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Variations in the microstructure and properties of multicomponent ferroelectric ceramics as a result of its modification by barium

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Abstract

The specific features of the microstructure of multicomponent solid solutions, based on relaxor ferroelectrics both unmodified and modified by barium, were observed. A reduction of tetragonal distortion in the unit cell in ceramics containing Ba, as well as an increase in the size of its crystallites (which is a consequence of this reduction), facilitates domain reorientation owing to an increase in their mobility. This is the main reason for the sharp increase in the relative permittivity $\varepsilon_{33}^{T}/\varepsilon_0$ of the poled samples of modified ceramics, and the variations of some parameters that characterize the piezoelectric response.

Keywords: Microstructure; Crystallites; Relaxor ferroelectrics; Dielectric constant

1. Introduction

The bases of most piezoceramic materials (PCM), used in various applications, are solid solutions (SS) of multicomponent systems with morphotropic phase boundaries, often including classical ferroelectrics (antiferroelectrics) ($PbTiO_3$, $PbZrO_3$, etc.) and relaxor ferroelectrics ($PbMg_{1/3}Nb_{2/3}O_3$, $PbZn_{1/3}Nb_{2/3}O_3$, $PbNi_{1/3}Nb_{2/3}O_3$) [1–4]. Clear advantages of multicomponent systems over binary ones are improving the processability, including an enlargement of the SS formation possibilities, and achieving a greater variety of properties. The latter allows the selection of compositions with required combinations of parameters for specific applications [5,6], and design of materials [1,2]. In part, the above-mentioned advantages are a result of an increase in the dimension of the morphotropic region, within or near which the parameters of materials are extreme. In addition, the crystal-chemical features of the multicomponent SS, with heterovalent ions in similar structural positions, lead to the generation of additional defects (vacancies) in the process of synthesis. This provides intensification of diffusion processes and, as a consequence, the optimum microstructure (polycrystalline structure) and piezoelectric responses of PCM [7–9].

Another way to control the microstructure and electrophysical characteristics of PCM is to modify ceramics; i.e. to incorporate small additives (not more than 10%) of simple compounds (oxides, carbonates, etc.) of different elements into the PCM, that results in selective variations of ceramic properties [10,11].

To create PCM with ultra-high dielectric constants for application in the low-frequency technique, one usually chooses compositions based on relaxor ferroelectrics, and also introduces modifiers (alkaline earth elements: calcium, strontium, barium) into a base medium [12–15]. The mechanism of their influence on the properties of SS of binary [12–17], ternary [15,17–25], and quaternary [26–28] systems consists of a reduction in the electronegativity, polarizing effect and, consequently, in the attenuation of the degree of A–O covalent bonds, leading to ferroelectric 'softening' of SS [17,26–29]. The effect of alkaline earth elements (especially Ba) on the polycrystalline structure of PCM is considered to a lesser extent [15,30]. Taking into account a significant dependence on the PCM properties from the microstructure [5,27,31], and based on its detailed research, the role of Ba in its formation is discussed in this paper.

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2. Experimental procedure

The objects of the study were multicomponent ceramic compositions $Pb_{(1-x)}Ba_x(Mg_{1/3}Nb_{2/3})_m(Zn_{1/3}Nb_{2/3})_y(Ni_{1/3}Nb_{2/3})_n Ti_zO_3$ (x=0 and 0.05, m=0.451, y=0.0982, n=0.1477, z=0.3), prepared by solid-state synthesis with elements of the columbite method, and sintered by conventional ceramic technology [28]. The sintering temperatures, T_{sint}, were identified as optimal when the maximum densities of ceramics, ρ_{exp}, were achieved. XRD studies were carried out on the diffractometer DRON 3.0 (filtered $Co_{K\alpha}$ – radiation, the Bragg–Brentano focusing geometry).

For microstructural studies the specimens were polished on a TegraPol-11 (Struers) machine. To visualize the polycrystalline structure of ceramics, two modes of thermal etching were used. The temperature of etching, T_{et}, was used in the range of 1100–1150 °C, and exposure time, τ_{et}, varied from 5 to 15 s for the 'high-temperature' technique. In the 'low-temperature' procedure, T_{et} and τ_{et} values were 800–850 °C and 50–3 min, respectively. Through these procedures, microgrooves along the grain boundaries were formed on the polished surfaces. Then, after being prepared in this way, sample surfaces were studied on optical microscopes, Axio Imager.Z1m (Carl Zeiss) and DMI5000 M (LEICA).

The relative permittivity of the poled samples ($\varepsilon_{33}^T/\varepsilon_0$), dielectric loss tangent ($tg\delta$), piezomodulus ($|d_{31}|$), electromechanical coupling coefficient of planar oscillation mode (K_p), mechanical quality factor (Q_M), and sound velocity (V_1^E) were determined with the help of precision impedance meter, 6500B Wayne-Kerr.

