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Phase Picture And Macroresponse In "Ferroelectric-Soft" Multicomponent System (Pb, Sr, Ba) (Ti, Zr, Nb, Zn, Mg)O_3.

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ABSTRACT

In the presented study phase diagram of the system (Pb, Sr, Ba) (Ti, Zr, Nb, Zn, Mg)O_3 was plotted and it was established that there is correlation between structural, dielectric, piezoelectric, elastic and dissipative properties of the materials. It was demonstrated that extremeness of values of solid solutions can be achieved in the vicinity of transition zone between three-phase and two-phase conditions. Also, it was established that it is possible to produce the developed ferroelectric-soft materials using regular ceramics technology with parameters, which allow to use them in various piezoelectric devices.

Keywords: Solid Solutions, Multicomponent Systems, Phase Diagram, Regular Ceramic Technology

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INTRODUCTION

Recently there are active attempts to develop new ferroelectric-soft (FS) materials with high dielectric permeability, electrostriction, piezoelectric and dissipative properties based on multicomponent systems modified by alkaline-earth metals with ferroelectrics-relaxors [1-2], which have prospects in application in low-frequency detectors (hydrophones, microphones, seismic detectors), as well as in precision moving devices. Tendency for civil industry applications of piezo-devices requires to search for cheaper and more available alternatives to very expensive method of hot pressing (HP) (which has expensive production tools); only HP allows to provide extremeness of properties of that kind of materials, and that's why it is applied so far.

However, attempts to use regular ceramic technology (RCT) instead of HP for production of FS materials had failed due to ~ 40% loss of piezo-characteristics [3]. In that regard, the aim of the presented study is the development of new FS materials with target characteristics without application of HP, while retaining the properties of materials produced using HP technology.

OBJECTS, METHODS OF PRODUCTION AND STUDY OF SPECIMENS

Object of the study were specimens of solid solutions (SS) of the multicomponent system $\left(Pb_{1-\alpha_1-\alpha_2}Sr_{\alpha_1}Ba_{\alpha 2}\right)\left[Ti_xZr_y\left\langle(Nb_{2/3}Zn_{1/3})(Nb_{2/3}Mg_{1/3})\right\rangle_{1-x-y}\right]O_3$, where α_1 = 0.02÷0.12, $\Delta\alpha_1$ = 0.02, α_2 = 0.0073÷0.045, x = 0.395÷0.42, y = 0.412÷0.437. SS were produced using RCT, which includes two stage synthesis with the following sintering without pressure ($T_{synt.1}$ = 1140 K, τ = 5 h, $T_{synt.2}$ = 1160 K, τ=5 h; $T_{sint.}$ = 1570 K).

X-Ray studies were carried out using powder X-Ray diffraction analysis method using DRON-3 diffractometer and powder dispersion analyzer (PDA) (FeK_α-radiation, Mn-filter; FeK_β-radiation; Bragg-Brentano focusing scheme). Experimental density ($\rho_{exp.}$) of specimens was measured by means of hydrostatic weighing in octane.

X-Ray density ($\rho_{x\text{-}ray.}$) was calculated using the formula: $\rho_{x\text{-}ray.} = 1.66\cdot M/V$, where M – weight of formula unit, g, V – volume of perovskite cell, Å. Relative density ($\rho_{rel.}$) was calculated using the equation (($\rho_{exp.}/\rho_{x\text{-}ray.}$)·100%). Identification of piezoelectric, dielectric and ferroelectric-elastic characteristics (relative dielectric permeabilities of polarized ($\varepsilon_{33}^T/\varepsilon_0$) and non-polarized ($\varepsilon/\varepsilon_0$) specimens, piezomodules (d_{31}, d_{33}), coefficient of electromechanical coupling planar oscillation mode (K_p), mechanical Q factor (Q_M), Young modulus (Y^E_{11}), speed of sound (V^E_1), Curie temperature (T_c), dielectric dissipation factor ($tg\delta$), piezoelectric coefficients (piezo-sensitivity) (g_{31}, g_{33})) was carried out at room temperature according to BS (branch standart) 11 04487 [4]. High-temperature dielectric spectra (relationships $\varepsilon/\varepsilon_0(T)$ at various frequencies (f) of alternating measuring electric field) were studied using the laboratory bench, which was designed at Physics Research Institute of the Southern Federal University with implementation of high-precision LCR-meters Agilent 4980A. Measurements were caried out in the range of temperatures (300…1000) K (on forward movement (heating) and backward movement (cooling)) with the range of frequencies of (20…10^6) Hz. For the experimental studies of dissipative properties of the produced materials in the range of frequencies of (1.0÷9.0) GHz we used the device based on E8363B 10 Hz – 40 GHz Series PNA Network Analyzer produced by Agilent Technologies. As the main parameter characterizing microwave absorption of electromagnetic radiation by the objects of the study we used element of scattering matrix S_{21}.

