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ABSTRACT

The Pb(Zr$_{0.56}$Ti$_{0.44}$)O$_3$ (PZT) ceramics was subjected to a pressure-induced activation at 320 MPa in a Bridgman anvil, where a load pressure was combined with a shear deformation. The induced changes in the linear and angular parameters of a unit cell, in the ratio of coexisting rhombohedral (*R3m*) and tetragonal (*P4mm*) phases as well as in the dielectric properties were analyzed.

1. Introduction

A wide range of useful physical properties of Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (PZT) ceramics, such as good reproducibility and stability under different temperatures, pressures, humidity as well as resistance to radiation impact, explains popularity of PZT materials as active functional elements or executive mechanisms. The ferroelectrics with the perovskite structure of general formula ABO$_3$, where A stands for Pb, while the B-site cations are Zr^{4+} and Ti^{4+} are of particular interest.

The isovalent metal cation substitution in the BO$_6$ oxygen octahedrons is a classical but not unique method of tuning physical properties of ABO$_3$ perovskites. Pressure-induced activation or mechano-activation was shown to allow for purposeful variation of the physical properties of relaxor ferroelectrics such as PbIn$_{0.5}$Nb$_{0.5}$O$_3$, PbSc$_{0.5}$Ta$_{0.5}$O$_3$ and PbFe$_{0.5}$Nb$_{0.5}$O$_3$ [1,2,16,18]. A correlation between the structural parameters characterizing the real structure of ferroelectric relaxors, and their structurally sensitive properties was revealed. Under strong electric fields and mechanical stresses both the phase composition and the average concentration of coexisting tetragonal (T) and rhombohedral (R) phases in a PZT material will change [3,14]. For example, a certain combination of monoclinic phase with *Cm* symmetry and R-phase with *R3c* symmetry in the PbZr$_{0.54}$Ti$_{0.46}$O$_3$ material was transformed into the combination of

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T-phase with *P4mm* symmetry and increased fraction of R-phase under temperature of 400 K and a pressure of more than 1 GPa [7]. In another case the microstructure and ions displacement in the $PbZr_{0.45}Ti_{0.55}O_3$ material under applied pressures was studied by the Rietveld refinement of T-phase with *P4mm* symmetry [8]. It was also shown that the pressure reduces the phase-transition temperature from segneto- to para-phase. These references provide evidence that pressure is an effective tool for influencing the physical properties of PZT.

The scope of this work is to find a relation between the applied mechanical load (mechano-activation) and physical properties of the $PbZr_{0.56}Ti_{0.44}O_3$ ceramics.

2. Experimental

The PbO, TiO_2 and ZrO_2 metal oxides of "chemically pure" quality were weighted to obtain a final composition of $PbZr_{0.56}Ti_{0.44}O_3$. The metal oxides were thoroughly mixed with alcohol in an agate mortar for two hours. The synthesis was carried out in a closed platinum crucible by a two-stage method, known as "columbite" method. The temperature of the first and second stages was 1150°C and 1250°C, respectively. The duration of each stage was 2 h. The $PbZrO_3$ filling was added to compensate a partial sublimation of lead oxide [2,16]. The product was grinded for 0.5 h, and will be referred to as initial powder.

Equal weight portions (seven in total) of the initial powder were subjected to a mechanical impact load of 320 MPa between the Bridgman anvils, where the lower anvil was rotated 360° counterclockwise. To ensure a quasi-hydrostatic character of the pressure, a metal ring was placed between the anvils, confining the powder. Then, all portions of powder were grinded together in an agate mortar, resulting in so-called mechano-activated powder. The parameter ζ, characterizing a shear deformation, was determined to be equal to 12 from the formula [17]:

$$\zeta = \ln(\upsilon r/d),$$

where υ is the rotation angle, r is the radius of the anvil, d is the thickness of the sample.

The same weight portions of initial powder (the reference sample) and of mechano-activated powder (the activated sample) were pressed into discs. Sintering was performed at 1150°C for 2 h in an atmosphere of $PbZrO_3$. The resulting ceramic discs were with 1 mm in thickness and 10 mm in diameter.

