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Ceramics International 38 (2012) 3835–3839

CERAMICS INTERNATIONAL

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Preparation, structure and piezoelectric properties of PZN-PMN-PT ceramics in the composition range of large PZN concentrations

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Received 23 December 2011; accepted 12 January 2012
Available online 21 January 2012

Abstract

A method of preparation of multicomponent Ba-doped $PbNb_{2/3}Zn_{1/3}O_3$-$PbNb_{2/3}Mg_{1/3}O_3$-$PbTiO_3$ (PZN-PMN-PT) solid solution system in the range of large PZN concentrations was developed. Structural peculiarities of these solid solutions were studied. Correlations between the crystal structure and piezoelectric properties were established.

Keywords: C. Piezoelectric properties; Relaxor ferroelectrics; Polycrystalline materials; Crystalline structures; Multi compounds solid solutions

1. Introduction

The development of novel highly effective piezoelectric materials based on relaxor ferroelectrics with a perovskite-type structure has been increasingly attracting attention of many researchers in recent years. A typical feature of this class of dielectrics is the exceptionally large values of the dielectric permittivity, electrostrictive and piezoelectric parameters at room temperature exceeding those in other materials [1]. Single crystals of the relaxor solid solution systems $PbNb_{2/3}Mg_{1/3}O_3$ (PMN)-$PbTiO_3$ (PT) and $PbNb_{2/3}Zn_{1/3}O_3$ (PZN)-PT possess the highest piezoelectric properties [2]. However, preparation of these solid solutions (SS) in the form of ceramics is hindered by the tendency of reagents to produce the parasitic phases with a pyrochlore-type structure [3–6] (stable intermediate compounds formed in the process of synthesis of $Pb(Nb_{1-x}B_x)O_3$-type perovskites [7–9]). Even small concentrations of pyrochlore phase lead to a drastic decrease of piezoelectric characteristics of perovskite materials [3–6,10]. These phases may often be eliminated by several ways including variation of the preparation conditions, doping by small amounts ($\leq$5%) of elements or simple compounds and designing of multicomponent systems. In particular, PMN-based SS free of parasitic phases can be obtained by the ''columbite'' method [11] or by the mechanochemical activation [12]. However, application of these procedures to the PZN-based compositions possessing the highest piezoelectric parameters [12] did not lead to the desirable result. To stabilize their structure, improve the electrophysical properties and extend a variety of their combinations it is more attractive to design the multicomponent systems. This method possesses a number of advantages, namely: (1) a larger dimension of the morphotropic region (MR) (a region of coexistence of different-symmetry phases characterized by the extreme properties of corresponding SS) enabling one to extend a selection of SS with desirable parameters; (2) a possibility to vary composition and, consequently, the SS characteristics; (3) a larger variety of material properties and their combinations, and (4) wider manufacturing opportunities. Therefore, the search for the novel relaxor-based multicomponent piezoelectric materials, the methods of stabilizing their crystal structure and the development of technology ensuring realization of the desirable electrophysical parameters remain a pressing problem.

2. Sample preparation and experimental procedure

We studied the multicomponent PZN-PMN-PT solid solution system in the PZN-rich concentration range. To avoid

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0272-8842/$36.00
doi:10.1016/j.ceramint.2012.01.033

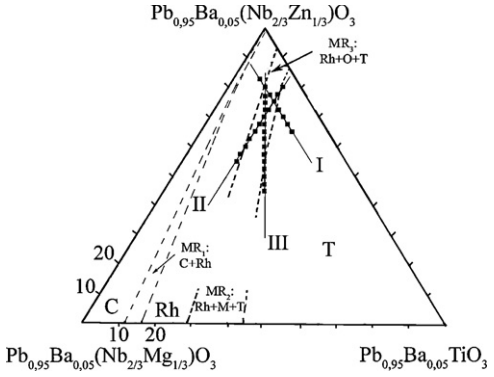

Fig. 1. Phase diagram of the ternary system $PbNb_{2/3}Zn_{1/3}O_3$–$PbNb_{2/3}Mg_{1/3}O_3$–$PbTiO_3$ modified with barium (+5% Ba) and the Sections under study.

