Liudmila A. BLIZNYUK[1], Aliaksei A. KLIMZA[1], Vera V. FEDOTOVA[1], Czesław KARWAT[2]

Scientific-Practical Materials Research Center of NAS of Belarus (1), Lublin University of Technology (2)

Dependencies of grain structure formation in dielectric materials based on solid state solutions $Ba_xSr_{1-x}(R_{0,5}Nb_{0,5})O_3$ with R = Ho, Er, Tm, Yb and Lu

Abstract. *Dielectric ceramic materials based on the $Ba_xSr_{1-x}(R_{0.5}Nb_{0.5})O_3$, where R= Ho, Er, Tm, Yb and Lu, obtained by means of mechanical activation, have been investigated. A mechanical activation effect on phase composition of synthesized solid solutions, densification temperature, microstructure and dielectric properties was studied. The use of mechanical activation process was shown to influence the physical-chemical properties of the solid substances including their reaction efficiency.*

Streszczenie. *Badaniom poddano ceramiczne materiały izolacyjne oparte na związkach $Ba_xSr_{1-x}(R_{0.5}Nb_{0.5})O_3$, gdzie R = Ho, Er, Tm, Yb oraz Lu, otrzymanych metodą aktywacji mechanicznej. Przeanalizowano wpływ aktywacji mechanicznej na skład fazowy, temperaturę zagęszczania, mikrostrukturę oraz właściwości dielektryczne syntezowanych roztworów stałych. Zaprezentowano zastosowanie procesu aktywacji mechanicznej w celu wpływania na właściwości fizykochemiczne substancji stałych, w tym ich wydajność w reakcjach chemicznych. (**Zależności formowania struktury ziarnistej w materiałach izolacyjnych opartych na roztworach stałych $Ba_xSr_{1-x}(R_{0,5}Nb_{0,5})O_3$ z R = Ho, Er, Tm, Yb oraz Lu).***

Keywords: dielectric material, mechanical activation, complex perovskite ceramics.
Słowa kluczowe: materiał izolacyjny, aktywacja mechaniczna, złożone spieki perowskitu.

Introduction

New technique puts in a more rigid claim to used materials and methods of their preparation, therefore one can consider a search of new materials, technology of their synthesis and methods of technologic parameters perfection as an important scientific and industry problem.

Large group of complex perovskite-like compositions may be obtained by substitution of one or two cations in perovskite structure with general formulae ABO_3 for some type of cations with different valence. Wide application of dielectric ceramic materials $Ba_xSr_{1-x}(B'_yB''_{1-y})O_3$ (B' - rare earth element, B''= Nb or Ta), named complex perovskites, is hampered with complexity of qualitative ceramics preparation at low synthesis temperatures what is important imperfection of given material class [1, 7], for which annealing temperature is 1550-1700°C.

We present the results of the study of dielectric ceramic materials based on $Ba_xSr_{1-x}(R_{0.5}Nb_{0.5})O_3$ system (R= Ho, Er, Tm, Yb, Lu), prepared using mechanical activation. The mechanical activation effect is investigated on phase composition of the solid solutions, their annealing temperature, microstructure and dielectric properties. The mechanical activation application is shown to influence physical-chemical properties of solid substances, including the reaction efficiency.

Experiment

There were used high purity oxides R_2O_3, Nb_2O_5, and carbonates $BaCO_3$, $SrCO_3$. Components taken in stoichiometric ratio were mixed thoroughly. Synthesis was performed at 1200°C during 4 h. X-ray diffraction phase analysis was performed at each study stage at room temperature using diffractometer DRON 4 (Cu_α - radiation, automatic regime with step of 0.05°, angle diapason 10°-60°).

From one part of the synthesized solid solution powder the samples have been prepared using standard ceramic technology. Solid solutions with addition of 3 weight % of binding material have been grinded thoroughly and product have been pressed as pellets of 12 mm diameter and 2-5 mm thickness under pressure of 150 MPa. Annealing was performed in air at temperatures (1450-1600)°C during 4-6 h.

Another part of synthesized solid solution powder has been exposed to mechanical activation stage in chalcedony grindability drum of ball planetary mill. Chalcedony grinding balls were of 10-12 mm diameter. Fine-dispersed grinding was performed with adding of ethyl alcohol during 2.5-12.5 h. After each grinding the powder was dried. There were 3 height % of binding added, product was grinded, obtained masse was pressed into pellets with diameter of 12 mm and thickness of 2-5 mm, under pressure of 150 MPa. Annealing was performed in air at (1220-1450)°C during 4 h.

