Peculiarities of the dependences of the dielectric properties of solid solutions of multicomponent systems on the electronegativity of their constituent cations

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Solid solutions (SS) of 3- and 4-component systems based on lead titanate–zirconate were prepared by the method of solid-phase reactions and uniaxial hot pressing. The dependences of the relative permittivity of polarized samples on the electronegativity (EN) of their constituent cations have been studied. The ferro-hardness of the SS (the stability of the domain structure to external influences) is shown to be directly dependent on the EN of elements B in the corresponding oxidation states, i.e., the degree of covalence of the B–O bond. The deviation from this dependence in SS with Ni and Cd is explained by their individual features, which result in changes in the degree of bond covalence in both cationic sublattices. The conducted crystal-chemical analysis made it possible to choose promising SS when creating ferroelectric materials, including textured piezoelectric ceramic materials for piezoelectric transducers for various purposes: Piezotransformers, piezoelectric motors, ultrasonic emitters, filter devices, ultrasonic flaw detectors, accelerometers, etc.

Keywords: Solid solutions; multicomponent systems; lead titanate–zirconate; electronegativity; dielectric properties.

1. Introduction

The targeted development of new materials that meet the requirements of the modern era has led to the need to create compositions that combine a high level of functionality and its self-control. This determined their belonging to the group of the smart compound, the leading position which is occupied by those with special electrical properties — ferroelectrics, including textured piezoelectric ceramic.[1–4] At the same time, the recent demand for their accelerated design in order to quickly introduce them into the industrial sphere has shifted the main emphasis in the production process towards the initial stage of macroresponse prediction based on already known correlations with the crystal-chemical status of the cationic composition. This article discusses the features of the dependences of the dielectric properties of the solid solutions (SS) of a number of multicomponent systems based on lead titanate–zirconate on the electronegativity (EN) of their constituent cations.

2. Objects, Methods of Obtaining and Research

The objects of study are SS of 3- and 4- component systems of the form: $PbZrO_3–PbTiO_3–PbB'_{1-\beta}B''_{\beta}O_3$; $PbZrO_3–PbTiO_3–PbNb_{2/3}Zn_{1/3}O_3–PbB'_{1-\beta}B''_{\beta}O_3$ (I), $PbZrO_3–PbTiO_3–PbNb_{2/3}Mn_{1/3}O_3–PbB'_{1-\beta}B''_{\beta}O_3$ (II), $PbZrO_3–PbTiO_3–PbSb_{2/3}Mn_{1/3}O_3–PbB'_{1-\beta}B''_{\beta}O_3$ (III) (B'– Nb/W; B''– Ni, Mg, Co, Zn, Mn, Cd).

The synthesis of samples was carried out by a one- or two-stage method of solid-phase reactions (with intermediate grinding and granulation of powders). Sintering was carried out using the method of uniaxial hot pressing, which, under certain conditions, provides texturization of the microstructure of ceramics, using mechanical activation procedures that lead to a change in the reactivity of solids, as well as acceleration of chemical reactions due to the occurrence of elastic and plastic deformations, additionally contributing to the texturization of the grain landscape of objects. Optimal regulations for the technological process of obtaining objects were established on the basis of X-ray data and density measurements for each studied composition.

Search measuring samples were made in the form of discs of Ø10×1 mm. After mechanical treatment, electrodes were applied to the flat surfaces of the samples by two-time firing of a silver-containing paste at 1073 K for 0.5 h.

X-ray studies were carried out by powder diffraction using DRON-7 and ADP diffractometers (Co_{K_α} radiation; Bragg–Brentano focusing scheme). Volumetric and crushed ceramic objects were studied, which made it possible to exclude the influence of surface effects, stresses, and textures that arise during the manufacture of ceramics. The calculation of the

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structural parameters was carried out according to standard methods.[5]

The experimental density (ρ_{exp}) of the samples was determined by hydrostatic weighing in octane. Calculation of the X-ray density ($\rho_{X\text{-ray}}$) was carried out according to the formula: $\rho_{X\text{-ray}} = 1.66 \cdot M/V$, where M is the weight of the formula unit in grams, V is the volume of the perovskite cell in Å. Relative density (ρ_{rel}) was calculated by the formula ($\rho_{exp}/\rho_{X\text{-ray}}$)·100%.