EXPERIMENTAL RESULTS AND DISCUSSION

Fig.1 presents the fragments of diffraction patterns of SS of the studied system with various values of α_1, which demonstrate the change of profiles of diffraction reflections (200)c for various concentrations of SS components. All discussed SS are located in multi-phase morphotropic region (MR). In turn, that region is divided into a number of zones, which differ in phase composition, with coexisting tetragonal (T), rhombohedral (Rh), pseudocubic (Psc) phases (the latter phase is the phase with unclear symmetry). For specimens with α_1 = 0.10 and α_1 = 0.12 the presence of Psc phase is not obvious due to small value of ratios of T-cell parameters, c/a and low intensity of reflection peaks, however, significantly bigger width of X-Ray line 002 as compared to width of the line 200 of T indicates presence of Psc with cell parameter close to c. Substitution of Pb toms by Sr and Ba atoms in the mentioned ratios leads to a certain shift of SS on the phase diagram in the direction of Rh zone, but in the limits of MR, which is similar to the situation occurring in the system $PbZr_{1-x}Ti_xO_3$ (ZTL), when Ti concentration decreases [6-7]. Fig. 2 presents the relationships of densities, structural, electrophysical and dissipative characteristics of the discussed SS and α_1. It is obvious that the obtained SS has considerably high values of $\rho_{rel.}$, which correspond to ultimate values that can be obtained using RCT (~95%), which is indicative of the high quality of ceramics. The increase of the concentration of Sr leads to the increase of cell parameter *a*; the decrease of the values of the parameters *c*, *c/a* occurs monotonously. Firstly, volume of the cell is decreasing, then (at $\alpha_1 = 0.06$) it increases forming maximum at $\alpha_1 = 0.08$; after that it decreases. For $\rho_{exp.}$ and $\rho_{x\text{-}ray.}$ different speeds decrease is observed, which defines a certain increase of $\rho_{rel.}$.

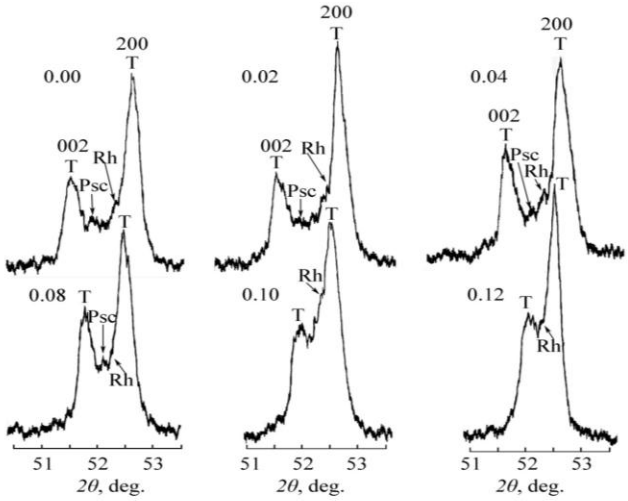

Fig. 1. Fragments of diffraction patterns of SS of the studied system. Values near the curves represent concentration of Sr (α_1) in arb. units.

