UDC 621.762.8:621.319.4:621.794.61 doi 10.33609/0041-6045.85.11.2019.75-83

O.I. V'yunov*, L.L. Kovalenko, A.G. Bilous

SYNTHESIS AND INVESTIGATION OF BARIUM TITANATE STANNATE SOLID SOLUTION

V.I. Vernadsky Institute of General and Inorganic Chemistry of the National Academy of Sciences of Ukraine, 32/34 Academic Palladin Avenue, Kyiv, 03142, Ukraine
* *e-mail:* vyunov@ionc.kiev.ua

Solid solutions of barium titanate-stannate, Ba(Ti,Sn)O_3 have been investigated. The sequence of phase transformations during the synthesis by solid state reactions technique has been determined, crystallographic and microscopic examinations of polycrystalline ceramics based on Ba(Ti,Sn)O_3 solid solutions have been carried out. The laws governing the change in crystallographic parameters and the average grain size as a function of tin content have been shown. Electrophysical investigations of the obtained ceramics have been carried out. It has been found that the dielectric parameters (ε and tgδ) of Ba(Ti,Sn)O_3-based ceramics can be improved and their sintering temperature can be reduced by the addition of 0.5 wt.% manganese oxide(IV) and 2 wt. % of low-melting glass-forming admixture AST (Al_2O_3–SiO_2–TiO_2). It has been shown that the obtained materials have promise in creating ceramic capacitors based on them.

Keywords: solid solutions, barium titanate-stannate, admixtures, crystallography, electron microscopy, dielectric measurements.

INTRODUCTION. The capacitor materials used in modern electronics must have a high permittivity ($\varepsilon \geq 10000$) and low dielectric loss (tg δ). One of the possible directions of creation of capacitor materials with high permittivity values is the use of solid solutions based on barium titanate $BaTiO_3$ [1]. Large room temperature permittivity is due to the existence of ferroelectric properties of barium titanate. In barium titanate, the transition from ferroelectric to paraelectric state (Curie temperature, *T*c) occurs at 120 °C. In substitution solid solutions Ba(Ti,Sn)O_3, however, *T*c shifts to the lower-temperatures region. In this case, the value of room temperature permittivity of the solid solution increases to 5000–8000 [2, 3]. During the sintering of ceramic samples based on Ba(Ti,Sn)O_3 solid solutions in air at high temperatures (~1400 °C), a partial reduction of titanium ($Ti^{4+} \rightarrow Ti^{3+}$) and an increase in average grain size are observed. This leads to an increase in dielectric loss and relaxation contribution to permittivity. the partial Ti^{3+} reduction, in particular at grain boundaries, can be prevented by adding transition $3d$-metal oxides (Fe_2O_3 and MnO_2) to the ceramic [4], which segregate on the surface of grains and form a core/shell structure [5], which leads to a reduction in dielectric loss [6]. The fine-grained structure is formed due to sintering temperature reduction when adding low-melting glass-forming compounds [7]. The AST admixture (Al_2O_3–SiO_2–TiO_2 in a 1:1:0.5 ratio) proved to be efficient for control of the sintering temperature of $BaTiO_3$ based semiconducting ceramics [8]. It may be expected that by adding admixtures that affect the processes of partial reduction of titanium and formation of ceramic microstructure one can improve the dielectric parameters (reduce the dielectric loss) of ceramics based on $Ba(Ti,Sn)O_3$ solid solution and create capacitor materials with properties required for practical use.

The aim of this work was to investigate the formation conditions of $Ba(Ti,Sn)O_3$ solid solutions in their synthesis by the solid-state reactions technique and the effect on the electrophysical properties of MnO_2 and AST (Al_2O_3–SiO_2–TiO_2) admixtures.

EXPERIMENT AND DISCUSSION OF THE RESULTS. The synthesis of $Ba(Ti,Sn)O_3$ solid solutions was carried out by solid-state reactions technique. The starting reagents for the synthesis of $Ba(Ti,Sn)O_3$ were highly pure barium carbonate, tin and titanium oxides. To reduce the sintering temperature and to form a fine-grained core/shell structure of ceramic samples, 2 wt. % low-melting AST admixture and 0.5 wt. %. manganese oxide MnO_2 were added. The mixing and milling of the starting reagents were carried out in a Fritsch Pulverisette planetary mill. Samples were pressed from the obtained powders. Sintering was performed at 1100–1400 °C for 2 h in a KSL1700X high-temperature furnace, which allowed us to obtain dense (5.75–5.8 g/cm^3) ceramics. The X-ray phase analysis was carried out on a DRON-4-07 diffractometer (CuK_α- radiation, Ni-filter). Certified SiO_2 (2Θ standard) and Al_2O_3 (intensity standard) were used as external standards. To interpret the data, the PDF-2 (ICDD) database was used. The microstructure was investigated on a SEC miniSEM SNE 4500MB scanning electron microscope (SEM). The elemental composition of films was studied with the aid of EDAX Element PV 6500/00 F spectrometer, which is part of this microscope.