Shape and size of powder particles after treatment were investigated using electron microscope LEO 1455VP.

Results and discussion

Analysis of phase composition of all the samples prepared by standard ceramic technology has shown a presence of R_3NbO_7 composition beside the main crystalline phase (Fig. 1).

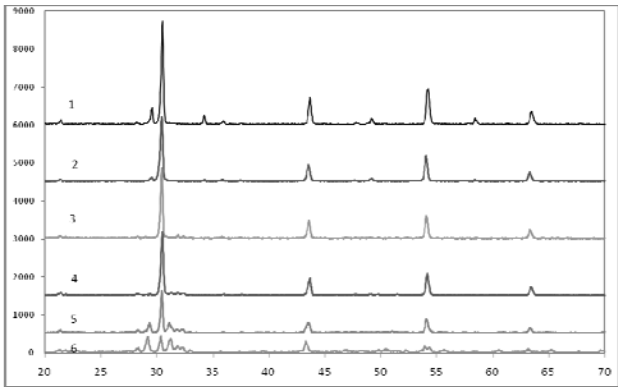
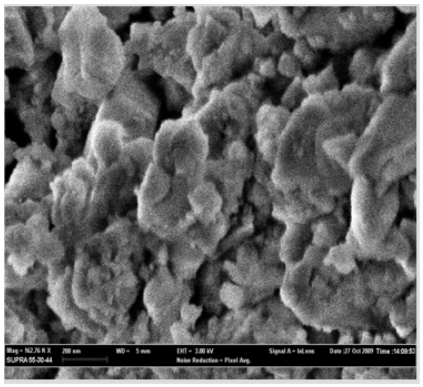


Fig.1. X-ray diffraction patterns of the samples of $Ba_xSr_{1-x}(Er_{0.5}Nb_{0.5})O_3$ system at different grinding duration: 1 – samples prepared by standard ceramic method; 2 – mechanical activation duration was 2.5 h; 3 – 5 h; 4 – 7.5 h; 5 – 10 h; 6 – 12.5 h

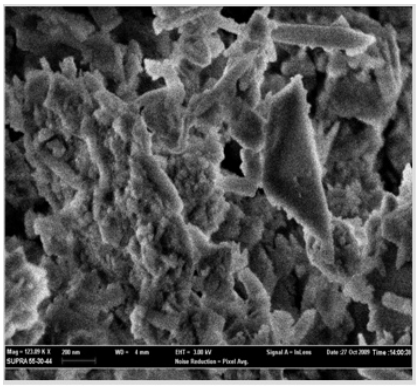
Fig. 2 demonstrates the X-ray diffraction patterns of the samples obtained at different grinding duration for material composition $Ba_{0.4}Sr_{0.6}(Er_{0.5}Nb_{0.5})O_3$: 1 – samples obtained by standard ceramic method; 2 – duration of solid solution mechanical activation was 2.5 h; 3-5 h; 4-7.5 h; 5-10 h; 6-12.5 h. Note, that such a character of phase composition

dependence on method of preparation is typical for all the compositions distinguishing with type of rare earth ions of yttrium group in B – positions of perovskite structure (R - Ho, Er, Tm, Yb, Lu).

a)



b)



c)

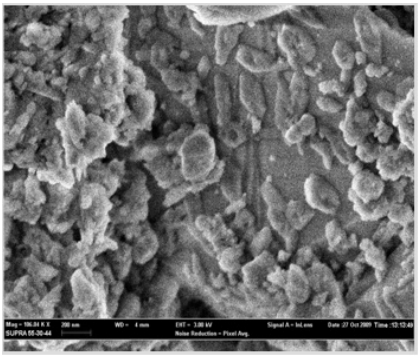


Fig.2. Powders after 12.5 h grinding: *a* – $Sr_{1-x}Ba_x(Er_{0.5}Nb_{0.5})O_3$, *b* – $Sr_{1-x}Ba_x(Yb_{0.5}Nb_{0.5})O_3$, *c* – $Sr_{1-x}Ba_x(Lu_{0.5}Nb_{0.5})O_3$

For all the materials based on the $Ba_xSr_{1-x}(R_{0.5}Nb_{0.5})O_3$ system (R= Ho, Er, Tm, Yb, Lu), obtained by standard ceramic method at 1500°C, we have not managed to prepare dense ceramic samples. The samples were incoherent, with enlarged volume.