A scanning electron microscope (SEM) Supra 25 (Zeiss) was used to estimate the size of crystallites in powder. X-ray phase analysis was carried out using D2 PHASER (Bruker) diffractometer with CuK_α radiation in Bragg-Brentano geometry. For a full-profile refinement by the Rietveld method, the Powder Cell software package was used [10]. Dielectric measurements were carried out using a computer-connected E7-20 immittance meter (MNIPI, Bielorrusia). Infrared spectra were collected on a FTIR spectrometer FSM-1202 (Infraspec, Russia) with 2 cm^{-1} resolution and by means of the KBr pelleting technique.

3. Results and discussion

The dissipation of mechanical energy supplied to the powder in the Bridgman anvil occurs through various channels, such as heating and dispersion of crystallites, the generation of
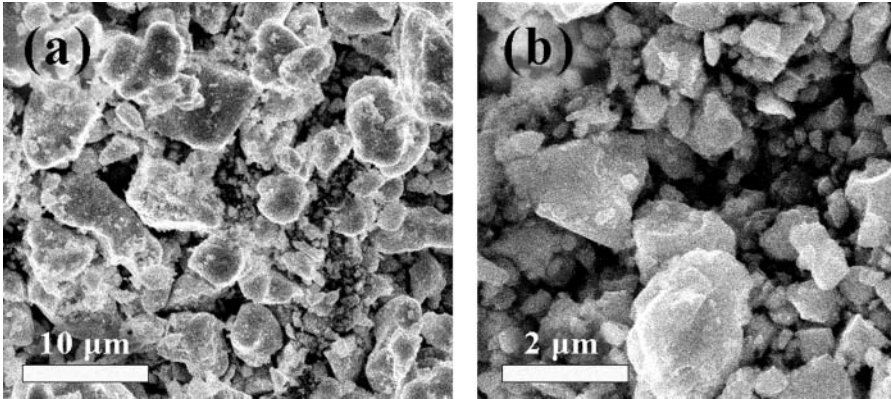
Figure 1. SEM micrograph of the reference (a) and activated (b) samples.

dislocations and point defects and their diffusion. Depending on the applied load, the as-activated material ends up in various metastable states, suggesting different activation energies for the volume diffusion processes during the sintering of ceramics. There are structural differences between them too.

The size distributions of crystallites in compacted powders depend largely on the magnitude of the applied pressure and on the parameter ζ. The particles of the activated sample were found to fall within the range of 0.004-0.95 μm (Fig. 1). The larger particles visible in Fig. 1 are agglomerates consisting of fine particles (smaller than 1 μm). Agglomeration during mechano-activation is a characteristic feature of all piezoelectric materials.

Figure 2 presents the XRD patterns of the reference and the activated samples of $PbZr_{0.56}Ti_{0.44}O_3$ ceramics. Miller's indices of reflexes are shown only for T-phase of the reference sample for the sake of clarity. No monoclinic phase of Cm symmetry [7,12] was observed in this material.
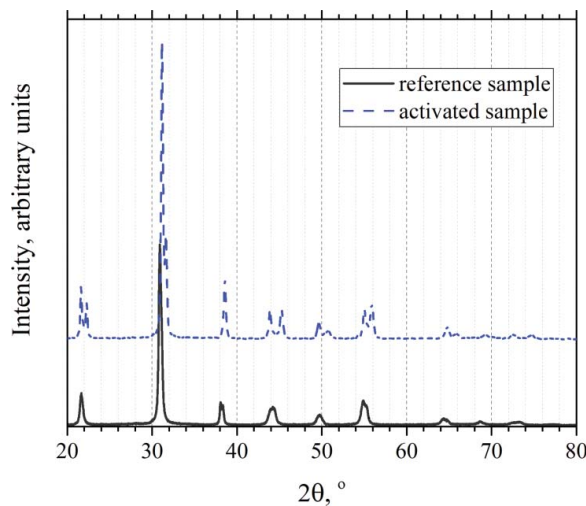

Figure 2. X-ray diffraction patterns of the reference (solid black line) and activated (dashed blue line) samples.

