

Complex electrical impedance and dielectric spectroscopy studies of BaTiO₃-BaSnO₃ ceramics obtained via sol-gel method.

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Abstract: In view of the practical applications of the piezoelectric ceramics produced from barium titanate (BaTiO₃) and barium stannate (BaSnO₃), (the BT-BS system), the dielectric behavior of such materials was studied. The starting components (powder of both BaTiO₃ and BaSnO₃) were synthesized and structurally characterized in advance. Bulk samples of BT-BS (formed as tablets with addition of PVA plasticizer) were prepared using the sol-gel method by varying the BT-BS composition percentage. The samples were characterized by complex electrical impedance spectroscopy and dielectric spectroscopy in the frequency range from 0.1 Hz to 1 MHz. As compared to BaTiO₃, an increase with at least 50 % was measured for the value of the room-temperature dielectric constant (ϵ' – the real part of the dielectric permittivity) of the BT-BS samples containing 15 wt% BaSnO₃. In contrast, the 50 wt% content of BaSnO₃ led to a decrease of ϵ' value of BT-BS by a factor of 3.5, due to relatively low ϵ' value of BaSnO₃. Analyses of the frequency spectra of complex electrical impedance and complex dielectric permittivity revealed the dielectric relaxational behavior of the BaTiO₃+BaSnO₃ system. The results obtained for ϵ' of BT-BS dielectrics as a function of the temperature were correlated with the data from structural studies. In particular, a specific enhancement of ϵ' was observed in temperature range around 120 °C for the BT-BS samples containing 15 wt% BaSnO₃. Corresponding conclusions were done. The effects observed show that the synthesized BaTiO₃-BaSnO₃ ceramics are promising materials for piezoelectric and dielectric applications, e.g., in energy storage devices.

Keywords: SOL-GEL, BATIO₃, BASNO₃, IMPEDANCE SPECTROSCOPY

I. Introduction

Alkaline earth oxides are interesting compounds in terms of their dielectric properties. Solid solutions in the BaTiO₃-BaSnO₃ (BTBS) system have attracted attention in recent years in the field of nanocapacitors. Synthetic BaTiO₃, prepared by conventional solid phase method shows great performance with high ϵ_r value of ~ 1900 at room temperature (30 °C), low dielectric loss $\delta \sim 0,01$ and piezoelectric constant $d_{33} \sim 191$ pC/N [1]. BaTiO₃ has five polymorphic structures showing different phases that vary with temperature [2]. The phase transition of BaTiO₃ at the Curie temperature (T_c) significantly changes its properties, which are ferroelectric and non-ferroelectric.

The BaTiO₃ ferroelectric shows a hexagonal structure at 1460 °C and a cubic structure at over 120 °C [3]. On the other hand, the ferroelectric properties of BaTiO₃ exist in three different polymorphic crystal structures, which are tetragonal, orthorhombic and rhombohedral. Zheng et al. [4] studied the effect of grain size on the dielectric constant and piezoelectric properties of BaTiO₃. They report that the dielectric constant and piezoelectric properties increase significantly by reducing the grain size. The maximum grain size was reached around 0.94 μm due to the density of the domain structure and the area decreased with decreasing grain size. BaSnO₃ has a cubic perovskite structure that exhibits n-type semiconductor behavior at room temperature [5, 6]. BaSnO₃ is thermally stable up to 2000 °C, but has a high absorption of moisture compared to other species [6]. Thus, it is currently used for thermally stable capacitors and humidity sensors [7, 8]. Meanwhile, completely dense BaSnO₃ ceramics can be achieved by synthesizing them at temperatures above 1594 °C [6]. Huang reported that in order to obtain single-phase BaSnO₃, it is necessary to heat it to 1200 °C and achieve a significant amount of grain porosity [9, 10].

In addition, Azad confirmed that grain porosity can be reduced by milling BaSnO₃ at 1600 °C [11]. The initial report on materials based on the findings found that BaSnO₃, synthesized at 1200 °C, has a dielectric constant $\epsilon_r \sim 14$ at 25 °C [6]. Kumar reported that BaSnO₃ was sintered at 1200 °C for 12 hours using the solid state method. A huge dielectric behavior of BaSnO₃ has recently emerged, where the dielectric constant ϵ_r value reaches ~ 6000

when measured at 220 °C and at a frequency of 1 kHz. The ϵ_r value of BaSnO₃ is two orders of magnitude higher than previously reported studies [12, 13]. However, the dielectric constant decreases with decreasing temperature. Therefore, it is assumed that the lack of oxygen leads to a reduction of Sn⁴⁺ to Sn²⁺ in BaSnO₃ samples, which contributes to an anomaly in the value of the giant dielectric constant ϵ_r when the samples were sintered at very high temperatures of T °C ≥ 1450 °C [13-16].