a complication of the system the modification in accordance with the formula $(Pb_{0.95}Ba_{0.5})[(Nb_{2/3}Zn_{1/3})_x\ (Nb_{2/3}Mg_{1/3})_yTi_{1-x-y}]O_3$ has been made as an alternative to using $BaTiO_3$ as a stabilizer [14]. Fig. 1 shows the phase diagram of the system where the crystallographic phases are indicated as expected based on the known phase diagrams of the corresponding binary systems in which cubic (C), tetragonal (T), rhombohedral (Rh), and orthorhombic (O) phases have been observed. The chosen experimental points are also shown. We studied the system in three sections. Section I was parallel to the side formed by the binary PZN-PT system with the constant PMN content (10 mol%) and the PZN concentration ranging from 82.5 mol% to 65 mol%. Section II was parallel to the side formed by the binary PZN-PMN system with the constant PT content (15 mol%) and the PZN concentration ranging from 80 mol% to 52.5 mol%. Section III was directed along the bisectrix of the angle adjacent to the PZN apex with the PZN content from 80 mol% to 45 mol%. In all these cases a concentration step was chosen as $\Delta x = 2.5$ mol%, where x is the PZN concentration.

All the samples, including the powders of the binary systems constituting a multicomponent SS, were synthesized by means of solid state reactions using the ''columbite'' method. Synthesis of zinc and magnesium niobates was performed in two stages: calcination at 1000 °C for 6 h and 4 h, respectively, and at 1100 °C for 4 h for both substances. The SS of final composition were obtained by one-stage synthesis from PbO and TiO_2, $BaCO_3$ and the preliminarily prepared $ZnNb_2O_6$ and $MgNb_2O_6$ at 950 °C for 4 h. The ceramics were sintered by the conventional ceramic technology at (1160–1180 °C) (depending on composition) for 3 h. The samples for measurements were disks of 10 mm in diameter and 0.5 or 1 mm in thickness. The flat surfaces were processed with the help of a diamond instrument using the 6th grade of fit. Electrodes were performed by means of two-fold burning-in of the Ag-containing paste at $T = 800$ °C for 0.5 h.

Phase content and synthesis completeness were assessed by x-ray diffraction. Precise structural studies were carried out on the sintered and ground ceramic samples by the X-ray powder diffraction method with DRON-3 and DRON-7 diffractometers using filtered Co Kα-radiation (the Bragg–Brentano focusing). The lattice parameters (linear–a, c and angular–α) and the perovskite cell volume (V) were calculated using the standard procedures [15].

The sample density (ρ_{meas}) was determined by the method of hydrostatic weighing in octane. The X-ray density ($\rho_{X\text{-ray}}$) was calculated by the formula $\rho_{X\text{-ray}} = 1.66\ M/V$, where M is the formula unit weight in grams and V is the perovskite cell volume in Å. The relative density (ρ_{rel}) was determined from the relation $\rho_{rel} = \rho_{meas}/\rho_{X\text{-ray}}$.

Dielectric, piezoelectric and elastic parameters of SS were measured using the resonance–antiresonance method [16]. The following parameters were determined: the relative dielectric permittivity of poled ε_{33}^T and unpoled ($\varepsilon/\varepsilon_0$) samples, the dielectric loss in a low electric field (loss tangent, tan δ), the piezoelectric modulus (d_{31}), the electromechanical coupling factor of planar vibration mode (K_p), the mechanical quality factor (Q_m), Young's modulus (Y_{11}^E), and the sound velocity (V_1^E). The accuracy of these measurements was $\leq \pm 1.5\%$ for $\varepsilon_{33}^T/\varepsilon_0$, $\leq \pm 2.0\%$ for $K_p \leq \pm 4.0\%$ for $|d_{31}| \leq \pm 12\%$ for Q_m, and $\leq \pm 1.0\%$ for Y_{11}^E [17].

3. Experimental results and discussion

Chosen technological conditions enabled us to obtain PZN–PMN–PT samples with the highest possible for conventional ceramic method densities $\rho_{rel} = 94$–96% which increased with increasing the $PbTiO_3$ concentration. Fig. 2a–c) show the densities ρ_{meas} and ρ_{rel}, the lattice parameters and the cell volumes as a function of composition of ceramics at Sections I, II and III, respectively. The phases of SS as determined using X-ray diffraction analysis are labeled. The phases which cannot be identified due to weak splitting and/or large broadening of X-ray diffraction peaks are referred to as pseudocubic (Psc). Section I possesses the most complicated phase composition due to a comparatively large variation in concentration of $PbTiO_3$ properties of which are drastically different from the properties of other components of the system. In Sections II and III the phase pattern is simpler because the $PbTiO_3$ content decreases. Furthermore, in some cases the chosen concentration step seems not to allow the determination of the regions of the intermediate phase states the extensions of which may be very small.