The dielectric parameters were studied by means of Tesla VM 560 Q-meter (at a frequency of 10^6 Hz) and impedance spectroscopy in a frequency range 1–10^7 Hz using 1260 Frequency Response Analyzer and 1296 Dielectric Interface (Solartron). The data were analyzed using the Zview software (Solartron). The obtained frequency dependences of the complex impedance, $Z'' = f(Z')$ were used to calculate permittivity and dielectric loss: $\mathrm{tg}\,\delta = Z'/Z''$; $Y'' = Z''/(Z'^2 + Z''^2)$; $\varepsilon' = Y''/2\pi f\varepsilon_0$, where $\omega = 2\pi f$; where f is the frequency, Hz, ε_0 is the dielectric constant ($8.854\cdot10^{-12}$ F/m).

The sequence of phase transformations during the synthesis of $Ba(Ti,Sn)O_3$ solid solution was studied by differential thermal and X-ray phase analyzes (fig. 1, *a*, table 1). The DTA curves exhibits only one endo effect at 820 °C, which is associated with the polymorphic transformation of barium car-

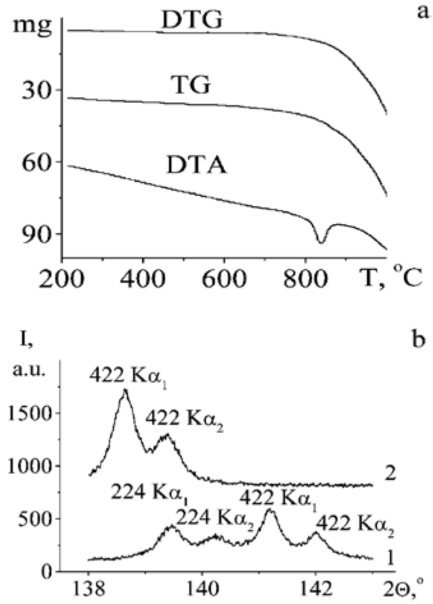

Fig. 1. Thermograms of a $BaCO_3$–TiO_2–SnO_2 mixture (*a*) and X-ray pattern of $Ba(Ti,Sn)O_3$ ceramic (*b*) depending on tin content (mol. %) 0 (*1*), 0.25 (*2*). T_{sint} = 1400 ºC.

Table 1

Phase composition of the $BaCO_3$–TiO_2–SnO_2 mixture during the synthesis of $Ba(Ti,Sn)O_3$

T, °C	Phase composition
20–600	γ-$BaCO_3$, SnO_2, TiO_2
700	γ-$BaCO_3$, SnO_2, TiO_2
800	γ-$BaCO_3$, SnO_2, TiO_2, $BaTiO_3$
900	β-$BaCO_3$, SnO_2, Ba_2TiO_4, TiO_2, $BaTi_4O_9$ $BaTiO_3$
1000	β-$BaCO_3$, SnO_2, $BaTiO_3$, Ba_2TiO_4, TiO_2, $BaTi_4O_9$
1100	$Ba(Ti,Sn)O_3$
1200	$Ba(Ti,Sn)O_3$
1300	$Ba(Ti,Sn)O_3$

bonate: the change of γ-$BaCO_3$ to β-$BaCO_3$. It is known that individual barium carbonate decomposes at a temperature above 1360 °C [9–11]. However, the decomposition of barium carbonate in a mixture is accompanied by temperature decrease [12, 13] and is a long-duration process [14], which occurs in a wide temperature range and terminates at about 1100 °C. According to the results of X-ray phase studies, a gradual decrease in the percentage of the barium carbonate and titanium dioxide phases and a gradual increase in the percentage of the barium titanate phase are observed in the temperature range of 600–900 °C. In the temperature range 900–1000 °C, intermediate phases of barium orthotitanate (Ba_2TiO_4) and barium tetratitanate ($BaTi_4O_9$) phases have been found. The formation of intermediate phases is explained by the long-duration process of barium carbonate decomposition in the mixture for the synthesis by solid-state reactions technique.