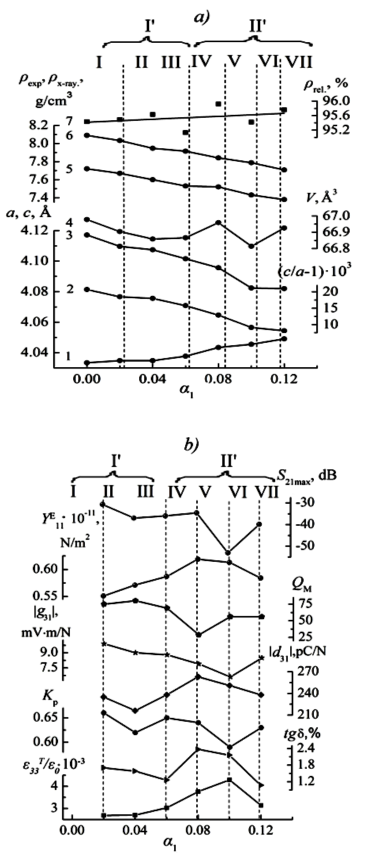

Fig. 2. Relationships of densities, structural (*a*) and electrophysical (*b*) parameters studied for SS for concentration *Sr* (α_1): 1- *a*, 2- *c/a*, 3- *c*, 4-*V*, 5, 6, 7- densities experimental, X-Ray and relative, respectively.

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The data presented in Fig. 2, *b* indicates that compositions with α_1 = 0.02÷0.04 have medium position between materials with high dielectric permeability and highly sensitive materials from the point of view of main parameters [3]. Values of $\varepsilon^T_{33}/\varepsilon_0$ of those materials, which can be called average, are advantageous for applications in middle frequency range. SS with content of α_1 = 0.06÷0.12 have reasonably high $\varepsilon^T_{33}/\varepsilon_0$, which allow to attribute them to the group of FS materials aimed for application in low-frequency devices. In addition, realization of very strong microwave absorption in them (SS with α_1 = 0.10) makes it possible to consider such materials as the basis for absorption of complexes.

All materials have high specific sensitivity, which considers internal resistance of detector and is proportional to value $d_{33}/\sqrt{\varepsilon^T_{33}/\varepsilon_0}$; that fact allows to implement these materials not only for applications at low and middle frequencies, but also in medical diagnosis equipment, which uses load with low input resistance that provides coherence of transformer working at high frequencies with it. As it can be seen, values of all electrophysical characteristics of the developed materials and other known materials, which are, generally, produced using HP, are adequate, which allows to make conclusion about possibility of development of FS materials without need for HP.

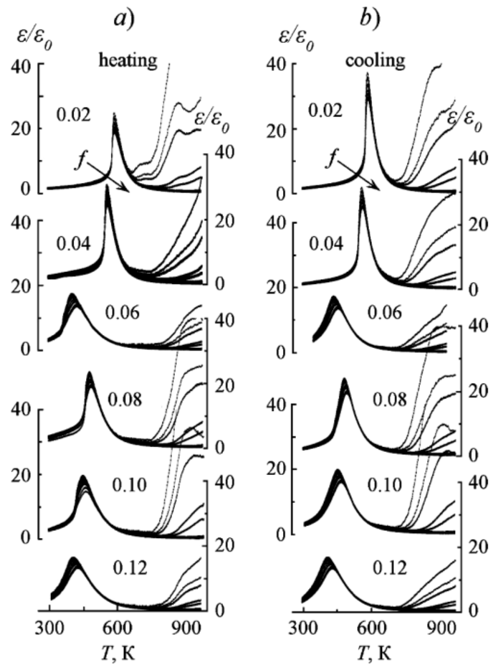

Fig. 3. Dielectric spectra of SS of the studied system in heating mode (*a*) and cooling mode (*b*). Numbers near the curves represent concentration of Sr (α_1) in arb. units.

Fig. 3 presents dielectric spectra of the studied SS. It can be seen that for α_1 = 0.02 relationships of $\varepsilon/\varepsilon_0(T)$ for various *f* and temperature has λ-shape (direct movement) with clear maximums, which do not become blurred and don't change their position for increase of *f*; maximums $(\varepsilon/\varepsilon_0)_{max}$ are high (~27000); there is no dispersion of $\varepsilon/\varepsilon_0$ to the left from the Curie point (T_c), it appears in the moment of ferroelectric (FE) – paraelectric transition and remains to the right from it in the narrow temperature range (590÷620) K.