**Table 1.** Linear and angular parameters of the elementary cells of the reference and activated samples.

Sample	P, MPa	a_T, Å	c_T, Å	a_R, Å	α, °	V_T, Å³	V_R, Å³
Reference	0	4.018(7)	4.138(5)	4.064(8)	89.46	66.805	67.121
Activated	320	4.084(8)	4.122(4)	4.082(9)	89.59	68.751	68.017

Considering the morphotropic phase boundary diagram for PZT [5], the $PbZr_{0.56}Ti_{0.44}O_3$ composition is situated in the morphotropic phase transition boundary (MPB) region, where both R- and T-phases coexist. Hence, we used a combined $R3m+P4mm$ symmetry model for the Rietveld refinement of the structure with Pseudo-Voigt 1 profile function. We found that in the activated sample the fraction of R-phase $R3m$ became 0.76 (after mechano-activation) instead that of 0.22 in the reference sample. The values of the profile factor, R_p, were 6 and 6.2 for the reference and activated samples, respectively.

The XRD pattern of the activated sample is characterized by the broadening of the reflexes with a decrement in their intensities. There is no sign of amorphization of the structure after the pressure of 320 MPa. The linear and angular values of the unit cell for both samples are given in Table 1. Table 1 illustrates that the unit cell parameter a of both T- and R-phases, its volume and rhombohedral angle α - all have grown after mechano-activation except some decrease of the linear parameter c of T-phase.

Under applied pressure the temperature in the center of the Bridgman anvil can exceed the Curie temperature. When the pressure is removed from the anvil, the transition to the ferroelectric phase is accompanied by the preservation of a certain concentration of structural defects whose elastic field of deformation prevents the crystallite structure from returning to the initial state. The most sensitive to the applied pressure of 320 MPa was the lattice parameter a of T-phase and the rhombohedral angle α of R-phase.

Infrared spectroscopy (IR) has been employed for decades in studies of ferroelectric phase transitions in perovskites [11]. This vibrational technique was employed to reveal the impact of mechanical activation on the physical properties of the $PbZr_{0.56}Ti_{0.44}O_3$ ceramics. Fig. 4 shows the normalized FTIR spectra of the reference and activated samples in the 450–750 cm^{-1} spectral interval, which is sufficient to describe the vibrational profile of the perovskite unit cell. This range contains the absorbance band of a complex shape composed
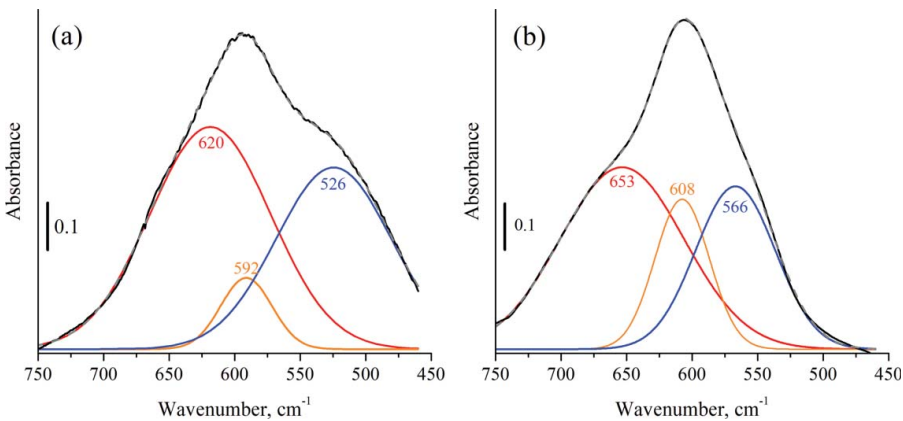
Figure 3. FTIR spectra of the reference (a) and activated (b) samples.
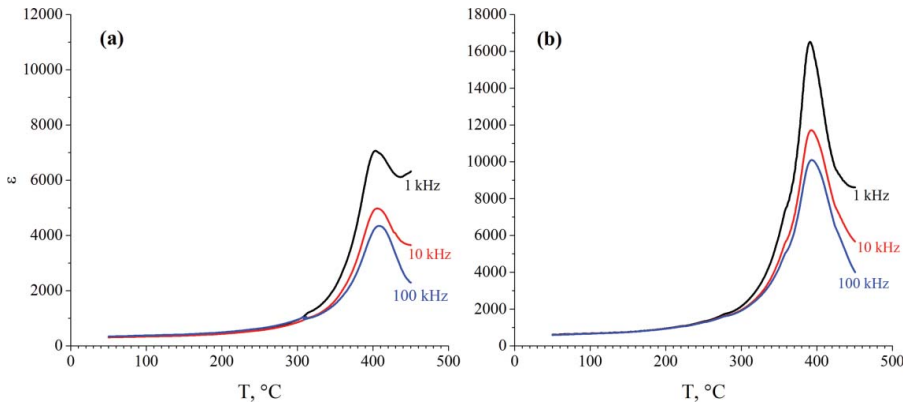
Figure 4. Temperature dependence of dielectric permittivity of the reference (a) and activated (b) samples for different frequencies of the applied electric field.