Measurements of dielectric, piezoelectric and ferroelastic parameters of SS at room temperature were carried out by the resonance method in accordance with Ref. 6. The relative permittivity of polarized samples ($\varepsilon_{33}^T/\varepsilon_0$), dielectric losses (dielectric loss tangent) (tgδ), electromechanical coupling coefficient of the planar vibration mode (K_p), piezomodules ($|d_{31}|$, d_{33}), piezosensitivities ($|g_{31}|$, g_{33}), mechanical quality factor (Q_M), Curie temperature (T_C) and relative change in the resonant frequency in the temperature range ($\delta f_0/f_r$) were determined.

3. Experimental Results and Discussion

The dependences were established between the electrophysical parameters of the SS of some systems $PbZrO_3 - PbTiO_3 - \Sigma_n(PbB'_{1-\beta}B''_{\beta}O_3)_n$ ($n = 1 - 3$) and crystal chemical characteristics of cations B′, B″.[7] It is shown that the ferro-hardness of the SS (resistance of the domain structure to external influences) is directly dependent on the EN of the B″ elements in the corresponding oxidation states, that is, on the degree of the covalences of B–O bond.

Following the logic of Ref. 7, in the SS of systems under consideration, with an increase in the effective EN (taking into account the fraction of elements in different valence states), that is, in the order of increasing the degree of bond covalence, the permittivity ($\varepsilon_{33}^T/\varepsilon_0$ of polarized samples) should decrease in the series Mg → Cd → Co → Zn → Ni → Mn. At the same time, it should be taken into account that the oxidation states of Mg^{2+}, Cd^{2+}, Zn^{2+} are stable and the effective values of the EN of Co and Mn are equal to the sum of the equity contributions of the EN of Co^{2+}, Co^{3+}, Mn^{2+}, Mn^{3+}, Mn^{4+} which were presented in the SS of the indicated type[7] with an approximate ratio of the proportion of the indicated cations $Co^{2+}:Co^{3+}$ = 5: 1 to 1: 1 (depending on the composition); $Mn^{2+}:Mn^{3+}:Mn^{4+}$ = 8: 5: 2 (estimated data from thermogravimetric analysis). This is illustrated in Figs. 1 and 2, built on the basis of the patent data (triple SS systems) and the results of our studies (SS of four-component systems - I, II, III). The SS with Ni^{2+} and Cd^{2+} do not satisfy the established regularity: The first shows the highest values of $\varepsilon_{33}^T/\varepsilon_0$, the second shows the lowest. At the same time, in the case of Ni^{2+}, the higher of the two given values $\varepsilon_{33}^T/\varepsilon_0$ remains outside the curves (according to different authors). Correspondence of the dependence $\varepsilon_{33}^T/\varepsilon_0$ on EN_B occurs with a significant decrease (by ~ 25%) in $EN_{Ni^{2+}}$ and an increase (by ~ 20%) in $EN_{Cd^{2+}}$. Therefore, in multicomponent systems, Ni^{2+} exhibits a significantly lower EN, while Cd^{2+} exhibits a higher EN. In this sense, in the specified row of elements, Ni^{2+} should move to the left, that is, toward a more ionic bond and be located in front of Mg^{2+}, and Cd^{2+} should move to the right, towards a more covalent bond.