Mechanical activation application during 2.5 h allows to obtain good dense samples of ceramics (shrinkage is more than 12%) at annealing temperature 1450°C. X-ray pattern 2 in Fig. 2 evidences the second phase presence to be insignificant.

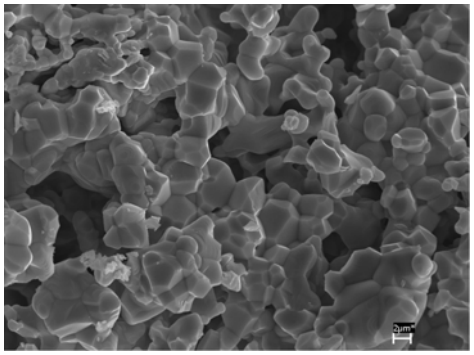
Increasing activation duration else by 2.5 h allows to lower the annealing temperature by 50-70°C and obtain the dense ceramic samples (shrinkage more than 12%) at temperatures 1400-1380°C, at that worth note that as far as rare-earth ionic radii decrease by approaching to the end of lanthanide row the annealing of the samples takes place at lower temperatures. After 5 h activation (Fig. 2, x-ray pattern 3) the samples were single-phase. Further increase of grinding duration by 2.5 h allows to lower the annealing temperature down to 1350-1300°C.

So the application of mechanical activation during 5-7.5 h enhances the reaction efficiency of solid solution and allows to prepare dense (with samples porosity less than 4%), at main phase content of 95%.

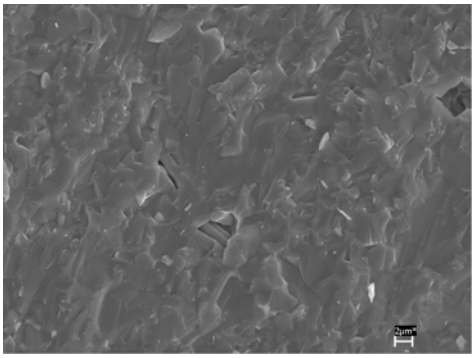
Mechanical activation during 10 h leads to the lowering of annealing temperature down to 1300-1240°C, however a number of new compositions appear beside the main phase. Mechanical activation during 12.5 h leads to the formation of multi-phase structure where beside main phase a set of compositions occurs: $Ba_6Nb_2O_{11}$, $SrNb_2O_6$, $Ba_3Nb_5O_6$ and Er_2O_3 (R_2O_3). The samples were synthesized at rather low temperature for this class of compositions – 1260-1220°C, however their porosity was more than 7%.

Investigations of powders after 12.5 h activation have shown the particles to be of irregular fragment-like shape (Fig. 2), and the powder consists of both separate particles and their conglomerations, with main dimensions in the range from 50 to 150 nm.

a)



b)



c)

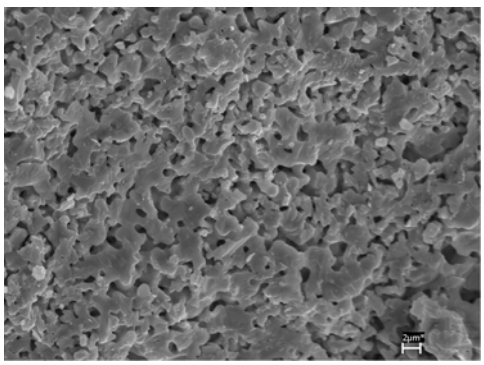


Fig.3. Break surface of ceramics system $Ba_{0.4}Sr_{0.6}(Er_{0.5}Nb_{0.5})O_3$: *a* – prepared by the standard ceramic method, *b*, *c* – with using mechanical activation during 5 and 12.5 h.

Investigations of the break surface of ceramics based on $Ba_{0.4}Sr_{0.6}(Er_{0.5}Nb_{0.5})O_3$ system using the scanning electron microscopy have shown the microstructure of the samples prepared by the standard ceramic method to have grains with clear boundaries and dimensions of 5-12 μm (Fig. 3a). Break surfaces of the samples obtained with mechanical activation application during 5 and 12.5 h (Fig. 3b and 3c) allow to evaluate changing shape and size of ceramics grains as well as a character of their boundaries and packing. Clear grain boundaries disappear, their main sizes are 0.02-2 μm. The formation of ceramics grains is demonstrated in the Table.