by the stretching modes of Ti—O и Zr—O bonds in BO_6 octahedra. It is known from the literature [4], that TiO_6 octahedron presents four distinct modes of vibration: ν_1-stretching at a higher frequency and ν_2-torsion, ν_3-bending and ν_4-cation-(TiO_3) vibrations at lower-frequencies. In order to reveal the vibrational components, the experimental profiles were fitted by the last-square method using three Gaussian curves. The fitting results are shown in Fig. 3; the maxima of components are peaking at 653, 608 and 566 cm^{-1} for the activated sample, and they are at 620, 592 and 526 cm^{-1} for the reference one. From their comparison, it follows that all three components for the activated sample are shifted to higher frequencies (blue-shifted) in respect to the reference ones by 33, 16 and 40 cm^{-1}, respectively. Another observation is the relative rise of intensity (two times) of the middle component at 592–608 cm^{-1}.

The assignment of the vibrational components can be made on the basis of what has been published. Both $PbZrO_3$ and $PbTiO_3$ compounds are known to give a couple of bands peaking at 738 and 554 cm^{-1} and 700 and 562 cm^{-1}, respectively [9]. The complex and asymmetric band profiles in Fig. 3 suggest a certain composition of both isolated $PbZrO_3$ and $PbTiO_3$ spectra. Since the ν_2, ν_3 and ν_4 occur below 400 cm^{-1} [13], the observed vibrational components can be attributed to ν_1-stretching modes of Ti–O and Zr–O bonds in the BO_6 octahedron of the ABO_3 structure [19]. It is worth noticing that a double rise of relative intensity of the component at 592–608 cm^{-1} correlates with a triple increase of the fraction with R-phase *R3m* symmetry.

High sensitivity of PZT solid solutions in the MPB region to external impact is due to the fact that the number of possible directions of the spontaneous polarization vector, P_s, are equal to eight for the rhombohedral system and to six for the tetragonal system. In the same region, the coercive field passes through a minimum, and the contribution of the 90- and 71 (109) degree boundaries to the motion of the domain walls is the highest one [15].

It is known, that 90-degree domain walls are characteristic for ferroelectric T-phases. They are always strained. Due to the nonuniform distribution of elastic fields, some macroscopic ceramic samples, like $PbTiO_3$, are getting destroyed spontaneously. Only the 180 and 71 (109) degree walls that are less strained than 90-degree are characteristic for ferroelectrics of R-phase. The homogeneous strain parameter, δ, characterizes a spontaneous polarization. For a tetragonal cell its value, expressed as $\delta = c/a—1$, is about 3.2 times larger for the

reference sample than for the activated one. In case of rhombohedral cells, δ is proportional to $\cos\alpha$ and equals to 0.009 and 0.007 for the reference and activated samples, respectively. The decrease of δ value for the sample after mechano-activation can be explained by a significant prevalence of the volume occupied by the R-phase over the volume of the T-phase in the total macroscopic volume of the sample. Hence, the parameter δ provides a qualitative estimate of phase amount in solid solutions of $Pb(Zr_{1-x}Ti_x)O_3$ in the MPB region.