At a temperature of 1000 °C, traces of titanium oxide, barium orthotitanate and tetratitanate of have been found, and the intensity of barium titanate reflections increases. At 200–1000 °C, a tin oxide phase is observed. Only at temperatures of 1100 °C and higher, a shift in the position of barium titanate reflections is fixed, indicating the formation of a Ba(Ti, Sn)O_3 solid solution. In the temperature range 1100–1400 °C, a single-phase barium titanate-stannate solid solution is formed.

When the tin content is increased to 15 mol. %, a transition of the tetragonal phase to a cubic one is observed (X-ray patterns show a decrease in the splitting of lines with Miller indices 224 and 422) in the $Ba(Ti,Sn)O_3$ system at room temperature (fig. 1, *b*)). The transition of the tetragonal phase to cubic at room temperature occurs at a tin content of 12 mol. %. Increasing the tin content of the Ba(Ti, Sn)O_3 solid solution leads to an increase in the unit cell volume (fig. 2).

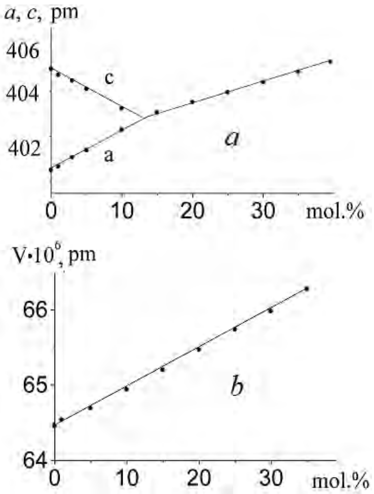

Fig. 2. Dependence of the unit cell parameters (*a*) and volume (*b*) of the Ba(Ti,Sn)O_3 ceramic on tin content. T_{sint} = 1400 °C.

Photographs of the microstructure of Ba(Ti, Sn)O_3 solid solutions as a function of tin content are shown in fig. 3. When the degree of isovalent substitution of titanium by tin increases, the ceramic grain size increases from 50 μm (0 mol %) to 130 μm (15 mol %).

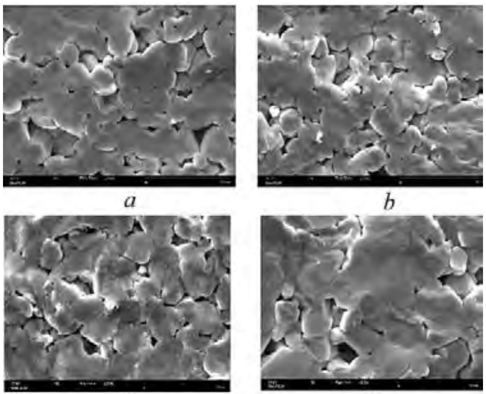
a *b*
c *d*

Fig. 3. Microstructure of the Ba(Ti,Sn)O_3 ceramics with different tin (mol.%): 9 (*a*); 11 (*b*); 13 (*c*); 15 (*d*); ×1000. T_{sint} = 1400 °C.

The increase in the average size of ceramic grains on the substitution of titanium by tin in barium titanate can be accounted for by several factors. The first factor is the formation of a eutectic liquid phase between grains during ceramic sintering, which was proved by the identity of the positions of thermal effects on the derivatograms of the systems $BaTiO_3$–$BaCO_3$–SnO_2 and $BaTiO_3$–$BaCO_3$–TiO_2 in the temperature range of the formation of the $BaTiO_3$–$Ba_6Ti_{17}O_{40}$ eutectic phase [15, 16]. Besides, when an ion of smaller size ($Ti^{4+}_{CN=6}$ = 60.5 pm) is substituted by an ion of larger size ($Sn^{4+}_{CN=6}$ = 69 pm), mechanical stresses and strains appear in crystals, which contribute to the acceleration of diffusion processes and give rise to grain growth [17, 18].

