ISSN 1027-5495. Functional Materials, 27, No.1 (2020), p. 192-196.
doi:https://doi.org/10.15407/fm27.01.192

Influence of the isomorphism of the solid solutions of barium strontium titanates on segnetoceramic properties

***G.N.Shabanova*[1], *S.M.Logvinkov*[2], *A.N.Korohodska*[1], *E.V.Khrystych*[3], *V.V.Deineka*[3], *D.V.Taraduda*[3]**

[1]National Technical University "Kharkiv Polytechnic of Institute",
2 Kyrpychova Str., 61002 Kharkiv, Ukraine
[2]S.Kuznets Kharkov National University of Economics,
9a Nauky Ave., 61000 Kharkiv, Ukraine
[3]National University of the Civil Defence of Ukraine,
94 Chernyshevska Str., 61023 Kharkiv, Ukraine

Received August 7, 2019

This scientific paper gives the research data relating to the opportunity for variation of the properties of segnetoceramic materials due to hetero- and isovalent substitutions in the cation sublattices of solid solutions by varying the parameters of crystalline lattice and basic material characteristics at maintaining monophasicity. For the materials based on barium and strontium titanates, the admixtures were used that enabled the variation of the cation substitution of barium, strontium and titanium. The parameters for the stable synthesis of the similar materials of a preset composition were defined experimentally. The compositions for segnetoceramic materials with appropriate performance characteristics have been developed.

Keywords: segnetoceramics, perovskite structure, isomorphic substitution, doping admixture, nonlinearity of volt-ampere characteristics.

Приведены результаты исследования возможности варьирования свойств сегнетокерамических материалов за счет гетеро- и изовалентных замещений в катионных подрешетках твердых растворов с изменением параметров кристаллической решетки и основных характеристик материала при сохранении однофазности. В материалах на основе титанатов стронция и бария применяли добавки, которыми варьировали катионное замещение бария, стронция и титана. Экспериментально определены параметры устойчивого синтеза подобных материалов заданного состава. Разработаны составы сегнетокерамических материалов с необходимыми эксплуатационными характеристиками.

Вплив ізоморфізму твердих розчинів барій-стронцієвих титанатів на властивості сегнетокераміки. *Г.М.Шабанова, С.М.Логвінков, А.М.Корогодська, О.В.Христич, В.В.Дейнека, Д.В.Тарадуда*.

Наведено результати дослідження можливості варіювання властивостей сегнетокерамічних матеріалів за рахунок гетеро- та ізовалентних заміщень у катіонних підгратках твердих розчинів зі зміною параметрів кристалічної решітки та основних характеристик матеріалу при збереженні однофазності. У матеріалах на основі титанату стронцію та барію застосовували добавки, якими варіювали катіонні заміщення барію, стронцію та титану. Експериментально визначено параметри сталого синтезу подібних матеріалів заданого складу. Розроблено склади сегнетокерамічних матеріалів з необхідними експлуатаційними характеристиками.

1. Introduction

An increase in the efficiency of functional materials and a reduction of the overall dimensions of microelectronics devices enable the creation of a wide range of radiotechnical devices on their basis, in particular sensory and medical ultrasonic diagnostic devices, different optic devices, high-capacity memory units, etc. To attain required performance characteristics of segnetoceramic materials based on the compositions of solid solutions of barium strontium titanates, the investigation of the influence of the initial segnetoceramics ingredients on the morphology and grain size of materials formed at specific synthesis conditions is of interest [1, 2]. It is known that the origination of substantial internal stress fields required for the manifestation of magnetoelectric effects is possible in the compounds with the structure of a perovskite type having the general formula of ABO_3 [3].

