

An essential factor ensuring the production of complete end products with optimal characteristics is the use of productive and energy efficient synthesis methods. An adequate solution can be considered the application of sol-gel technology, providing a number of advantages [30-37]: use of available raw materials and consumables, use mainly of standard equipment, control of the parameters of the reaction medium and the individual technological stages, synthesis of mono - and polyphase products with planned characteristics, thermal treatment of the compositions at relatively low temperature values in comparison with classical energy-intensive high-temperature methods and others.

The aim of the present work is to study the structure and properties of La-subsidized barium-titanate ceramics synthesized by the sol-gel method. The prepared test specimens were examined by X-ray phase analysis and infrared spectroscopy. With an increase in the amount of La introduced into the experimental compositions, an increase in the registered values of dielectric constant (21000 at 0.05 mol% La) and a tendency to transition from tetragonal to cubic phase were found. The phase changes during the intermediate stages of the decomposition processes of the used raw materials are studied.

2. Experimental part

Synthesis of La donated barium titanate ceramics was performed by sol gel method in the following sequence: La_2O_3 (0.3g) was dissolved in dilute nitric acid under heating. Barium acetate - 8.938 g - is dissolved in 15 ml of distilled water with very good homogenization. The titanium butoxide sol is obtained after dissolving in 50 ml of absolute ethanol and 25 ml of acetic acid with vigorous stirring. To the synthesized sol of $[Ba(Ac)_2]$ the dissolved lanthanum oxide is added - thus a sol is obtained, which is slowly and with good homogenization added to the sol of $Ti(OBu)_4$. The resulting final sol gels in air - under the action of moisture. Drying followed and the resulting xerogel was treated in an oven at 1000°C. Ceramics $Ba_{0.95}La_{0.05}TiO_3$ were synthesized and the phase composition was determined by XRD. IR spectroscopy was also performed to prove the result of the X-ray phase analysis. The predominant phase is tetragonal shown in Fig. 1. A tablet is then formed from the powder samples and baked at 1240°C. Relative dielectric constant is measured on the samples thus obtained with a gradual increase in temperature.

3. Results and discussion

X-ray phase analysis was performed using a Bruker D8 Advance apparatus with a solid state LynxEye detector.

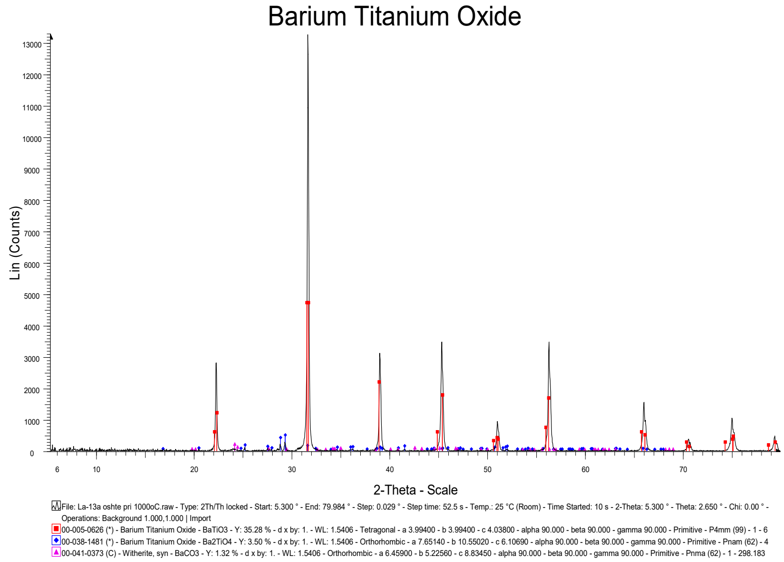

Fig. 1. XRD analysis of $Ba_{0.95}La_{0.05}TiO_3$

The main phase of fig. 1 is of $BaTiO_3$. The presence of a non-stechiometric Ba_2TiO_4 phase is observed, but according to additional studies this phase does not have a negative effect on the desired properties of the final product.

Figure 2 shows the infrared spectroscopy of La donated $BaTiO_3$.