Activation of $PbZr_{0.56}Ti_{0.44}O_3$ powders at intermediate pressures has shown the existence of the "threshold" pressure of 160 MPa. Above this value, generation of point defects is more likely than dislocations which are prevailing at lower pressures. A detailed analysis of this phenomenon is beyond the scope of the present work. This "threshold" value coincides with the values of 160–240 MPa reported earlier for relaxor lead-containing ferroelectrics [2,16,18]. "Ballistic" diffusion processes in PZT powders induced by a combination of load impact with a shear deformation are accompanied by the formation of micro- and mesoscopically homogeneous regions being different in terms of structural parameters and phase composition. However, for solid solutions of $PbZr_{1-x}Ti_xO_3$ with different phase composition there are differences in the values of electrophysical parameters, as we have seen.

Figure 4 shows the temperature-frequency dependences of the dielectric permittivity of the reference (in the inset) and activated samples. The maximum value, ε_m, of dielectric constant for the activated sample is twice larger than that for the reference sample. Such difference is mostly determined by the volume fraction of the dominant phase and by the porosity of the ceramic. The maximum value of temperature, T_m, at 1 kHz decreases from 403 to 391°C after mechano-activation, while the frequency dispersion of the dielectric permittivity is slightly suppressed, and the blurring of the phase transition decreases. It is worth mentioning here, that the density of the ceramic samples measured by hydrostatic weighing is in average 96% of the theoretical value.

Thus, the experimental results we have obtained as well as the published data [3,14] show that the pressure applied to the solid solutions of PZT from the MPB region leads to a change in the concentrations of coexisting T- and R-phases. In our opinion, such a situation occurs in two cases only.

Let us assume that the increase of the R-phase fraction after mechano-activation of the $PbZr_{0.56}Ti_{0.44}O_3$ powder is due to the "release" of some PbO and TiO_2 oxides which migrate to the crystallite surface under the same stoichiometry conditions, but with other indices of the stoichiometric formula. Then in macroscopic homogeneous volumes of crystallites-domains, the centers of BO_6 octahedrons should be predominantly occupied by Zr ions, whose atomic mass is approximately twice the mass of the Ti atom. In this case, on morphotropic phase boundary diagram for PZT, the mechano-activated compound should be located to the left of $PbZr_{0.56}Ti_{0.44}O_3$. It is well known that for the elements of the same group of the periodic system, such as the Zr and Ti ions, the frequencies of stretching vibrations decrease with the increasing mass of the central ion in the oxygen octahedron [6]. The experimental results of this work show an unambiguous increase in frequencies of stretching vibrations after mechano-activation, which is inconsistent with this assumption.

Another reason for the increase in the R-phase concentration may be the reorientation of the spontaneous polarization vector P_s of a part of the T-phase volume from the [001] direction to the [111] direction of the unit cell under the applied pressure. In

this case, the average concentration of the components in the sample should be preserved, while the observed blue-shift of stretching vibrations may be due to the additional contribution of the defective subsystem of the crystal lattice.

4. Conclusions

Based on the obtained results, it can be concluded that mechano-activation with the Bridgman anvil leads to the nano-structuring of the synthesized $PbZr_{0.56}Ti_{0.44}O_3$ powders and to the generation of structural defects in the form of dislocations and point defects that play an important role in the diffusion processes during sintering of ceramics.

Mechano-activation of the synthesized powder samples alters the defect subsystem of the crystal lattice, which in turn affects the dielectric and vibrational spectra, the structural parameters of the crystal lattice of the coexisting T- and R-phases and their ratio as well. By choosing the loading pressure and the shear strain value, it is possible to purposely tune the physical properties (including the concentration and type of defects) of PZT ceramics.

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References

[1] K. G. Abdulvakhidov, E. N. Ubushaeva, I. V. Mardasova, M. A. Vitchenko, B. K. Abdulvakhidov, V. G. Zaletov, A. A. Amirov, I. K. Kamilov, A. S. Manukyan, P. S. Plyaka, and G. B. Sukharina, Phase transitions, magnetic and dielectric properties of $PbFe_{0.5}Nb_{0.5}O_3$, *Ferroelectr.* **494**, 182–191 (2016).

[2] K. G. Abdulvakhidov, M. A. Vitchenko, I. V. Mardasova, and E. N. Oshaeva, Properties of the ferroelectric ceramics $PbSC_{0.5}Ta_{0.5}O_3$ fabricated from an ultradispersed powder, *Tech. Phys.* **53**, 661–663 (2008).