The Ca, Sr, Cd, Ba, and Pb titanates have the perovskite type structure ($CaTiO_3$) and are crystallized in the cubic system [3, 4]. In this crystalline system, a Ti^{4+} ion can be substituted by tetravalent Zr^{4+}, Hf^{4+}, Th^{4+} and other ions and a bivalent Ca^{2+} can be substituted by Ba^{2+}, Sr^{2+}, and Pb^{2+}. Non-isovalent substitution that includes cation sublattices of a different type is also possible. Nearly all the given titanates have a peculiarity that allows for the formation of substitutional solid solutions with unbounded solubility and this feature is successfully used to adjust the properties of the ceramic materials produced using the titanates. Different combinations of the binary and ternary solid titanate solutions can shift the Curie point to the side of higher or lower temperatures and provide the stability of properties in a wide temperature range [3].

Therefore, studying the possibility to change the properties of segnetoceramic materials due to hetero- and isovalent substitutions in the solid solution cation sublattices accompanied by appropriate changes in the parameters of crystalline lattice while maintaining the single-phase material were of interest. The cation substitution of barium, strontium, titanium and their combinations can be carried out in barium strontium titanates. $Al(NO_3)_3 \cdot 9H_2O$, Bi_2O_3, Nb_2O_5, SnO_2, $MnCO_3$, PbO_2, ZrO_2 (reagent grades) were used as dopants to initial raw materials: $BaCO_3$-barium carbonate, $SrCO_3$-strontium carbonate of the reagent grade TU48 PT 0516-10-95, and TiO_2 — pigment titanium dioxide "SUMTITAN R-202".

2. Experimental

2.1 Specimen synthesis: compositions and conditions

To synthesize the specimens of a specified phase composition, the following technical operations were performed, in particular, the dosing of raw components, grinding and mixing and also the molding and firing of the raw mixtures. The thorough grinding and mixing of raw components was performed in the laboratory ball mill using the "wet method" (the sludge moisture content was 35 mass%, the balls-to-material ratio was 1:7). The grinding fineness was controlled using the method of sieve analysis (full passage through the mesh aperture of No0063) [5]. The drying was conducted in the drying chamber at a temperature of up to 100°C. Prior to the firing, the raw mixtures were formed using the method of two-sided pressing at the specific pressure of 50 to 100 MPa. The briquettes were fired in silite and cryptol furnaces at preset synthesis temperatures and isothermal holding time. The temperature in the firing zone was measured using an optic pyrometer "Smotrich-5P-01" and a platinum-rhodium thermocouple. The compound synthesis completeness was controlled using the method of chemical analysis to check the absence of free barium oxide [6].

The admixtures were added to provide an appropriate variation of the properties of obtained segnetoceramic $(Ba_{1-x}Sr_x)TiO_3$-based materials; the strontium sublattice nonstoichiometry coefficient was 0.12, i.e. $(Ba_{0.88}Sr_{0.12})TiO_3$ and the admixture content was of 1 to 3 mass % (Table 1).

It was experimentally proved that the addition of doping Bi^{3+}, Nb^{5+} and Mn^{2+} cations to the developed segnetoceramic materials failed to provide a required nonlinearity for the properties [7]. Possibly, the composition was unbalanced due to the multivariance of cation substitutions and unordered vacancy (V) distribution:

$$3Ba^{2+} \rightarrow 2Bi^{3+} + V;$$

$$5Ba^{2+} \rightarrow 2Nb^{5+} + 3V; \quad Ba^{2+} \rightarrow Mn^{2+}.$$

In addition, manganese can easily change its valence and it can partially provide the isovalent cation substitution in the titanium sublattice of the solid solution:

$$Ti^{4+} \rightarrow Mn^{4+}.$$

Table 1. Specimen synthesis: compositions and conditions

No.	Initial ingredients	Firing temperature, °C/time, h	Compacting pressure, MPa
1	$BaTiO_3$, $SrTiO_3$, TiO_2, Bi_2O_3, Nb_2O_5, $MnCO_3$	1200/3	50
2	$BaTiO_3$, BaO	1350/3	70
3	$SrTiO_3$, 1350/2, 120		
5	$Ba_{0.88}Sr_{0.12}TiO_3$	1370/2	100
6	$Ba_{0.88}Sr_{0.12}TiO_3$ with 0.3 % of $Al(NO_3)_3$ solution	1350, 1370/2	100
7	$Ba_{0.5}Sr_{0.5}SnO_3$	1350/2	100
8	$Ba_{0.88}Sr_{0.12}TiO_3$ + 3 % additive of $Ba_{0.5}Sr_{0.5}SnO_3$	1350/2	100
9	$Ba_{0.88}Sr_{0.12}TiO_3$ + 3 % additive of $Ba_{0.5}Sr_{0.5}ZrO_3$	1350/2	100
10	$Ba_{0.5}Sr_{0.5}ZrO_3$	1350/2	100
11	$Ba_{0.88}Sr_{0.12}TiO_3$ + 2 % additive: 95 % BaO–ZrO–TiO_2 solid solution with 5 % of SrO–ZrO–PbO_2–TiO_2 solid solution	1300/2	100
12	$(Ba_{0.75}Sr_{0.25})(Ti_{0.95}Zr_{0.05})O_3$	1300/2	100

Table 2. Phase composition and chemical composition of the material of synthesized specimens

Phase composition	Chemical composition, wt %			
	BaO	SrO	TiO_2	ZrO_2
$(Ba_{0.75}Sr_{0.25})(Ti_{0.95}Zr_{0.05})O_3$	51.58	11.62	34.04	2.76

To increase the mobility of structural regroupings and provide an appropriate reduction of the relaxation time of the domain structure of the materials with the induced changes of electromagnetic field, we selected the method of the preliminary synthesis of the materials possessing a considerable individual dielectric permittivity and the basic composition analogous to that of barium-strontium sublattice ($Ba_{0.88}Sr_{0.12}TiO_3$).

When using fine-dispersed segneto-ceramic material admixture (fraction < 45 μm) consisting of the mixture of solid solutions (in equal portions) BaO–ZrO_2–TiO_2 and SrO–ZrO_2–PbO_2–TiO_2, a considerable linear shrinkage is observed during the firing and it is conditioned by the processes of decomposition of initial carbonates and sintering of the specimens. The versions of other studied compositions with the admixture require technological modification and o ptimization (insufficient mechanical strength < 50 MPa).

The compositions containing $BaTiO_3$ and $PbZrO_3$ or $PbTiO_3$ have the Curie point higher than 120°C; their nonlinear properties are manifested as weakly as those of barium titanate or even weaker. The compositions containing $BaTiO_3$ and small additions of $BaZrO_3$ or $BaSnO_3$ have the Curie temperature lower than 120°C and show better nonlinear properties in comparison with barium titanate and the compositions of $BaTiO_3$–$SrTiO_3$ system; this result correlates with the earlier research data [7].

3. Results and discussion

Consideration was given to barium-strontium stannate and barium-strontium zirconate ($Ba_{0.5}Sr_{0.5}SnO_3$ and $Ba_{0.5}Sr_{0.5}ZrO_3$) as to promising admixtures for the material doping.

For further investigations we selected the option of synthesized material whose phase composition and chemical composition are given in Table 2.

The completeness of the synthesis of the given phase was controlled in the specimens using the XRD method with a diffractometer DRON-3M (a CoKα tube was the radiation source, and the Fe filter was used). The obtained X-ray pattern clearly shows the diffraction peaks of the basic phase except for the $(Ba_{0.75}Sr_{0.25})(Ti_{0.95}Zr_{0.05})O_3$ solid solution: d(Å) = 3.982; 2.822; 2.303; 2.002; 1.992; 1.783; 1.628; and 1.409. In addition, a slight diffraction peak characteristic to ZrO_2, d = 2.985 Å is observed. The calculated amount of free ZrO_2 is about 1.5 to 2 %, which is indicative of the low solubility of ZrO_2 in the $(Ba_{0.75}Sr_{0.25})(Ti_{0.95}Zr_{0.05})O_3$ solid solution for selected technological parameters of the synthesis (Fig. 1).