In Sections I and III the parameter c diminishes with the increase of x while the parameter a increases causing a diminution of the c/a ratio. As the T phase disappears, one can observe small variations in the parameter a. Practically linear increase of V with increasing x is observed initially in the region of coexistence of T phases. In the region of coexistence of the T_2 and Psc phases one can observe the invar effect, i.e. constancy of the lattice parameters or V [18,19]. With a further x increase V increases too. A wavy growth in V with increasing x in the T phase may be related to the periodic process of formation, accumulation and elimination of vacancies and a crystallographic shear in Ti-rich objects as previously observed in the media containing the variable-valence elements [20].

Similar dependences for SS Section II are shown in Fig. 2b. The parameter a and the Rh cell volume increase slightly and

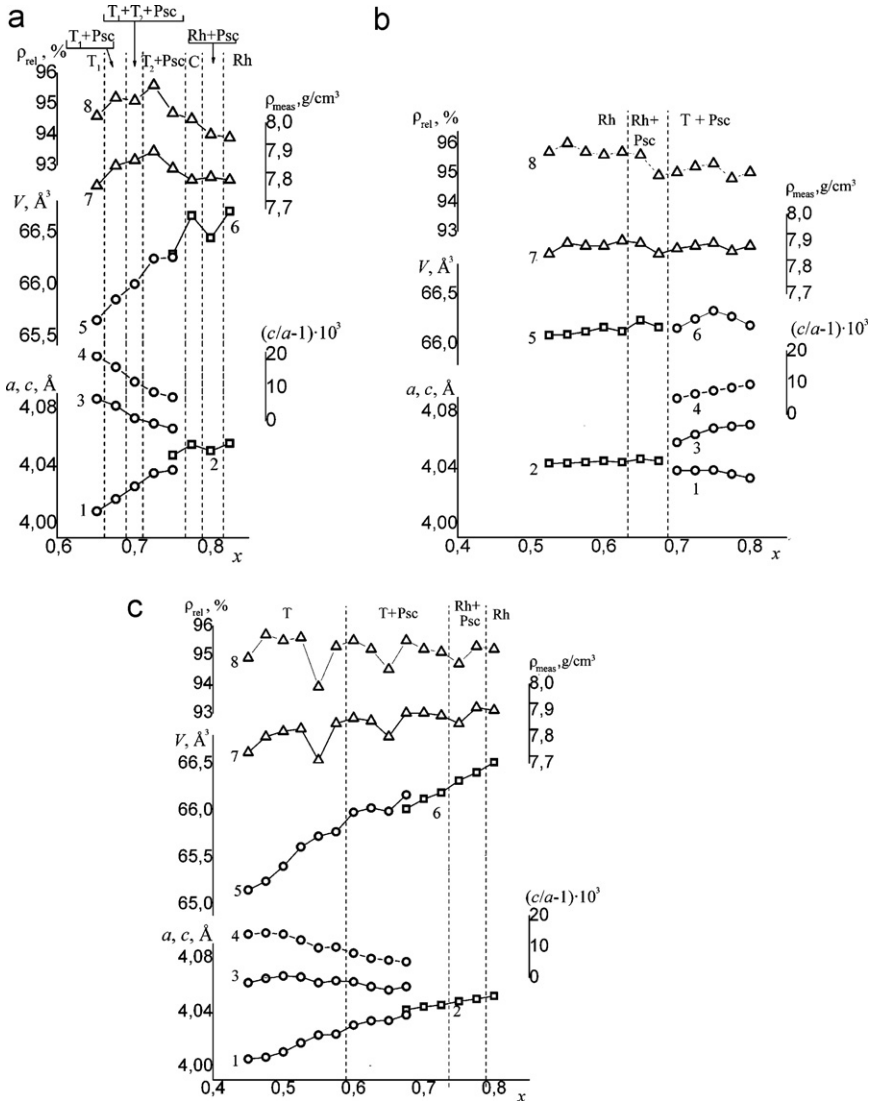

Fig. 2. Lattice parameters, cell volume and densities of the $(Pb_{0.95}Ba_{0.5})[(Nb_{2/3}Zn_{1/3})_x\ (Nb_{2/3}Mg_{1/3})_yTi_{1-x-y}]O_3$ system as a function of composition for the phase diagram sections (a) I, (b) II and (c) III. 1–a_T, 2–a_K, 3–c_T, 4–c/a, 5–V_T, 6–V_C; 7,8–are the experimental and relative densities, respectively.

non monotonically with the increase of PZN concentration. After the appearance of the T phase ($x > 0.7$) the parameter c and the c/a ratio increase while the parameter a decreases. In the range of $x = 0.5$–0.6, V slowly increases with increasing x. The invar effect manifests itself at the boundaries of mixed Rh, Psc and T, Psc phases. With the increase of PMN concentration the sample density increases, especially in the region of coexistence of the Psc and Rh phases. This is because of the large number of shear planes at the boundaries of different phases and the high structural imperfection of the ceramics having these compositions.