On the opposite movements the portraits are similar, however, it can be seen that $(\varepsilon/\varepsilon_0)_{max}$ are increasing to ~38000. For α_1 = 0.04 the relationships of $\varepsilon/\varepsilon_0$ and temperature (direct movement) are similar to those observed for SS with α_1 = 0.02, but with small differences, which are related to low dispersion in the range (300÷530) K, absence of dispersion to the right from Curie point T_c and considerably higher maximum of $(\varepsilon/\varepsilon_0)_{max}$ (~33000). For the opposite movement the portrait is, generally, the same, however in low-temperature range (300÷540) K there is no dispersion of $\varepsilon/\varepsilon_0$. The above allows to attribute the discussed SS to classical ferroelectrics (FE). At α_1 = 0.06 blurring of the phase portrait (PP) (direct movement) takes place accompanied by shift of $(\varepsilon/\varepsilon_0)_{max}$ in the zone of higher temperatures with increase of *f* ofmeasurement field and its rapid decrease (~18000), as compared to $(\varepsilon/\varepsilon_0)_{max}$ of SS at α_1=0.02 and 0.04; there is no dispersion of $\varepsilon/\varepsilon_0$ in the range (300÷360) K; the dispersion appears at temperatures of (360÷420) K. At the back movement the portrait is similar, however there is dispersion in the whole FE zone. At α_1 = 0.08 there is also blurring of PP (direct movement) with shift $(\varepsilon/\varepsilon_0)_{max}$ in the area of higher temperatures with increase of f of the measuring field, $(\varepsilon/\varepsilon_0)_{max}$ ~ 25000; there is dispersion of $\varepsilon/\varepsilon_0$ before and after T_c in the range of (300÷520) K. At the back movement the portrait is similar, but with lower dispersion of $\varepsilon/\varepsilon_0$. Behavior of relationships of $\varepsilon/\varepsilon_0$(T) of SS at α_1 = 0.10 is similar to the described behavior at α_1 = 0.06, however there is stronger dispersion before and after T_c and there are higher values of $(\varepsilon/\varepsilon_0)_{max}$ (~20000) both at direct and back movement. For SS at α_1 = 0.12 behavior of relationship $\varepsilon/\varepsilon_0(T)$ is almost similar to SS at α_1 = 0.06, however there is dispersion of $\varepsilon/\varepsilon_0$ in the whole SE region for both direct and back movements. The above allows to attribute the discussed SS to FE-relaxors, which, in turn, allow to consider them as prospective base materials for precision transmission devices. It worth mentioning that anomalies of $\varepsilon/\varepsilon_0$ appear in the high temperature range (~670÷770) K: rapid increase of $\varepsilon/\varepsilon_0$ at ~670 K at low f (25, 60, 100) Hz without formation of maximum and its formation at higher frequencies ((60, 100) Hz) (α_1 = 0.02, 0.08, 0.10). For SS at α_1 = 0.04, 0.06, 0.12 at T ~ 770 K only beginning of those processes is visible. The observed phenomenon is related to the change of the valence condition of Ti ions $Ti^{4+}\rightarrow Ti^{3+}$и $Nb^{5+}\rightarrow Nb^{4+}$ [8-9], which is accompanied by the formation of oxygen vacations [10] and, therefore, the development of Maxwell-Wagner relaxation processes. The results of the studies indicate that it is possible to produce FS materials using the technology, which doesn't comprise application of external pressure; the wide range of electrophysical characteristics provides the wide range of opportunities for engineering implementation of the developed media for the one multi-element compound.

CONCLUSION

In the presented study the correlation between structural, dielectric, piezoelectric, elastic and dissipative characteristics of solid solutions of the system (Pb, Sr, Ba) (Ti, Zr, Nb, Zn, Mg)O_3 was investigated. Also, it was established that it is possible to produce the developed ferroelectric-soft materials using regular ceramics technology with parameters, which allow to use them in various piezoelectric devices.

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