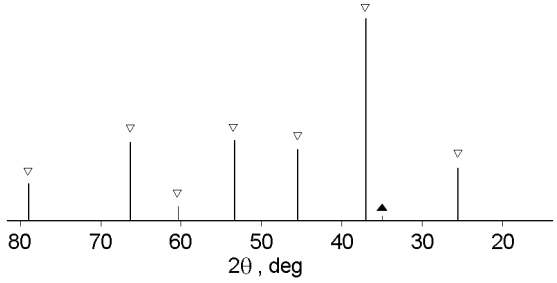

Fig. 1. The bar X-ray pattern of segnetoceramic material of a $(Ba_{0.75}Sr_{0.25})(Ti_{0.95}Zr_{0.05})O_3$ composition: (∇ — $(Ba_{0.75}Sr_{0.25})(Ti_{0.95}Zr_{0.05})O_3$, ▲ — ZrO_2.

The studies of the electric characteristics of different segnetoceramic materials, first of all the solid solutions of barium titanate with isomorphic doping admixtures, showed that some solid solutions manifest more pronounced temperature dependence of dielectric permittivity and the others manifest it less explicitly. The compositions with a high value of dielectric permittivity show a considerable change in the Curie point as a function of the intensity of electric field. The nonlinearity degree of segnetoelectrics, the Curie temperature and the value of ε turned out to be the interrelated values to a certain extent [8].

It is known that the segnetoelectric materials show the highest nonlinearity of electric properties near the Curie point. For the hands-on use of segnetoelectric materials developed for high-voltage devices the phase transition point of the synthesized lot of materials is within 45°C, i.e. it exceeds the room temperature. Hence, the experimental specimens of segnetoceramics were studied in the temperature range of 25 to 80°C. A relative dielectric permittivity of such specimens is in the range of $4{\cdot}10^3$ to $1.2{\cdot}10^4$ for the fields with $E = 10^6...5{\cdot}10^6$ V/m that meets the preset performance characteristics.

Fig. 2 shows the experimental dependences of dielectric permittivity and electric induction of the segnetoceramic material of a basic $(Ba_{0.75}Sr_{0.25})(Ti_{0.95}Zr_{0.05})O_3$ composition on the electric field intensity. Fig. 3 gives the micro-images of the surface of the segnetoceramic specimen of this basic composition that was synthesized using the developed technology. The image (Fig. 3) is indicative of the fact that the obtained ceramic structure corresponds to the basic material structure. The X-ray analysis data prove the formation of segnetoceramics of the preset phase composition and the absence of any incidental crystalline admixtures. The specific features of microstructure, in particular, the value of mechanical stresses, the size and shape of pores and their volume distribution depend on the specificity of fabrication processes and define the final properties of obtained materi-

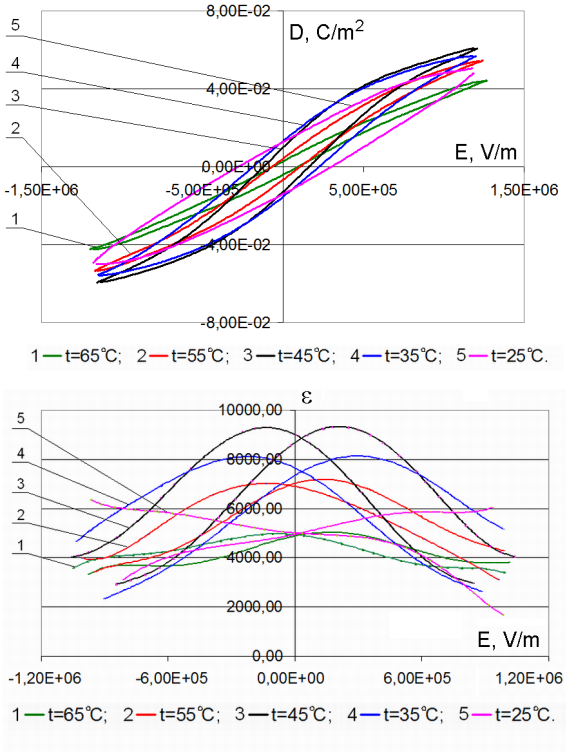

Fig. 2. The dependences of dielectric permittivity (D) and electric induction (e) of the segnetoceramic material with a $(Ba_{0.75}Sr_{0.25})(Ti_{0.95}Zr_{0.05})O_3$ composition on the electric field intensity (E).