However, the Ni^{2+} by the degree of covalence of bond, having an unfinished 18-electron outer shell $[(d^8)s^2]$,[8] which is characterized by significantly greater polarization properties (and the ability to deform and exert a polarizing effect[9])
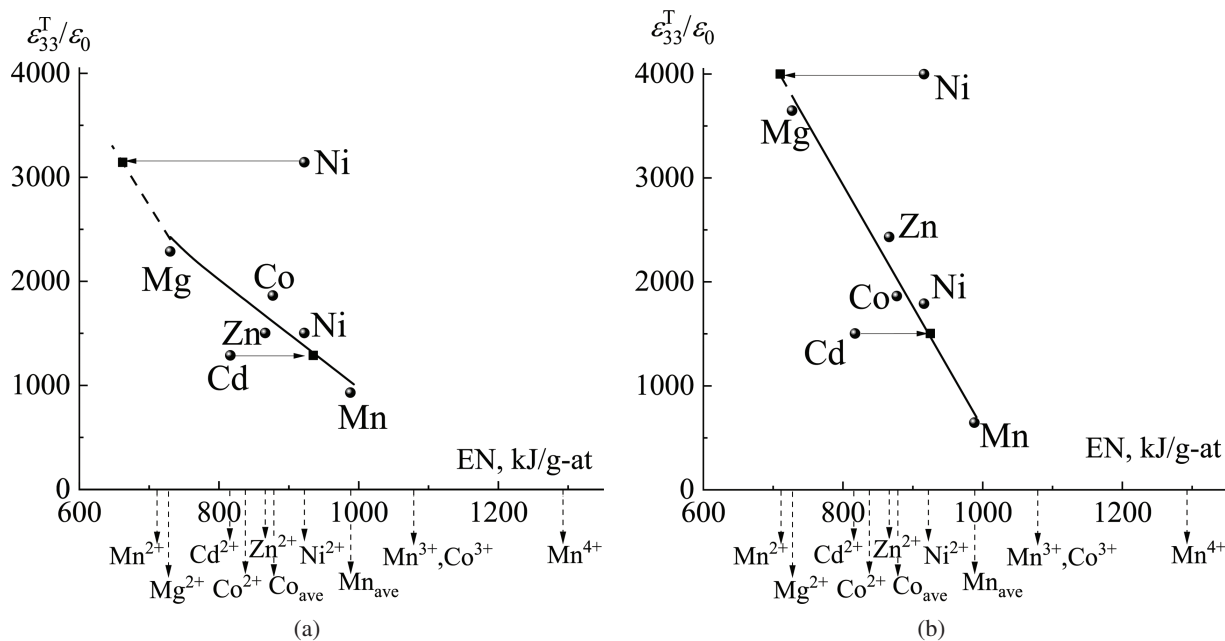

Fig. 1. Dependences of the relative permittivity of polarized samples of SS of three-component systems $PbZrO_3–PbTiO_3–PbB'_{1-\beta}B''_{\beta}O_3$ on the EN of B″-ions (B′ = Nb (a), B′ = W (b)).

compared to the ions of the type of inert gas with the same charge and close radius as Mg^{2+} forms an Ni–O bond that is more covalent than Mg–O.

Therefore, the reason for the displacement of Ni^{2+} in the EN series should be sought in the specifics of its behavior in the SS structure: The possibility of reducing the degree of oxidation, decreasing the concentration, falling under the influence of neighboring ions, which can change the nature of the B–O bonds. It was with the latter that the observed anomalous behavior $\varepsilon_{33}^T/\varepsilon_0$ in Ni-containing four-component SS was associated in Ref. 7.

The mechanism of this effect, according to the authors, is associated with the appearance of B′-cations in lower oxidation states in amounts that depend on the individual characteristics of B″ ions. This will lead to a change in the degree of covalence not only of the B′–O, but also of the B″–O bond, i.e., to a change in the EN_B''.

Since the observed changes in EN are significant, the concentrations of B′ ions of lower valence should be noticeable (in any case, commensurate with the ground state of the elements). And this is impossible, since under the thermal conditions of synthesis of the considered solid solutions, when the mixtures are heated in air, the W^{6+}, Nb^{5+}, Ta^{5+} cations can only be slightly reduced without changing, in general, the oxidation state. This is confirmed both by the thermogravimetric analysis data, which did not reveal W^{5+}, Nb^{4+}, Ta^{4+} in the reaction mixtures, and by the measurements of the electrical conductivity of the samples. The exception is B′ = Sb, for which the joint presence of Sb^{5+} and Sb^{3+7} in the ratio ≈ 1:1 is characteristic in the synthesis temperature range, and therefore the interpretation of experimental results given in Ref. 7

is valid only for this case. But since the anomalous behavior $\varepsilon_{33}^T/\varepsilon_0$ is also characteristic of SS without Sb, it is clear that its cause is not in the concentration variations of different valence B′ ions. The transition $Ni^{2+} \to Ni^{1+}$, which would be accompanied by a decrease in EN,[7] also seems unlikely. Thus, the mechanism of reducing the effective EN of Ni^{2+} by reducing its amount in regular octahedral sites of the SS structure seems to be the most acceptable.