The results of studying the dielectric characteristics (ε and tg δ) of Ba(Ti,Sn)O_3 solid solutions in a temperature range of 20–70 °C as a function tin content are shown in fig. 4. When the tin content is increased, the position of the maximum ε_{max} is shifted towards room temperature (from 40 to 20 °C) with simultaneous increase in ε_{max} value from 4500 to 6500 (fig. 4, *a,b)*). Further increasing the tin content results in a shift of the position of the maximum ε_{max} to below room temperature (fig. 4, *c,d*)). In the room temperature range, the permittivity value decreases in accordance with Curie-Weiss law, i.e. proportionally with 1/*T*. This temperature dependence of ε is typical of paraelectrics near the phase transition region.

The plots of dielectric loss *vs* temperature for Ba(Ti,Sn)O_3 solid solutions also axhibit maxima in the phase transition

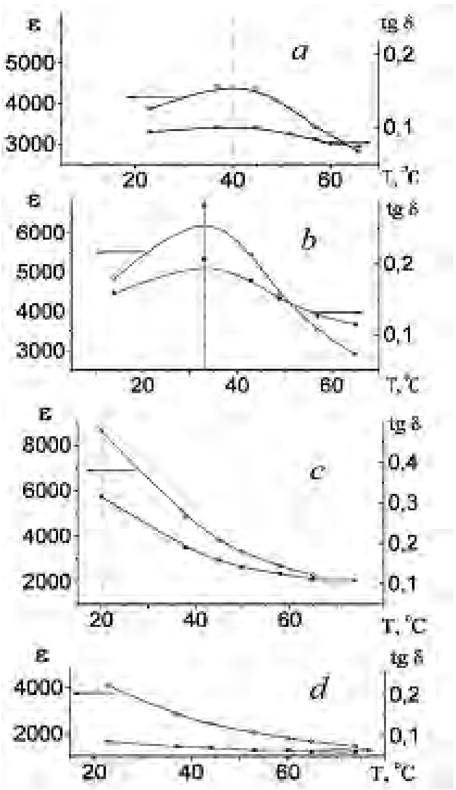

Fig. 4. Plots of ε and tgδ *vs* temperature for the Ba(Ti,Sn)O_3 ceramic at a frequency of 1 MHz depending on tin content (mol.%): 9 (*a*); 11 (*b*); 13 (*c*); 15 (*d*). T_{sint} = 1400 °C.

region, and the higher the $\varepsilon_{\max}$ value, the higher tg δ. For instance, at 1 MHz at a tin content of 9 mol. %, $\varepsilon_{\max}$ and tgδ are 4500 and 0.1, respectively, and at a tin content of 11 mol.%, 6500 and 0.2 (fig. 4, *a*,*b*)). The increase in dielectric loss tgδ depending on the tin content of the Ba(Ti, Sn)O_3 solid solution is associated with an increase in average grain size.

To reduce the grain size by decreasing the sintering temperature and thus to improve the dielectric characteristics, 0.5 wt. % MnO_2 and 2 wt. % of low-melting glass-forming admixture AST were added to the Ba(Ti,Sn)O_3 solid solution. In this case, ceramic with a maxi-mum density (5.75–5.8 g/cm^3) is formed at a sintering temperature of 1100 °C, where as without admixtures, ceramics with this densi-ty are formed only at high temperatures (1400–1450 °C).

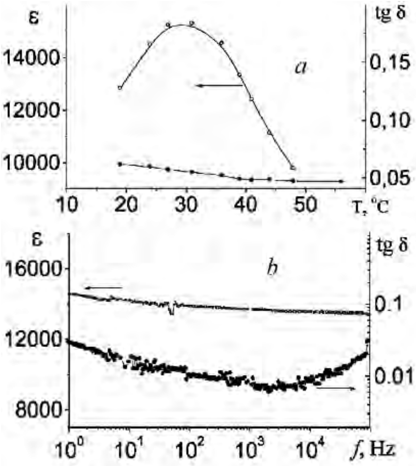

Fig. 5. Plots of ε and tgδ at 1 MHz *vs* temperature (*a*) and frequency (*b*) for the Ba($Ti_{0.89}Sn_{0.11}$)O_3 ceramic with manganese oxide and AST admitures (*b*). T_{sint} = 1100 °C.