II. Experimental part

Organic precursors such as barium acetate, titanium butoxide and stannous acetate were used to synthesize the ceramic samples. The process is carried out according to the sol-gel method, with the ratio of the starting components being 1:1:1.6. The solutions were prepared in the presence of acetic acid, distilled water and acetylacetone. Each of the indicated solutions was homogenized independently using a magnetic stirrer for 30 minutes. After mixing the components, the total solution was homogenized for 5 hours. The synthesis and stabilization of the sol thus carried out allows the deposition of thin layers on various monolithic substrates. One part is allowed to gel. The gel was dried in an oven at 120 °C for 24 hours. Next is annealing at 800 °C and holding for 8 hours. After obtaining the desired BaTiO₃ and BaSnO₃ phases, tablets are formed and pressed in the presence of polyvinyl alcohol. The finished samples are calcined in a furnace at a temperature of 1100 °C until the plasticizer burns out. The deposition of layers by the immersion method is carried out by means of a dip-coater

III. Results and discussion

Characterization of the resulting phases was performed by X-ray analysis using a Bruker D8 Advance automatic powder X-ray diffractometer with CuK α radiation (Ni filter) and registration by a LynxEye solid-state detector. The X-ray spectrum was recorded in the angular range from 10 to 80° 2 θ with a step of 0.02° 2 θ and a counting time of 17.5 s/step. Qualitative phase analysis was performed using the International Center for Diffraction Data (ICDD) PDF-2(2022) database. In fig. 1 and 2 are presented X-ray photographs of the prepared samples of BaTiO₃-BaSnO₃ in the ratio (85%:15%) and BaTiO₃-BaSnO₃ in the ratio (50%:50%). Figure 2 shows the distinct peaks of the BaTiO₃ and BaSnO₃ phases. We

have the presence of TiO₂ in two nonstoichiometric compositions between 24° and 25° and nonstoichiometric SnO₂ at 27°. The result may be due to the not good homogeneity during the preparation of the tableted samples or incorrectly conducted temperature mode of baking. When adjusting the percentage ratio of the BaTiO₃-BaSnO₃ system (85%:15%), we have a monophasic characteristic of the BaTiO₃-BaSnO₃ structure.