Table. Formation of grain depending on conditions of preparation

grinding	Min volume, μm^2	Max volume, μm^2	Main size of grain, μm	Average size of grain, μm
Without grinding	2.90	275.5	2.90-19.63	4.02
2.5 h	1.29	98.00	0.41-11.09	3.12
2.5+2.5 h	0.81	75.00	0.90-8.4	3.06
2.5+2.5+2.5 h	0.57	50.06	0.57-2.85	1.70
2.5+2.5+2.5+ 2.5 h	0.094	3.10	0.094-0.47	0.73
2.5+2.5+2.5+ 2.5+2.5 h	0.004	20.9	0.02-1.20	0.86

Dielectric parameters of prepared samples (relative permitivity, dielectric loss tangent and their temperature dependences in the temperature range -20…200°C) have been investigated at the frequency 1 MHz. The results have shown that the mechanical activation of solid solution powder during 2.5-10 h does not affect the permittivity values. All the obtained samples have high quality factor (dielectric loss tangent tgδ is less than 0.0005) and thermal stable in the whole investigated temperature range (thermal coefficient of permittivity $TK_{\varepsilon} \approx 0$ in the whole temperature range). Increase of mechanical-chemical activation duration up to 12.5 h leads to the lowering of permittivity values by 50% and enhancement of tgδ.

Conclusion

On the base of performed analysis one can conclude that the mechanical activation of the synthesized powder solid solutions $Ba_xSr_{1-x}(R_{0.5}Nb_{0.5})O_3$ (R=Ho, Er, Tm, Yb, Lu) allows to enhance significantly their reaction efficiency and obtain high-frequency ceramic materials with high electro-physical parameters at low temperatures for the given material class. However, one should take into account that large duration of activation process results in "nano-composites" formation in which the main part of substance consists of inter-phase surfaces (interfaces).

So, selecting correctly the method and conditions of mechanical activation of polycrystalline substance and taking into account the crystal structure peculiarities and chemical bond character one can achieve significant results in creation of new materials and technological processes advantageous in economical aspect.

REFERENCES

[1] Reaney I.M., Coola E.L., Setter N., Dielectric and Structural Characteristics of Ba- and Sr-based Complex Perovskites as a Function of Tolerance Factor, *Japanese Journal of Applied Physics*, 33 (1994), 3984-3990

[2] Takahashi T., Wu E.I., Van Der Van A., Ceder G., First-principles Investigation of B-site Ordering in $Ba(Mg_xTa_{1-x})O_3$ Microwave Dielectrics with the Complex Perovskite Structure, *Japanese Journal of Applied Physics*, 39, (2000), 1241-1248

[3] Khalam A., Sreemoolanathan H., Ratheesh R., Mohanan P., Sebastian M.T., Preparation, characterization and microwave dielectric properties of $Ba(B_{1/2}'Nb_{1/2})O_3$ [B′ = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Yb and In] ceramics, *Materials Science and Engineering: B,* 107 (2004), 264-270

[4] Sebastian M.T., Dielectric materials for wireless communication, Elsevier Science and Technology Publishers, Oxford (2008)

[5] Varma M.R., Biju S., Sebastian M.T., Preparation of phase pure $Ba(Zn_{1/3}Ta_{2/3})O_3$ nanopowders for microwave dielectric resonator applications, *Journal of European Ceramic Society*, 26, (2006), 1903-1907

[6] Barwick M., Azough F., Freer R.J., Structure and dielectric properties of perovskite ceramics in the system $Ba(Ni_{1/3}Nb_{2/3})O_3$–$Ba(Zn_{1/3}Nb_{2/3})O_3$, *Journal of European Ceramic Society*,26, (2006), 1767-1773

[7] Akimov A.I., Ges A.P., Klimza A.A., Properties of $A(R_{1/2}B_{1/2})O_3$ dielectrics with a complex perovskite structure, *Proceedings of the National Academy of Sciences of Belarus: Series of Physical-Mathematical Sciences*, (2007), No. 1, 97-100 (in Russian)

[8] Patent No. 13589 RB: The method of dielectric ceramic material preparation for ultrahigh frequency technique (In Russian)

Authors: *res. fel. Liudmila A. Bliznyuk, res. fel. Aliaksei A. Klimza, Dr. Vera V. Fedotova, Scientific-Practical Materials Research Center of NAS of Belarus, 19, P.Brovka, 220072, Minsk, Belarus, e-mail: klimal@physics.by*

prof. Czesław Karwat, Lublin University of Technology, Department of Electrical Devices and H.V. Technology, 38a Nadbystrzycka Str., 20-618 Lublin, Poland, E-mail: c.karwat@pollub.pl.