This can be a consequence of either the "precipitation" of impurity phases or the introduction of Ni^{2+} into vacant irregular positions. However, the absence of by-products of solid-phase synthesis (thermogravimetric, X-ray diffraction and microstructural analyses) in the considered number of the investigated SS indicates that Ni^{2+} enters the lattice almost completely.

It remains to assume that a part of Ni^{2+} leaves the regular octahedral positions and fills some vacancies in the irregular structure. This is possible if we take into account, on one hand, the tendency of certain transition metal oxides (W, Nb, Ti) to form anion-deficient nonstoichiometry and to the exclusion of the point defects by a crystallographic shift,[10] generating vacancies in an irregular structure (tetrahedral and octahedral unoccupied positions inside channels formed by columns of blocks, hexagonal tunnels, etc.),[10] on the other hand, the tendency in such oxide systems of cations, which found themselves after even a slight loss of oxygen in a strongly asymmetric environment, to change their coordination number (c.n.) and form "fivefold, quadruple, triple and double groupings".[11,12]

Most of all, Ni^{2+} is prone to this due to the specifics of the electronic structure of d-layers and the influence of the
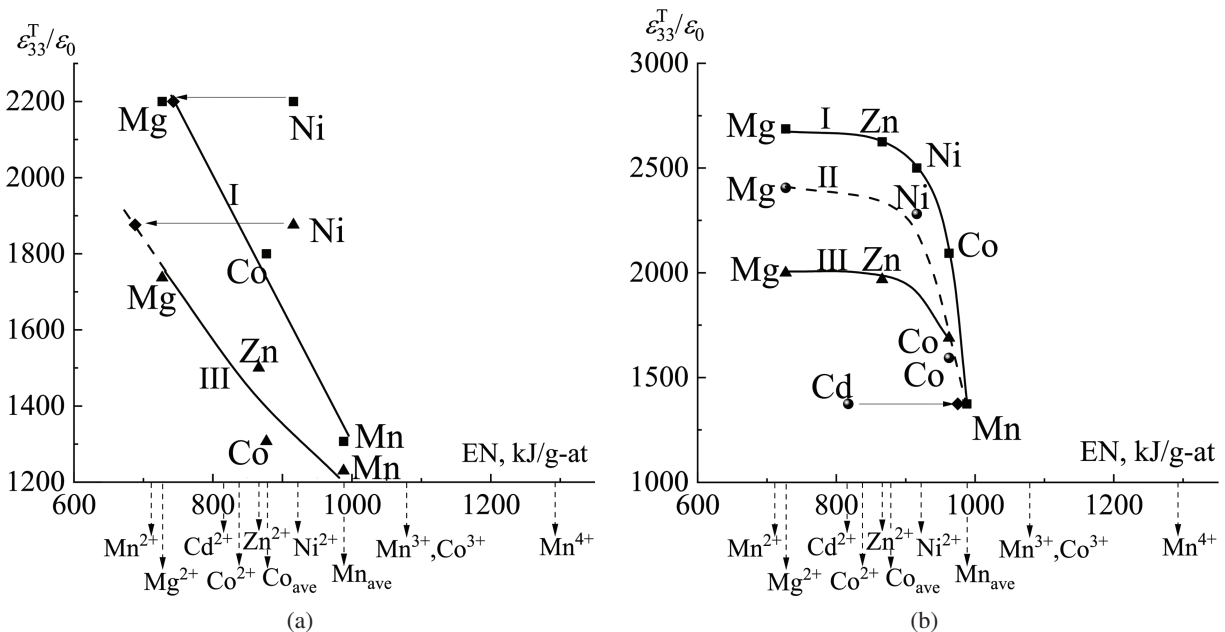

Fig. 2. Dependences of the relative permittivity of the polarized samples of the SS of quaternary systems of the form $PbZrO_3 - PbTiO_3 - \Sigma_n(PbB'_{1-\beta}B''_\beta O_3)_n$ ($n = 2$) on the EN of B″-ions (B′ = Nb (a), B′ = W (b)). The numbers next to the curves correspond to the numbers of the SS series adopted in the text.