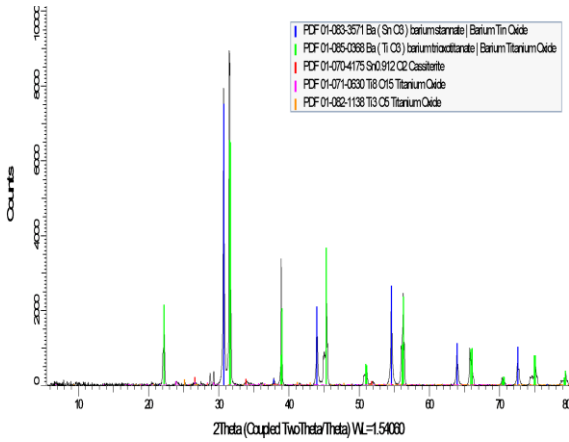


Fig. 1. System BaTiO₃ + BaSnO₃ in ratio (50% : 50%) ceramic

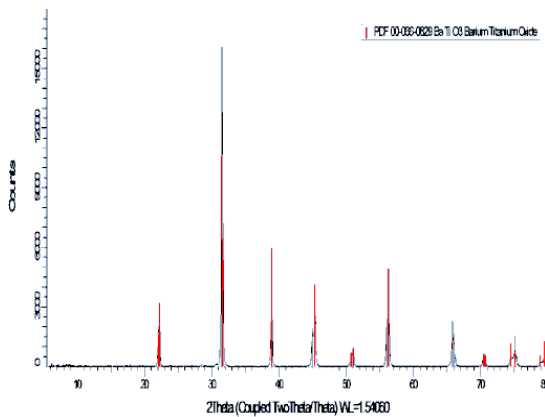


Fig. 2. System BaTiO₃ + BaSnO₃ in ratio (85% : 15%) ceramic

Description of impedance spectra

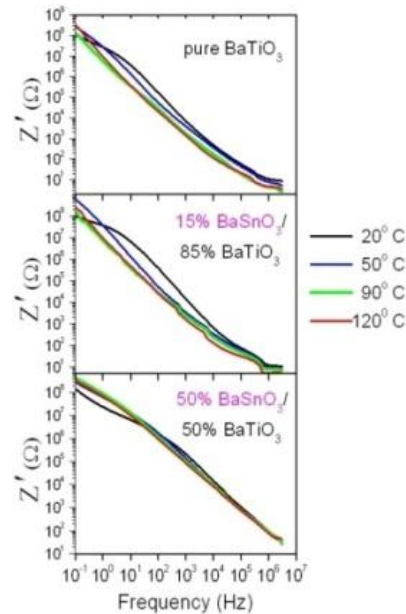
Experimental data were obtained by EIS. By this technique, both real (*ReZ*) and imaginary (*ImZ*) parts of the complex electrical impedance $Z^* = ReZ + i ImZ$ are simultaneously measured as a function of the frequency *f* of the alternating-current (AC) electric field applied. The frequency spectra of Z^* of the produced sample were recorded by electrical impedance-meter Bio-Logic SP-200, in the range 0.1 Hz – 1 MHz, at various temperatures (Fig.4). By the measurements, for all the samples were kept identical experimental conditions. Silver paste was applied on both sample surfaces, serving as electrodes. The amplitude of the AC voltage applied between the electrodes of ceramic cylinders was 2 V_{RMS} (sine function). The dimensions of the two round electrodes were 2.0 cm in diameter, the distance between them varied 1-4 mm.

Dielectric Spectroscopic Analysis
Dielectric Permittivity

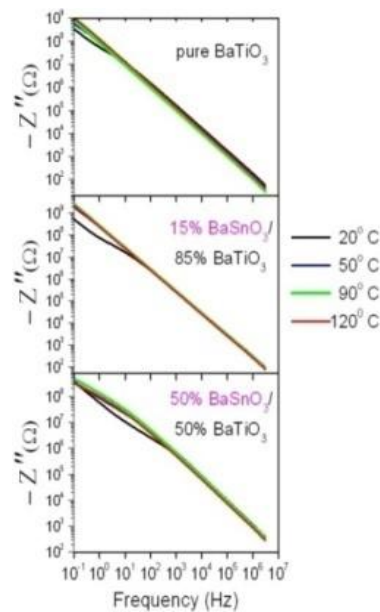
By means of the expressions

$$\epsilon'(f) = \frac{-Z''(f)d}{2\pi f \epsilon_0 A |Z(f)|^2} \text{ and } \epsilon''(f) = \frac{Z'(f)d}{2\pi f \epsilon_0 A |Z(f)|^2}$$

from the measured $Z'(f)$ and $Z''(f)$ spectra, we calculated the real (ϵ') and imaginary (ϵ'') parts of the complex dielectric function of the composites under study. The geometrical parameters were $A = XX \text{ cm}^2$ and $d = XX \text{ mm}$, and $\epsilon_0 = 8.85 \times 10^{-12} \text{ F.m}^{-1}$ was the value of the permittivity of free space. The dispersion curves for both ϵ' and ϵ'' had relaxational characteristics.



a)



b)

Fig. 4 Frequency spectra of real (Z') and imaginary (Z'') parts of complex electrical impedance measured for the samples at different temperatures

Conclusion:

BaTiO₃-BaSnO₃ ceramic phases were synthesized. XRD analysis showed a good phase structure in the ratio of 85%/ 15%. The studied physical and mathematical indicators showed good piezoelectric effects. With a view to future applications in electronics, the material will be further investigated both as dip-coating deposited thin layers and presented in subsequent developments by the team.

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References:

1. Eric A. Gabilondo, Shaun O'Donnell, Rachel Broughton, Jacob L. Jones, Paul A. Maggard, "Synthesis and stability of Sn (II)-containing perovskites: (Ba,SnII)HfIVO₃ versus (Ba,SnII)SnIVO₃", *Journal of Solid State Chemistry*, (2021), 302.
2. Amine Bendahhou, Pascal Marchet, Soufian El Barkany, Mohamed Abou-Salama, "Structural and impedance spectroscopic study of Zn-substituted Ba₅CaTi₂Nb₈O₃₀ tetragonal tungsten bronze ceramics", *Journal of Alloys and Compounds*, Elsevier, 2021, 882, pp.160-176.
3. Jinyu Lu, Gang He 1, Jin Yan, Zhenxiang Dai , Ganhong Zheng 1, Shanshan Jiang, Lesheng Qiao, Qian Gao, Zebo Fang, "Interface Optimization and Transport Modulation of Sm₂O₃/InP Metal Oxide Semiconductor Capacitors with Atomic Layer Deposition-Derived Laminated Interlayer", *Journal Nanomaterials*, 2021, 11, 3443.
4. Fayaz Hussain, Amir Khesro, Raz Muhammad, Dawei Wang, "Effect of Ta-doping on functional properties of K_{0.51}Na_{0.49}NbO₃", 2019, *Materials Research Express* 6, 106309.
5. Kezhen Yin, Jingwei Zhang, Zhenpeng Li, Jingxing Feng, Ci Zhang, Xinyue Chen, Andrew Olah, Donald E. Schuele, Lei Zhu , Eric Baer, "Polymer multilayer films for high temperature capacitor application", *Journal of applied polymer science*, 2018, DOI: 10.1002/app.47535.
6. Dong, N., Gao, X., Xia, F., Liu, H., Hao, H. & Zhang, S. (2019). Dielectric and Piezoelectric Properties of Textured Lead-Free Na_{0.5}Bi_{0.5}TiO₃-Based Ceramics. *Crystals*, 9 (4), 9040206-1-9040206-11.
7. L. Zhang, Y. Pu, M. Chen, Ultra-high energy storage performance under low electric fields in Na_{0.5}Bi_{0.5}TiO₃-based relaxor ferroelectrics for pulse capacitor applications, *Ceram. Int.* 46 (2020) 98–105. <https://doi.org/10.1016/j.ceramint.2019.08.238>.
8. Hend Kacem, Ah. Dhahri, Mohamed Amara Gdaiem, Z. Sassi, L. Seveyrat, L. Lebrun, V. Perrin, J. Dhahri, "Electrocaloric properties of lead-free ferroelectric ceramic near room temperature", *Applied Physics A* (2021) pp127:483.
9. Dash Smaranika, Pradhan Dhiren K., Kumari Shalini, Ravikant None, Rahaman Md. Mijanur, Cazorla C., Brajesh Kumar, Kumar Ashok, Thomas Reji, Rack Philip D., Pradhan Dillip K., "Enhanced ferroelectric and piezoelectric properties of BCT-BZT at the morphotropic phase boundary driven by the coexistence of phases with different symmetries", (2021) *Physical Review B*, Volume: 104; Journal Issue: 22.
10. Luo Huajie, Qi He, Sun Shengdong, Wang Lu, Ren Yang, Liu Hui, Deng Shiqing Chen Jun, Structural origin for the high piezoelectric performance of (Na_{0.5}Bi_{0.5})TiO₃-BaTiO₃-BiAlO₃ lead-free ceramics, *Journal Acta Materialia* Volume: 218, (2021) doi.org/10.1016/j.actamat.2021.117202.
11. F Medjaldi, A Bouabellou, Y Bouachiba, A Taabouche, K Bouatia and H Serrar, "Study of TiO₂, SnO₂ and nanocomposites TiO₂:SnO₂ thin films prepared by sol-gel method: Successful elaboration of variable- refractive index system", *Mater. Res. Express* 7 (2020) 016439.
12. B. Wodecka-Du's, M. Adamczyk-Habrajska, T. Goryczka, D. Bochenek, "Chemical and Physical Properties of the BLT4 Ultra Capacitor—A Suitable Material for Ultracapacitors", *Materials* 2020, 13, 659; doi: 10.3390/ma13030659.
13. Tae Yeon Kim, Je Oh Choi, Gopinathan Anoop, Jaegyu Kim, Seong Min Park, Shibnath Samanta, Woosoon Choi, Young-Min Kim, Seungbum Hong , Ji Young Jo, "(111)-oriented Sn-doped BaTiO₃ epitaxial thin films for ultrahigh energy density capacitors", *Ceramics International*, Available online 15 June 2021, 0272-8842.
14. Lyuben Lakov, Mihaela Aleksandrova, Vladimir Blaskov, Yordan Marinov, Veselin Petkov, „Technological regulation for creating a ceramic target from BaTiO₃ gel powders doped with Sn. Temperature dependence of the dielectric permittivity”, *Machines. Technologies. Materials*. Vol. 15 (2021), Issue 4, pg(s) 155-157.
15. Mihaela Aleksandrova, Bojidar Jivov, Lyuben 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, Scientific Technical Union of Mechanical Engineering INDUSTRY 4.0, 2020, ISSN:ISSN PRINT 2367-749X, ISSN WEB 2534-8477, 83-85.
16. Ku Noor Dhaniah Ku Muhsen, Rozana Aina Maulat Osman, Mohd Sobri Idris, "The effects of Ca, Zr and Sn substitutions into a ternary system of BaTiO₃-BaSnO₃-BaZrO₃ towards its dielectric and piezoelectric properties": a review, *Journal of Materials Science: Materials in Electronics*, Published online, June 2020.