Fig. 5 shows plots of ε and tg δ *vs* temperature (at 1 MHz) and frequency for the Ba(Ti, Sn)O_3 ceramic with admixtures of 0.5 wt. % MnO_2 and 2 wt. % AST. As is seen from fig. 5, *a*), when manganese oxide and AST ad-mixtures are added to the Ba(Ti,Sn)O_3 solid solution, the ceramic is characterized by high permittivity values at room temperature ($\varepsilon_{20\,°\mathrm{C}}$ ~13000), and at the phase transition temperature, $\varepsilon_{\max}$ reaches ~16000. The value of dielectric loss tgδ in the temperature range of question 20–70 °C does not almost change and is between 0.06 and 0.055 (at 1 MHz). Investigations of the dielectric parameters (ε and tgδ) of the Ba(Ti,Sn)O_3 ceramic showed the absence of significant dispersion of them in a wide fre quency range of 1–10^5 Hz (fig. 5, *b*).

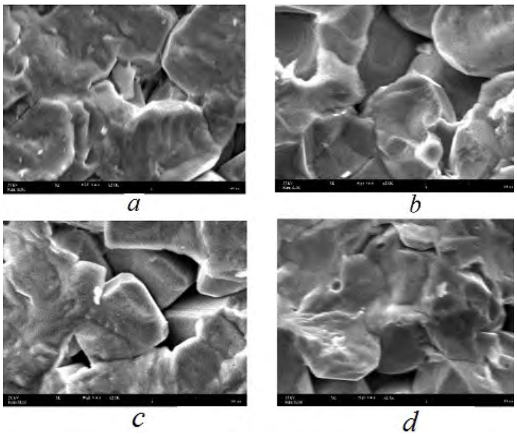

Fig. 6. Microstructure of the $Ba(Ti_{0.89}Sn_{0.11})O_3$ ceramic: without admixtures (*a*), with admixtures of AST (*b*), MnO_2 (*c*), AST and MnO_2 (*d*). T_{sint} = 1100 ℃.

Fig. 6 shows the microstructure of the $Ba(Ti,Sn)O_3$ ceramic without admixtures, with individual admixtures of AST, MnO_2 and with the addition of a mixture of AST and MnO_2 admixtures at a sintering temperature of 1100 °C. As is seen from the shown micrographs, the grain size of the $Ba(Ti,Sn)O_3$ solid solution does not change either on the addition of individual admixtures or on the addition of a mixture of admixtures. The improvement of dielectric characteristics (high ε values, low loss tgδ and low frequency dispersion of ε and tgδ) of the ceramic based on the $Ba(Ti,Sn)O_3$ solid solution with AST and manganese (IV) oxide admixtures is due to the formation of a fine-grained structure of the core-shell type at as low sintering temperature of the material as 1100 °C.

The obtained experimental data indicate the possibility of creating capacitor materials with high dielectric parameters (ε ~ 13000–16000, tgδ ~ 0.05–0.06 at 1 MHz) based on $Ba(Ti,Sn)O_3$ solid solutions. These materials have a low cost of starting reagents ($BaCO_3$, TiO_2), can be prepare by a simple technology (solid-state reactions technique, low sintering temperatures, short holding time, sintering in an air atmosphere) and can be used in the creating novel radio frequency materials for the effective solution of the problems of microminiaturization of modern electronic equipment.

CONCLUSIONS. Barium titanate-stannate solid solutions $Ba(Ti,Sn)O_3$ with isovalent substitutions have been investigated. The sequence of phase transformations in the process of the synthesis of the $Ba(Ti,Sn)O_3$ solid solution with the formation of intermediate barium orthotitanate (Ba_2TiO_4) and tetratitanate ($BaTi_4O_9$) has been established. Crystallographic and microscopic investigations of cera-mics based on $Ba(Ti,Sn)O_3$ solid solutions have been carried out. Laws governing the variation of crystallographic parameters (*a*, *c*, unit cell volume *V*) and mean grain size as a function of the tin content of $Ba(Ti,Sn)O_3$ have been shown. It has been found that by adding manganese oxide and low-melting admixture AST, the dielectric parameters (ε and tgδ) can be improved, and the sintering temperature of $Ba(Ti,Sn)O_3$-based ceramics can be reduced. The ceramics obtained at 1100 °C are characterized by large permittivity values at 1 MHz (ε ~13000–16000) and low dielectric loss ($tg\bar{\bar{\delta}}$ ~ 0.05–0.06) in room temperature range. It has been shown that the obtained materials have promise in creating ceramic capacitors based on them.