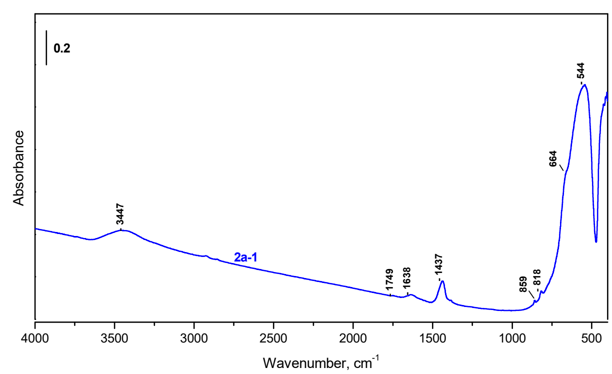

Fig. 2 IR spectrum of $BaTiO_3$ doped with La

The 544 cm^{-1} band and the 664 cm^{-1} arm refer to the valence oscillations of the Ti-O bond. The bands 1437 cm^{-1} and 1638 cm^{-1} are characteristic of the valence symmetric and asymmetric oscillations of the (COO-) groups. The wide band 3447 cm^{-1} is attributed to (OH) groups - weakly adsorbed water. Most likely the result of the preparation of tablets with KBr (It is known that La and its compounds tend to adsorbing water).

The relative dielectric constant presented in fig. 3 shows rather high values of $\varepsilon = 21000$ in comparison with the conducted literature studies, in which the obtained high values of ε are related to the production of materials by high-temperature synthesis methods.

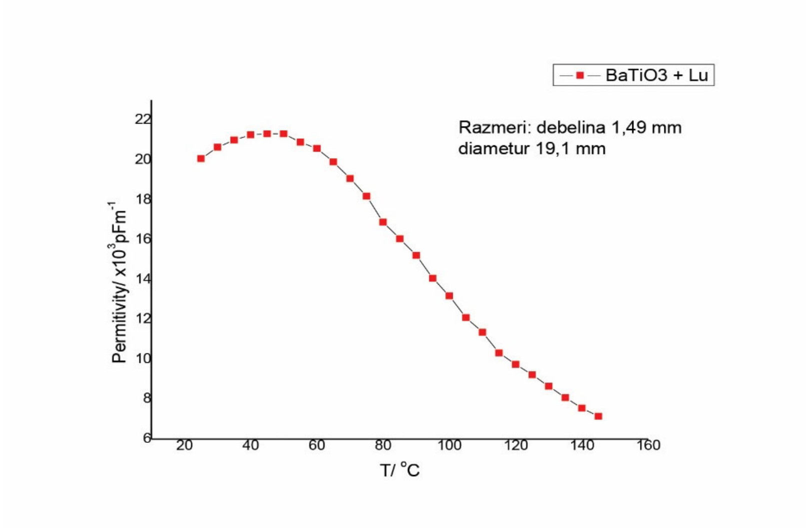

Fig. 3 Relative dielectric constant of modified $BaTiO_3$ with La

4. Conclusion

A phase of $Ba_{0.95}La_{0.05}TiO_3$ was obtained from the sol-gel synthesis. The results were characterized by XRD analysis proving the presence of this phase. The characterization was supported by further analysis by IR spectroscopy showing the appearance of characteristic bands at 544 cm^{-1} and 664 cm^{-1}. A high relative dielectric constant of 21000 was established from the molded sample. From the results thus obtained, we can establish that the material is suitable for the manufacture of capacitors used in electronics.