3. Experimental results and discussion

The introduction of Ba drastically reduced the optimal sintering temperature of samples (from 1220 °C for unmodified SS to 1180 °C for modified ceramics). This may be consequence of the formation of additional liquid phases (glassy phases). They could be formed during the synthesis of SS by the melting of thermally stable hydroxide $Ba(OH)_2$ (melting point 780 °C). It is the product of the hydrolysis of a small amount ($<5\%$) of unreacted starting material $BaCO_3$ [32]. Also, the liquid phases could be formed during the sintering through the formation of melts of Ba–Ti-containing media (interaction of products of raw components). Their melting points may drop significantly in the multi-element compositions in comparison with the binary system $BaO–TiO_2$ [33].

The experimental densities of both SS at the optimal T_{sint} (7.99 g/cm^3 for unmodified ceramics and 7.85 g/cm^3 for modified one) were approximately equal to 95% of the XRD densities (8.26 g/cm^3 and 8.22 g/cm^3). A slight ($<2.4\%$) reduction in ρ_{exp} (to a value of 7.66 g/cm^3) of modified ceramics at a higher temperature (1220 °C) may be a consequence of some coarsening of the microstructure. Thus, the difference between the values of ρ_{exp} of unmodified and modified SS is small ($<4\%$), as is also the case for samples of Ba-containing ceramics sintered at temperatures above 1180 °C [28]. These insignificant variations of ρ_{exp} allow us to compare the microstructures of both ceramic compositions sintered in the same conditions (T_{sint}=1220 °C).

As noted in [17,26,27], the modified-by-barium SS does not contain the ballast pyrochlore phases typical of 'pure' composition, because of the possibility of Zn transition in the four-coordinated state [34,35]. Stabilization of the perovskite structure is associated with a lower electronegativity of the ions Ba^{2+}(115 kcal/g-atom) compared to Pb^{2+}(170 kcal/g-atom) [36] and, as a result, with a decrease in the degree of covalence of the A–O bond and the polarizing action on B-cations [37]. Furthermore, Ba^{2+} ions have the stable octahedral coordination in an oxide. All this contributes to a reduction in the tendency of Zn to have a tetrahedral coordination relative to oxygen, and leads to the stabilization of the perovskite state.

The introduction of barium into the solid solution significantly changed its structural phase state (XRD-data). The quantity of the rhombohedral, Rh, phase decreased drastically (initial SS crystallized with a mixture of tetragonal, T, and Rh phases). In addition, the tetragonal distortion of unit cells decreased c_T/a_T-1, where c_T, a_T, the unit cell parameters, were

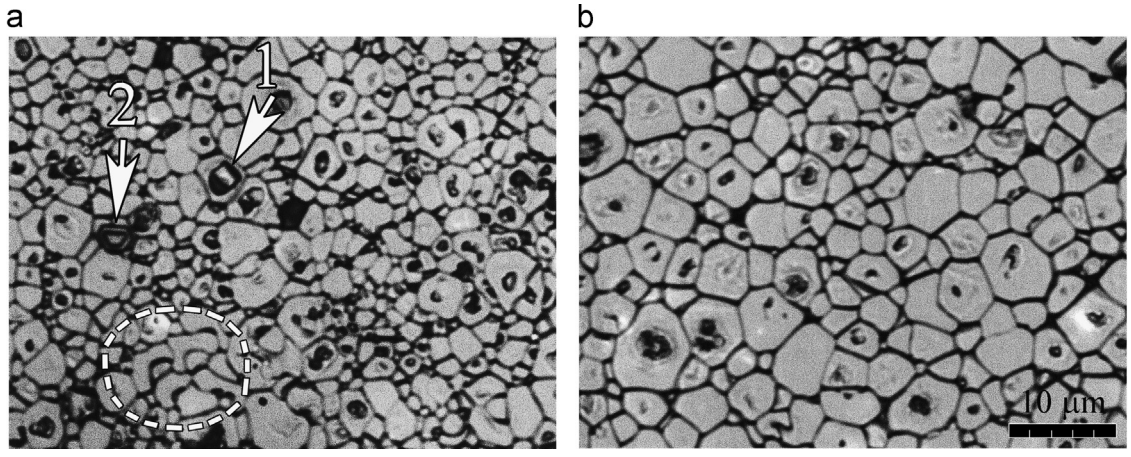

Fig. 1. Microstructure of ceramics (a) without Ba (parameters of thermal etching are T_{et}=1150 °C, τ_{et}=15 s); (b) with Ba (T_{et}=1150 °C, τ_{et}=7 s). Curved crystallites are inside the dashed circle. Arrow #1 indicates the euhedral 'sub-crystallite'. Arrow #2 indicates the euhedral crystallite.