СИНТЕЗ ТА ДОСЛІДЖЕННЯ ТВЕРДИХ РОЗЧИНІВ ТИТАНАТУ–СТАНАТУ БАРІЮ

О.І. В'ЮНОВ *, Л.Л. КОВАЛЕНКО , А.Г. БІЛОУС

Інститут загальної та неорганічної хімії
ім. В.І. Вернадського НАН України,
просп. Академіка Палладіна, 32/34, Київ,
03142, Україна
* *e-mail: vyunov@ionc.kiev.ua*

Визначено умови утворення твердих розчинів $Ba(Ti,Sn)O_3$, синтезованих методом твердофазних реакцій та досліджено вплив домішок MnO_2 та AST (Al_2O_3–SiO_2–TiO_2) на електричні властивості кераміки на їх основі. Домішки додавали для зниження температури спікання та утворення дрібнозернистої кераміки і структури зерен типу ядро/оболонка. Встановлено фазові перетворення при синтезі твердих розчинів на основі $Ba(Ti,Sn)O_3$. За допомогою досліджень рентгенівських порошкових дифрактограм показано, що при температурі 600–900 °C зменшення вмісту карбонату барію та оксиду титану супроводжується збільшенням вмісту титанату барію. При 900–1000 °C виявлено проміжні фази ортотитанату барію (Ba_2TiO_4) і тетратитанату барію ($BaTi_4O_9$). За температури 1100 °C і вище зміщення рефлексів на рентгенограмі титанату барію вказує на утворення твердого розчину $Ba(Ti,Sn)O_3$.

Збільшення вмісту Sn приводить до зростання середнього розміру зерен кераміки від 50 мкм при 0 % мол. Sn до 130 мкм при 15 % мол. Sn, що пояснюється утворенням евтектичної рідкої фази між зернами та механічними напругами і деформаціями, які прискорюють дифузійні процеси.

Досліджено параметри кристалічної структури (*a*, *c*, об'єм елементарної комірки *V*) та мікроскопічні особливості (середній розмір зерна) кераміки на основі $Ba(Ti,Sn)O_3$ у залежності від вмісту олова. При 12 % мол. Sn перехід від тетрагональної до кубічної фази відбувається за кімнатної температури.

Введення оксиду марганцю та низькоплавкої домішки AST у кераміку на основі $Ba(Ti, Sn)O_3$ покращує його діелектричні параметри (ε і tg δ) та знижує температуру спікання до 1100 °C. Кераміка з 0.5 % мас. MnO_2 і 2 мас. % AST на 1 МГц при кімнатній температурі характеризуються великою діелектричною проникністю і низькими діелектричними втратами ($\varepsilon \sim 13000$–16000, $\mathrm{tg}\,\delta \sim 0.05$–$0.06$). Ці експериментальні дані показали, що на основі твердих розчинів $Ba(Ti,Sn)O_3$ з досліджуваними домішками можуть бути розроблені конденсаторні матеріали з високими діелектричними параметрами. Такі матеріали мають низьку вартість хімічних реагентів ($BaCO_3$, TiO_2), просту технологію (метод твердофазних реакцій, спікаються при низькій температурі протягом короткого часу на повітрі) і є перспективними для розробки нових радіочастотних матеріалів для керамічних конденсаторів.

Ключові слова: тверді розчини, титанат–станат барію, домішки, кристалографія, електронна мікроскопія, діелектричні параметри.

СИНТЕЗ И ИССЛЕДОВАНИЕ ТВЕРДЫХ РАСТВОРОВ ТИТАНАТА-СТАННАТА БАРИЯ

О.И Вьюнов *, Л.Л. Коваленко , А.Г. Белоус

Институт общей и неорганической химии им. В.И. Вернадского НАН Украины, просп. Академика Палладина, 32/34, Киев, 03142, Украина
* *e-mail: vyunov@ionc.kiev.ua*

Исследованы твердые растворы титаната-станната бария $Ba(Ti,Sn)O_3$. Установлена последовательность фазовых превращений при синтезе методом твердофазных реакций, проведены кристаллографические и микроскопические исследования поликристаллической керамики на основе твердых растворов $Ba(Ti, Sn)O_3$. Показаны закономерности изменения кристаллографических параметров и среднего размера зерен в зависимости от содержания олова. Проведены электрофизические исследования полученной керамики. Установлено, что при дополнительном введении 0.5 % мас. оксида марганца(IV) и 2 % мас. легкоплавкой стеклообразующей примеси AST (Al_2O_3–SiO_2–TiO_2) можно улучшить диэлектрические параметры (ε і tg δ) и снизить температуру спекания керамики на основе $Ba(Ti,Sn)O_3$. Показано, что полученные материалы являются перспективными для создания на их основе керамических конденсаторов.