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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. 1330002-1-1330002-22.
3. Biscaglia M.T., V. Buscaglia, M. Viviani, P. Nanni, M. Hanuskova, Influence of foreign ions on the crystal structure of $BaTiO_3$, Journal of European Ceramic Society, 20, 2000, pp.1997–2007.
4. Yongping P., Y. Wenhu, C. Shoutian, Influence of rare earths on electric properties and microstructure of barium titanate ceramics, Journal of Rare Earths, 25, 2007, pp. 154-157.
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. Li Y.M., W. Chen, Q. Xu, J. Zhou, X. Gu, S. Fang, Electromechanical and dielectric properties of $Na_{0.5}Bi_{0.5}TiO_3$-$K_{0.5}Bi_{0.5}TiO_3$-$BaTiO_3$ lead-free ceramics, Mater. Chem. Phys. 94, 2-3, 2005, pp. 328-332.
8. Li Y., W. Chen, Q. Xu, J. Zhou, X. Gu, Piezoelectric and ferroelectric properties of $Na_{0.5}Bi_{0.5}TiO_3$-$K_{0.5}Bi_{0.5}TiO_3$-$BaTiO_3$ piezoelectric ceramics, Mater. Lett. 59, Issue 11, 2005. pp. 1361-1364
9. Song J. S., S. J. Jeong, I. S. Kim, D. S. Lee, E. C. Park, Piezoelectric and dielectric properties in grain oriented $(Bi_{0.5}Na_{0.5})TiO_3$-$BaTiO_3$ ceramics, Ferroelectrics, 338, 2006, pp. 3-8.
10. Hiruma Y., H. Nagata, T. Takenaka, Phase transition temperatures and piezoelectric properties of $(Bi_{1/2}Na_{1/2})TiO_3$–$(Bi_{1/2}K_{1/2})TiO_3$–$BaTiO_3$ lead-free piezoelectric ceramics, Japanese Journal of Applied Physics, Volume 45, Number 9S, 2006, pp. 7409.
11. Zhang S.T., B. Yang, W. Cao, The temperature-dependent electrical properties of $Bi_{0.5}Na_{0.5}TiO_3$-$BaTiO_3$-$Bi_{0.5}K_{0.5}TiO_3$ near the morphotropic phase boundary, Acta Mater. Vol. 60, Issue 2, 2012, pp. 469-475.
12. Trelcat J.-F., C. Courtois, M. Rguiti, A. Leriche, P.-H. Duvigneaud, T. Segato, Morphotropic phase boundary in the BNT-BT-BKT system, Ceram. Int., Vol. 38, Issue 4, 2012, pp. 2823-2827.
13. Tsur Y., T.D. Dunbar, C.A. Randall, Crystal and defect chemistry of rare earth cations in $BaTiO_3$, Journal of Electroceramics, 7, 2001, pp. 25-34.
14. Buscaglia M. T., M. Viviani, V. Buscaglia, C. Bottino, P. Nanni, Incorporation of Er3+ into $BaTiO_3$, Journal of the American Ceramic Society, 85, 2002, pp. 1569- 1575.
15. Kim J.H., S.H. Yoon, Y.H. Han, Effects of Y_2O_3 addition on electrical conductivity and dielectric properties of Ba-excess BaTiO3, Journal of the European Ceramic Society, 27, 2007, pp. 1113-1116.
16. Pinjari R.K., N.M. Burange, B.A. Aldar, Structural and electrical analysis of strontium substituted barium titanate, Int. J. Eng. Res. Technol. 3, 2014, pp. 209-213.
17. Morrison F.D., A.M. Coats, D.C. Sinclair, A.R. West, Charge compensation mechanisms in La-doped $BaTiO_3$, Journal of Electroceramics, 6, 2001, pp. 219-232.
18. Morrison F.D., D.C. Sinclair, A.R. West, Doping mechanisms and electrical properties of La-doped $BaTiO_3$ ceramics, Int. J. Inorg. Mater. 3, 2001, pp.1205–1210.
19. Wodecka-Dus B., D. Czekaj, Fabrication and Dielectric Properties of Donor Doped $BaTiO_3$ Ceramics, Archives of Metallurgy and Materials, Vol. 54, Issue 4, 2009, pp. 923-933.
20. 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.
21. Vijatovic M.M., B.D. Stojanovic, J.D. Bobic, T. Ramoska, P. Bowen, Properties of lanthanum doped $BaTiO_3$ produced from nanopowders, Ceramics International, 36, 2010, pp. 1817–1824.
22. Huang C.M., C.Y. Lin, J. Shieh, Relationship between the evolutions of the microstructure and semiconductor properties of yttrium-doped barium titanate ceramics, Journal of Physics D: Applied Physics, 44, 2011, pp. 345403.
23. Ianculescu A., Z.V. Mocanu, L.P. Curecheriu, L. Mitoseriu, L. Padurariu, R. Trusca, Dielectric and tunability properties of La-doped $BaTiO_3$ ceramics, J. Alloys Compd. 509, Issue 41, 2011. pp. 10040-10049.
24. Ganguly M., S.K. Rout, T.P. Sinha, S.K. Sharma, H.Y. Park, C.W. Ahn, I.W. Kim, Characterization and Rietveldrefinement of A-site deficient lanthanum doped barium titanate, J. Alloys. Comp. 579, 2013, pp. 473-484.
25. Billah M., A.A. Ahamed, A. Sen, M.M. Rahman, Influence of Lanthanum doping on the Crystallite Growth and Dielectric Properties of Barium Titanate ($BaTiO_3$) Ceramics, Conf.