The obtained results enabled us to refine the phase diagram as presented in Fig. 3 (shown is a fragment near PZN). It is different from the expected one (Fig. 1) by a wider region of the morphotropic phase boundary from Rh to T state and a more complex structure, i.e. a presence of coexistence regions of the phases of different symmetry (T, Rh, Psc and C) and phase states (T_1, T_2) with the different value of c.

Variations in the basic properties with phase and chemical composition of Sections I, II and III are shown in Fig. 4. High values of $\varepsilon_{33}^T/\varepsilon_0$ accompanied by low Q_m suggest that these SS belong to the group of soft ferroelectric materials [21]. The

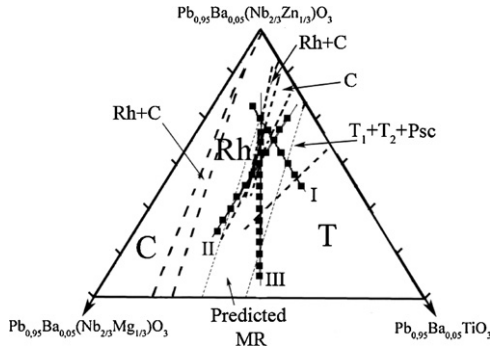

Fig. 3. A studied fragment of the phase diagram of the barium modified PZN–PMN–PT system with the refined phase boundaries.