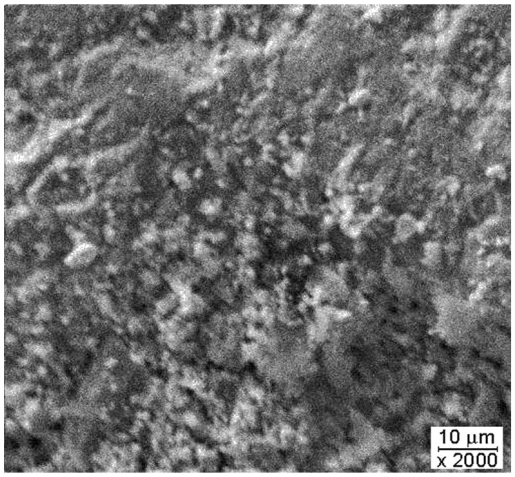

Fig. 3. The image of the surface of segnetoceramic specimen of a $(Ba_{0.75}Sr_{0.25})(Ti_{0.95}Zr_{0.05})O_3$ composition.

als. The indicated factors are not always recordable and therefore the specimens fabricated us ing the similar flowchart may show considerable variations in ε values, nonlinearity coefficients and other parameters of segnetoelectrics.

4. Conclusions

Based on the research data, an efficient method was selected to control the properties of barium strontium titanates for increasing the nonlinearity of their electromagnetic characteristics due to the adjustment of the structure parameters of solid solutions and the symmetry of individual crystalline sublattices using doping admixtures. The types of doping admixtures that have a synergetic effect on the enhancement of nonlinearity due to its isomorphism ability in all the cation sublattices can be formed up as $Ti^{4-} > Zr^{4+}$, $2Ba^{2+} - > Zr^{4+}$, $^{2Sr2+} - > Zr^{4+}$, $Ba^{2+} + Sr^{2+} - > Zr^{4+}$, $Ti^{4+} + 2Ba^{2+} - > 2Zr^{4+}$.

References

1. T.N.Verbitskaia. The Varactors, Gosenergoizdat, Moscow (1958) [in Russian].
2. G.A.Smolenskiy, V.A.Bokov, V.A.Isupov, Segnetoelectrics and Antisegnetoelectrics, Nauka, Leningrad (1971) [in Russian].
3. K.S.Aleksandrov, B.V.Beznosikov, Perovskite — like Crystals, Nauka, Novosibirsk (1997) [in Russian].
4. V.L.Balakevich. Engineering Ceramics, Stroyizdat, Moscow (1984) [in Russian].
5. E.V.Khristich, G.N.Shabanova, S.M.Logvinkov, Segnetoceramic Materials with Nonlinear Electrophysical Properties in the $BaO–SrO–TiO_2$ system. Refractory Materials and Engineering Ceramics, Moscow (2012) [in Russion].
6. G.N.Shabanova, A.M.Korogodska, O.V.Hristich, Cementing Materials. The Practicum on Discipline "ZTTHSM". Pidruchnik NTU "HPI", Kharkiv (2014) [in Ukrainian].
7. V.V.Vyitrishko, O.L.Rezinkin, E.V.Hristich, *Bulletin of NTU "KhPI"*, Kharkiv (2012) [in Russian].
8. M.M.Rezinkina, O.L.Rezinkin, R.P.Mygushchenko, *J.Mano-Electronic*, **10**, 02008 (2018).