Proc. International Conference on Mechanical, Industrial and Materials Engineering 2015, 11-13 December, 2015, Rajshahi, Paper ID: MS-28, pp. 1-6.
26. Farahin N., A. Hamid, R. Aina, M. Osman, M.S. Idris, M.R. Zakaria, Review on preparation and properties of high-K dielectric material based on Lanthanum doped Barium Titanate, Materials Science Forum Vol 819 (2015) pp. 173-178.
27. Vasilescu C.A., C. Marin, S.E. Corina, A. Gheorghe, G. Paul, R. Trusca, Lanthanum influence on the structure, dielectric properties and luminescence of BaTiO3 ceramics processed by spark plasma sintering technique, J. Alloys Comp. 706, 2017, pp. 538-545.
28. Devmunde B. H., S.B. Somwanshi, P.B. Kharat, M.B. Solunke, Rare Earth Ion (La^{3+}) Doped $BaTiO_3$ Perovskite Nanoceramics for Spintronic Applications, NANOMAT-2020, Journal of Physics: Conference Series 1644, 012055, 2020, pp. 1-5.
29. Lee J.K., K.S. Hong, J.W. Hong. Roles of Ba/Ti Ratios in the dielectric properties of $BaTiO_3$ ceramics, J. Am.Ceram. Soc. Vol. 84, Issue 9, 2001, pp. 2001-2006.
30. Che R.X., H. Gao, H.B. Zhao, J.X. Fang, Developing history and present situation of sol-gel science, Journal of Yunnan University, 2005, 27(3A), pp. 378-383.
31. Xinle Z., M. Zhimei, X. Zuojiang, C. Guang, Preparation and Characterization on Nano-Sized Barium Titanate Powder Doped with Lanthanum by Sol-Gel Process, J. Rare Earths, 24, 2006, pp. 82–85.
32. Fan H., L. Liu, Optimizing design of the microstructure of sol-gel derived $BaTiO_3$ ceramics by artificial neural networks, J. Electroceram., 22, 2009, pp. 291– 296.
33. Wang J., Ch. Li, B. Xu, Basic Principle, Advance and Current Application Situation of Sol-Gel Method, Chemical industry and engineering, 2009, 26(3), pp. 273-277.
34. Yordanov S.I., A.D. Bachvarova-Nedelcheva, R.S. Iordanova, I.D. Stambolova, Sol-gel Synthesis and Properties of Sm Modified TiO_2 Nanopowders, Bulgarian Chemical Communications 50, 2018, pp. 42-48.
35. Bachvarova-Nedelcheva A., S. Yordanov, R. Iordanova, I. Stambolova, Comparative Study of Sol-Gel Derived Pure and Nd-doped TiO_2 Nanopowders, Journal of Chemical Technology and Metallurgy 53(6), 2018, pp. 1167-1172.
36. **Aleksandrova M., B. Jivov, L. Lakov**, Summary of sol-gel synthesis of materials with electronic applications, International Scientific Journal Materials Science. Non-Equilibrium Phase Transformations, Year VI, Issue 3, 2020, Scienticic Technical Union of Mechanical Engineering INDUSTRY 4.0, 2020, pp. 83-85.
37. Tan W.K., H. Muto, G. Kawamura, Z. Lockman, A. Matsuda, Nanomaterial Fabrication through the Modification of Sol–Gel Derived Coatings, Review, Nanomaterials, 11, 181, 2021, pp. 1-30.