[3] A. Amin, R. E. Newnham, and L. E. Cross, Effect of elastic boundary-conditions on morphotropic $Pb(Zr,Ti)O_3$ piezoelectrics, *Phys. Rev. B.* **34**, 1595–1598 (1986).

[4] E. B. Araujo, C. A. Guarany, K. Yukimitu, J. C. S. Moraes, and J. A. Eiras, Structural phase transitions of $PbZr_{0.52}Ti_{0.48}O_3$ ceramic: An infrared spectroscopy study, *Ferroelectr.* **337**, 1317–1323 (2006).

[5] J. Bernard, R. William Jr, and J. Hans, *Piezoelectric ceramics* (London and New York, 1971).

[6] J. R. Ferraro, Infrared spectra of inorganic and coordination compounds (Nakamoto, Kazuo), *J. Chem. Educ.* **40**, 501 (1963).

[7] J. Frantti, Y. Fujioka, J. Zhang, S. Wang, S. C. Vogel, R. M. Nieminen, A. M. Asiri, Y. Zhao, and A. Y. Obaid, I. A. Mkhalid, High-pressure neutron study of the morphotropic lead-zirconate-titanate: Phase transitions in a two-phase system, *J. Appl. Phys.* 112 (2012).

[8] J. Frantti, Y. Fujioka, J. Zhang, J. Zhu, S. C. Vogel, and Y. Zhao, Microstrain in tetragonal lead-zirconate-titanate: The effect of pressure on the ionic displacements, *Rev. Sci. Instrum.* 85 (2014).

[9] C. A. Guarany, L. H. Z. Pelaio, E. B. Araujo, K. Yukimitu, J. C. S. Moraes, and J. A. Eiras, Infrared studies of the monoclinic-tetragonal phase transition in $Pb(Zr, Ti)O_3$ ceramics, *J. Phys. Condens. Matter.* **15**, 4851–4857 (2003).

[10] W. Kraus, and G. Nolze, POWDER CELL – A program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns, *J. Appl. Crystallogr.* **29**, 301–303 (1996).

[11] J. T. Last, Infrared-Absorption Studies on Barium Titanate and Related Materials, *Phys. Rev.* **105**, 1740–1750 (1957).

[12] B. Noheda, D. E. Cox, G. Shirane, J. A. Gonzalo, L. E. Cross, and S. E. Park, A monoclinic ferro-electric phase in the $Pb(Zr_{1-x}Ti_x)O_3$ solid solution, *Appl. Phys. Lett.* **74**, 2059–2061 (1999).

[13] C. H. Perry, and B. N. Khanna, G. Rupprecht, Infrared Studies of Perovskite Titanates, *Phys. Rev.* **135**, A408–A412 (1964).

[14] V. A. Saley, Y. A. Ponomaryev, V. V. Klimov, and Y. M. Poplavko, X-ray study of PZT solid solutions in the tetragonal-rhombohedral phase transition composition area, *Ferroelectr.* **22**, 805–807 (2011).

[15] G. Smolenskii, The Physics of Ferroelectric Phenomena, *Leningrad Izdatel Nauka* (1985).

[16] E. N. Ubushaeva, K. G. Abdulvakhidov, I. V. Mardasova, B. K. Abdulvakhidov, M. A. Vitchenko, A. A. Amirov, A. B. Batdalov, and A. G. Gamzatov, Nanostructured multiferroic $PbFe_{0.5}Nb_{0.5}O_3$ and its physical properties, *Tech. Phys.* **55**, 1596–1599 (2010).

[17] R. Valiev, Nanostructuring of metals by severe plastic deformation for advanced properties, *Nature Mater.* **3**, 511–516 (2004).

[18] M. A. Vitchenko, I. V. Mardasova, E. N. Oshaeva, K. G. Abdulvakhidov, and E. Y. Fain, Nanocrystalline $PbIn_{0.5}Nb_{0.5}O_3$ ceramics and its properties, *Tech. Phys. Lett.* **33**, 160–162 (2007).

[19] E. B. Wilson, J. C. Decius, and P. C. Cross, Molecular vibrations: the theory of infrared and Raman vibrational spectra, *Cour. Corp.* (2012).