REFERENCES\

1. Xu Y. *Ferroelectric materials and their applications.* (Amsterdam: North-Holland, Elsevier Science Publisher, B.V., 2013).
2. Bilous A., V'yunov O., Kovalenko L. $(Ba,Y)(Ti, Zr,Sn)O_3$-based PTCR materials. *Ferroelectrics.* 2001. **254** (1): 91.
3. Saravanan R. *Titanate Based Ceramic Dielectric Materials.* (Millersville, PA: Materials Research Forum LLC, 2018).
4. Miki T., Fujimoto A., Jida S. An evidence of trap activation for positive temperature coefficient of resistivity in $BaTiO_3$ ceramics with substitutional Nb and Mn as impurities. *Journal of applied physics.* 1998. **83** (3): 1592.
5. V'yunov O.I., Kovalenko L.L., Belous A.G. The effect of isovalent substitutions and dopants of 3*d*-metals on the properties of ferroelectrics-se-miconductors. *Condensed Matter Physics.* 2003. **6** (2): 213.
6. Vivekanandan R., KuttyT.R.N. Grain boundary layer ceramic capacitors based on donor-doped Ba $(Ti_{1-x}Sn_x)O_3$. *Materials Science and Engineering: B.* 1990. **6** (4): 221.
7. Holand W., Beall G.H. *Glass ceramic technology.* (New Jersey: John Wiley & Sons, 2012).
8. Belous A.G., Yanchevskii O.Z., V'yunov O.I. The effect of Al_2O_3–TiO_2–SiO_2 additives on properties of semiconductive $BaTiO_3$. *Ukrainian Che-mistry Journal.* 1995. **61** (1): 13.
9. Kresse R., Baudis U., Jäger P., Riechers H.H., Wagner H., Winkler J., Wolf H.U. Barium and barium compounds. *Ullmann's encyclopedia of industrial chemistry.* 2000: 621.
10. L'vov B.V., Ugolkov V.L. Kinetics of free-sur-face decomposition of magnesium, strontium and barium carbonates analyzed thermogravimetrically by the third-law method. *Thermochimica acta.* 2004. **409** (1): 13.
11. Maitra S., Chakrabarty N.,Pramanik J. Decomposition kinetics of alkaline earth carbonates by integral approximation method. *Cerâmica.* 2008. **54** (331): 268.
12. Berbenni V., Marini A., Bruni G. Effect of mechanical milling on solid state formation of $BaTiO_3$ from $BaCO_3$–TiO_2 (rutile) mixtures. *Thermochimica acta.* 2001. **374** (2): 151.
13. Manzoor U., Kim D.K. Synthesis of nanosized barium titanate powder by solid-state reaction between barium carbonate and titania. *Journal of Materials Science and Technology.* 2007. **23**(5):655.
14. Ashiri R., Nemati A., Ghamsari M. S., Sanjabi S., Aalipour M. A modified method for barium titanate nanoparticles synthesis. *Materials Research Bulletin.* 2011. **46** (12): 2291.

15. Lee W.H., Tseng T.Y., Hennings D.F.K. Effects of calcination temperature and A/B ratio on the dielectric properties of (Ba,Ca)(Ti,Zr,Mn)O_3 for multilayer ceramic capacitors with nickel electrodes. *Journal of the American Ceramic Soci-ety.* 2000 . **83** (6): 1402.

16. Makovec D., Drofenik M. Microstructural chan-ges during the reduction/reoxidation process in donor-doped $BaTiO_3$ ceramics. *Journal of the American Ceramic Society.* 2000. **83** (10): 2593.

17. Kolobov Y.R., Valiev R.Z., Graboveiskaya G.P., Zhilyaev A.P., Dudarev E.F., Ivanov K.V., Ivanov M.B., Kashin O.A., Naidenkin E.V. *Grain boundary diffusion and properties of nanostructured materials.* (Cambridge: Cambridge Int Science Publishing, 2007).

18. Wang J., Jiang S., Jiang D., Wang T.,Yao H. Ef-fects of Sn on the microstructure and dielectric properties in $BaTiO_3$-based ceramics. *Ceramics International.* 2013. **39** (4): 3657.

Received 15.07.2019