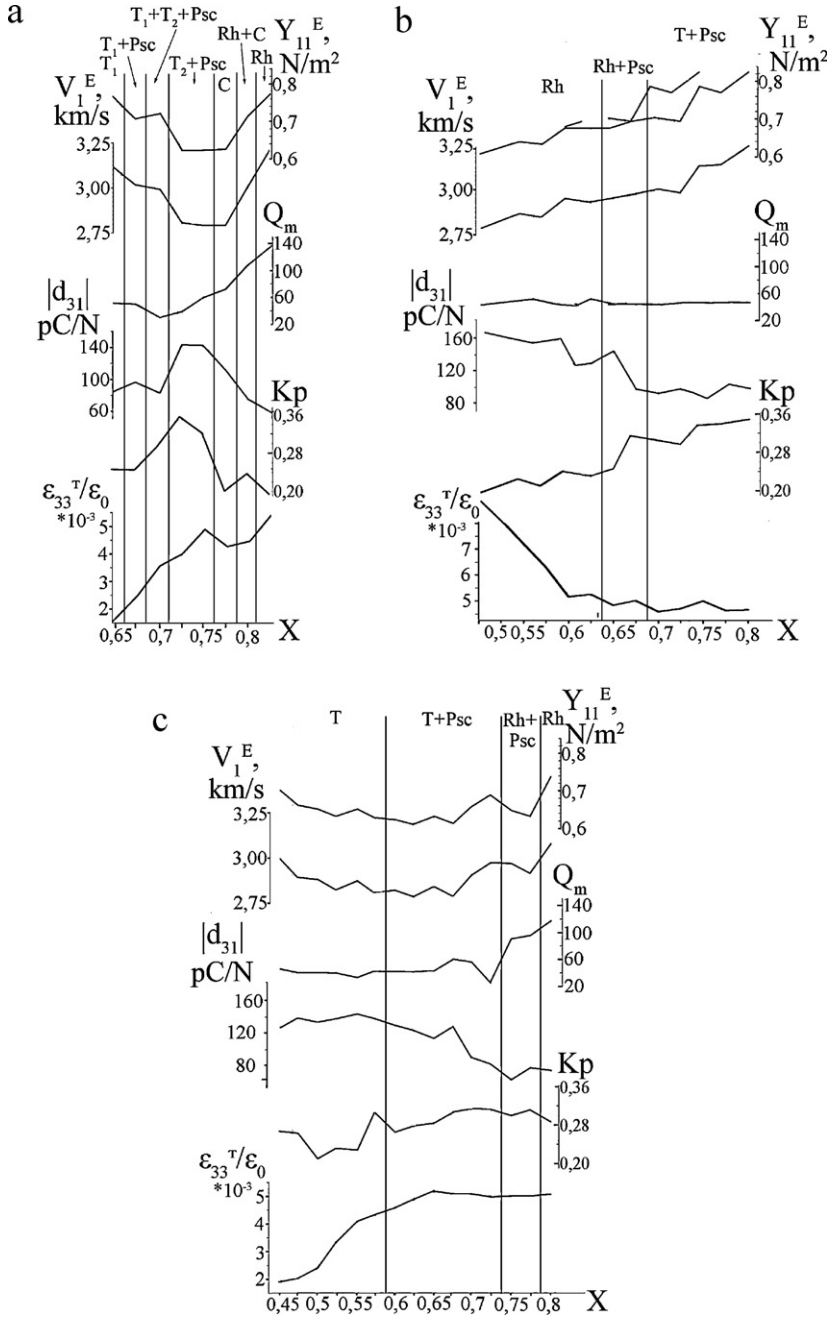

Fig. 4. Plots of measured characteristics of $(Pb_{0.95}Ba_{0.5})[(Nb_{2/3}Zn_{1/3})_x\ (Nb_{2/3}Mg_{1/3})_yTi_{1-x-y}]O_3$ ceramics as a function of composition corresponding to the phase diagrams sections (a) I, (b) II and (c) III.

shift of the $\varepsilon_{33}^T/\varepsilon_0$ maximum temperature observed earlier in Ref. [22] when varying a measuring field frequency indicates a relaxor origin of the PZN- and PMN-rich SS systems. The largest nonlinearity of composition dependences of the parameters with distinct maxima of piezoelectric (K_p, d_{31}) and dielectric ($\varepsilon_{33}^T/\varepsilon_0$) characteristics is observed in Section I ceramics. Maximum values of characteristics correspond to the region with $0.725 < x \leq 0.75$, where the T_2 and Psc phases coexist and the invar effect is observed. This is indicative of the maximum sensitivity of the ceramics with this composition to the external influence caused by structural instability. In this concentration range the V_1^E and Y_{11}^E values pass through the minimum related to the increased variety of structural elements at the domain and nanodomain levels and the increased imperfection of SS from the morphotropic region [20].

In Section II, a dramatic decrease of $\varepsilon_{33}^T/\varepsilon_0$ is observed with the increase of x up to $x = 0.6$, but then it does not change significantly while the K_p value increases fairly monotonically with a small local maximum in the range of $0.65 < x \leq 0.675$. Such a behavior of $\varepsilon_{33}^T/\varepsilon_0$ may be caused by the increase of the Curie temperature. The K_p and d_{31} maxima in the range of $0.65 < x \leq 0.675$ may be related to a transition between the Rh and T phases. Q_m remains practically unchanged when x

increases. For V_1^E and Y_1^E one can observe a nearly linear growth with the local maxima at $x = 0.6$ and $x = 0.75$.

The $\varepsilon_{33}^T/\varepsilon_0$ values for Section III ceramics increase with increasing x to 0.65, which may be due to the appearance of a low-symmetry phase and, as a consequence, the increased mobility of domain structure. This may be also related to the appearance a nanodomain structure typical of the relaxor state. With the increase of x, K_p slightly increases passing through two distinct maxima: the first, rather sharp one is in the region of the onset of a Psc phase ($x = 0.575$), and the second one, flatter and diffuse, is in the region preceding the appearance of a Rh phase. The value of d_{33} slowly increases in the region of existence of the T phase, but then with the appearance of the Pc phase, it begins to decrease passing through a sharp maximum at $x = 0.675$, which may be the result of the domain structure variation. The values of Q_m, V_1^E and Y_1^E do not practically change with the increase of x up to the appearance of the Rh phase and then they increase drastically passing through a local maximum at $x \sim 0.725$. Temperatures of the $\varepsilon_{33}^T/\varepsilon_0$ maxima for all the studied SS range from 80 to 200 °C [22].

4. Conclusion

The obtained results allowed us to choose the most promising $(Pb_{0.95}Ba_{0.5})[(Nb_{2/3}Zn_{1/3})_x(Nb_{2/3}Mg_{1/3})_yTi_{1-x-y}]O_3$]O_3 solid solutions for their following technological development as materials for low-frequency receiving devices, e.g. hydrophones, microphones and seismic detectors. The highest piezoelectric characteristics are found in solid solutions of Section I with $x = 0.725$ for which $\varepsilon_{33}^T/\varepsilon_0 = 4000$; $\tan\delta_. = 0.22$; $K_p = 0.36$; $|d_{31}| = 143$ pC/N; $Q_m = 62$; $V_1^E = 2.8$ km/s; $Y_{11}^E = 0.629 \times 10^{-11}$ N/m^2 and $T_c = 125$ °C.

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