field of surrounding anions in the process of electron pairing, which determines its high stereochemical activity[8] and distinguishes it from other elements of the considered B″-group. The latter creates favorable preconditions for its possible filling of the resulting vacancies, including tetrahedral ones. This is also allowed by the size factor (the ratio of the sizes of Ni^{2+} and oxygen is ~ 0.5), which is close to the upper limit of such ratios typical for the tetrahedral configuration (0.225–0.415).[13,14] In turn, the high emission capacity of Ni^{2+}, due to its small size and enhanced multicomponent SS by microdefective compositions (it is an SS disorder due to a large number of components, the presence of different sorts of ions in equivalent crystallographic positions, local nonstoichiometricity, due to redox processes and thermal dissociation as well as thermal disordering at the previous technological stages of the synthesis, sintering and the states and properties preserved due to hysteresis, the formation of the vacancies) makes it possible to realize these possibilities. It is also important that there are structure-forming cations W^{6+}, Nb^{5+}, Ti^{4+} in the SS compositions, the specificity of which was mentioned above. This opens up wider prospects for the emergence of a variety of vacancies. One more feature of Ni^{2+} should be noted: The possibility of simultaneous

coexistence of octahedral, tetrahedral and square forms with a complex mobile equilibrium and structural transitions which depend on the conditions for obtaining objects, the concentration of Ni^{2+}, the number and nature of the surrounding ions. It is known, for example, that the so-called anomalous behavior of Ni-complexes[8] is associated with these features of the Ni^{2+} structure. The discrepancies described above in the values $\varepsilon_{33}^T/\varepsilon_0$ given by various authors are probably due to differences in the conditions for obtaining SS, in particular, of the temperature, with an increase due to which the stability of the tetrahedral form increases.[8]

The departure of a part of Ni^{2+} from regular octahedral positions will lead, on one hand, to a decrease in the degree of B–O bond covalence, and, on the other hand, to the creation of vacancies and, as a consequence, interruption of the "polarization chains",[15] leading to a decrease of the spontaneous polarization and the spontaneous deformation of the perovskite cell and, as a result, to an increase in $\varepsilon_{33}^T/\varepsilon_0$ due to the dependences existing between them.[7]

The abnormally low value $\varepsilon_{33}^T/\varepsilon_0$ of SS with Cd^{2+}, in our opinion, is a consequence of its redistribution over the A- and B-positions, which is allowed by the size of Cd^{2+}, which satisfies both conditions for the stability of a perovskite-type

Table 1.   Electrophysical characteristics of promising SS based on the $Pb(Ti,Zr)O_3$ (PZT) system.

				Electrophysical characteristics of SS								
				tgδ, %								
				$E = 50$ V/cm	$E = 1$ kV/cm							
System	B′B″	T_c, K	$\varepsilon_{33}^T/\varepsilon_0$			K_P	$\|d_{31}\|$, pC/N	d_{33}, pC/N	$\|g_{31}\|$, mV·m/N	g_{33}, mV·m/N	$\delta f_0/f_r$, % (213–353 K)	Q_M
SSs resistant to mechanical and electrical influences for piezo transformers, piezoelectric motors, etc.												
I	NbMn	595–615	1300–1350	0.31–0.34	0.45–0.75	0.570–0.610	125–135	—	10.4–11.6	—	—	1250–1800
II	WMg	500–510	2050–2200	0.37–0.39	1.0–1.1	0.58–0.63	150–190	—	8.3–9.8	—	—	1400–1700
II	WMn	605	950	0.90	—	0.57	87	—	10.5	—	—	1400
SSs with high resonant frequency stability for filter devices												
I	NbMn	595	780	0.65	—	0.38	55	—	8.0	—	0.21–0.26	3300
II	WMn	585	930	1.6	—	0.44	80	—	9.7	—	0.25	1150
II	WMn	595	650	0.6	—	0.29	38	—	6.6	—	0.24	2100
SSs with low dielectric constant for high-frequency transducers												
I	NbMg	550	330	0.45	—	0.37	36	—	12.3	—	—	1800
II	WMn	590	360	0.33	—	0.45	46	—	14.5	—	—	2300
II	WMn	560	280	0.32	—	0.30	25	—	10.1	—	—	3500
SSs with medium and high dielectric constant for MF- and LF- transducers												
I	NbMg	595	2050	1.5	—	0.66	207	465	11.4	—	—	75
I	WMg	560	2850	1.3	—	0.67	250	540	9.9	—	—	65
SSs with highly piezosensitive for ultrasonic flaw detectors. accelerometers. etc.												
PZT	WCd	635	700	2.1	—	0.61	98	225	16.1	37.0	—	65
PZT	WCd	625	1350	1.5	—	0.66	165	365	14.2	30.0	—	110
SSs with high anisotropy of piezoelectric properties												
PT	WMn	720	185	1.1	—	0.065	5.6	57	3.4	34.8	—	1950

structure ($r_A \geq 0.9$ Å, 0.51 Å $\leq r_B \leq 1.1$ Å[5]). This is also not favored by the strength of the Cd–O bonds, which provokes an increased migration ability of this cation. The latter also manifests itself in low-temperature sublimation of CdO (1173 K),[16] as well as in the implementation of low temperatures of the onset of reactions of the formation of complex Cd-containing oxides (T_{sint} $PbW_{1/2}Cd_{1/2}O_3 = 563$–603 K, T_{sint} $PbW_{1/2}Mg_{1/2}O_3 = 673$–733 K[17]). Thus, already in the process of obtaining SS with Cd^{2+} with an increase in the heat-treatment temperature, when the diffusion of ions rapidly increases, a real possibility of redistribution of Cd^{2+} is created. This is probably related to the strong smearing of the phase transition in $PbW_{1/2}Cd_{1/2}O_3$. Partial replacement of lead with cadmium will lead to an increase in EN of ferroactive A-sublattice and the degree of covalence of A–O bonds, which, in turn, will enhance the covalence of the B–O bond[7] and, consequently, increase the effective EN ions in the position B. Thus, the low value $\varepsilon_{33}^T/\varepsilon_0$ in SS with Cd^{2+} is apparently the result of a change in the degree of bond covalence in both cationic sublattices.

The conducted crystal chemical analysis was used in the Department of Ferro-Piezomaterials, Instruments and Devices of the Research Institute of Physics of the Southern Federal University in the development of new industrially produced ferropiezoelectric materials with various combinations of electrophysical parameters, including those resistant to external influences (electrical, mechanical and temperature), with low, medium and high dielectric constants, high piezosensitivity, high anisotropy of piezoelectric properties, etc. They can become the basis of piezoelectric elements for piezotransformers, piezoelectric motors, ultrasonic emitters, filter devices, high-frequency and low-frequency transducers, ultrasonic flaw detectors, accelerometers, sensors with increased sensitivity to hydrostatic pressure, low-frequency receivers, etc. (Table 1). The choice of promising SS was carried out in the vicinity of the morphotropic phase transition of the systems under consideration (materials resistant to mechanical and electrical stress, with medium and high dielectric permittivity), in the tetragonal phase at a distance from the MPT (materials with high-resonant frequency stability), in the rhombohedral phase (materials with low-dielectric constant, high piezosensitivity).

4. Conclusions

The dependences of the relative dielectric permittivity of polarized samples were studied on the EN of cations that are part of SS of multicomponent systems of form $PbZrO_3 - PbTiO_3 - \Sigma_n(PbB'_{1-\beta}B''_\beta O_3)_n$, $n = 1 - 2$; B' – Nb/W; B″ – Ni, Mg, Co, Zn, Mn, Cd. The ferro-hardness of SS (the stability of the domain structure to external influences) is shown to be directly dependent on the value of the EN of elements B in the corresponding oxidation states, that is, on the degree of covalence of the B–O bond. The observed deviation from this dependence in SS containing Ni^{2+} and Cd^{2+} is

due to the features of the Ni^{2+} structure and the size of Cd^{2+}, which satisfies both stability conditions for a perovskite-type structure, which results in changes in the degree of bond covalence in both cationic sublattices. Based on the results obtained, promising SS of the studied systems were selected for the manufacture of piezoelectric transducers for various purposes, including piezotransformers, piezoelectric motors, ultrasonic emitters, filter devices, ultrasonic flaw detectors, accelerometers, etc.

The performed crystal chemical analysis is useful in modeling and creating ferroelectric materials, including textured piezoelectric ceramic materials with controlled (including production conditions) electrophysical parameters.

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