ISSN 1027-4510, Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques, 2017, Vol. 11, No. 3, pp. 677–679. © Pleiades Publishing, Ltd., 2017.
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Mechanical Activation and Electrophysical Properties of $Pb(Zr_{0.58}Ti_{0.42})O_3$

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Received October 23, 2016

Abstract—The influence of mechanical force action combined with shear deformation implemented via Bridgman anvils on the dielectric properties of synthesized $Pb(Zr_{0.58}Ti_{0.42})O_3$ powder is studied. It is ascertained that the physical properties of sintered ceramics can be controlled over a wide range upon varying the concentration and type of structural defects arising from the mechanical activation of powders.

Keywords: mechanical activation, structural defects, Curie temperature, Curie–Weiss constant

DOI: 10.1134/S1027451017030363

INTRODUCTION

Problems concerning the development of active piezoelectric materials for applied use are associated in one way or another with the optimization of existing technologies, the search for innovative methods, and their adaptation to specific compositions. Despite all discrepancies between techniques for obtaining the materials of active multifunctional components, the final tasks are the reproducibility and high stability of physical properties, as well as the low cost of hardware. In recent years, piezoelectric and ferroelectric materials have been actively prepared using the mechanical activation method, which is most often implemented at the initial stage of the manufacturing process with the help of planetary ball mills. However, in the majority of cases, physical-chemical processes taking place in an activated material and their role in the formation of the physical-chemical properties of piezoelectric ceramics are overlooked.

It is known that, in solid solutions of the $Pb(Zr_{1-x}Ti_x)O_3$ system, their physical properties are very sensitive to changes in both the Pb, Zr, and Ti ion concentrations and spatial meso- and macroscopic inhomogeneities [1, 2].

The goal of this work is to reveal how the concentration of structural defects and their type affect the dielectric properties and microstructure of $Pb(Zr_{0.58}Ti_{0.42})O_3$. Before the sintering of ceramics, the concentration and type of generated structural defects were varied via the intense force action method combined with shear deformations implemented with the help of Bridgman anvils, as in [3–5]. From a functional point of view, powder treatment between Bridgman anvils is practically identical to that in planetary ball mills and the stoichiometry of the treated powders is assumed to remain constant during mechanical activation. Except for grinding of the synthesized powders and the generation of structural defects, other effects caused by the dissipation of external mechanical energy delivered to the powders are not discussed below.

EXPERIMENTAL

The samples were prepared from chemically pure PbO, TiO_2, and ZrO_2. After preliminary 2-h synthesis in a lead-containing atmosphere at a temperature of 1150°C, the strictly dosed $Pb(Zr_{0.58}Ti_{0.42})O_3$ powder portion was placed between Bridgman anvils and subjected to force action with the constant shear strain. The lower anvil was rotated with the specified angular velocity. The applied pressure was varied from 80 to 320 MPa. In all experiments, the parameter characterizing the shear strain was six. As in [6], its value was determined from the formula

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

where υ is the angle of rotation expressed in radians (in this work, $\upsilon = 12$ rad) and r and d are the radius and thickness of the sample, respectively. A similar approach was used to treat seven portions of the powder from which a single sample (~1-mm-thick disk with a diameter of 10 mm) was sintered. The reference and working samples were simultaneously sintered in a closed platinum crucible under identical temperature–time conditions in a PbO atmosphere. The temperature and duration of sintering were $T = 1250$°C and $t = 2$ h, respectively. Upon completion of the synthesis and sintering processes, the phase composition

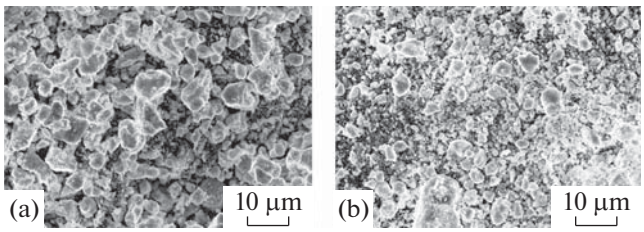

Fig. 1. Micrographs of the (a) reference and (b) working samples of the $Pb(Zr_{0.58}Ti_{0.42})O_3$ powder. The latter was activated at a pressure of 200 MPa.

and structural parameters of each sample were determined using an HZG-4B X-ray diffractometer. After mechanical action, the morphology and microstructure of the powders were studied with the aid of a Supra-25 electron microscope, and the dielectric properties were investigated by means of an E7-20 automated impedance meter. Electrodes were formed from a liquid paste of colloidal silver with a solvent, which was deposited onto the sample surface and annealed at a temperature of 750°C.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 presents micrographs of the reference (unactivated) and working (activated at $P = 200$ MPa) samples of the $Pb(Zr_{0.58}Ti_{0.42})O_3$ powder. Particle-size estimation performed by means of an electron microscope indicates that the particles have a multimodel distribution over sizes ranging from 40 nm to 5 μm. As is seen in Fig. 1, coarse particles arise from the agglomeration of smaller particles electrified due to mechanical activation.

The sizes of the coherent-scattering regions (CSRs) and microstrains $\Delta d/d$ were estimated via X-ray diffraction. The results of estimation demonstrated that the CSR size of $Pb(Zr_{0.58}Ti_{0.42})O_3$ powders decreases to 25 nm and quantities $\Delta d/d$ increase with growing (up to 120 MPa) pressure. A further increase in pressure is accompanied by the nonmonotonic behavior of the CSRs and $\Delta d/d$, which is caused by dynamic recrystallization processes developed upon mechanical activation. It should be noted that, at pressures exceeding 120 MPa, the concentrations of dislocations generated by mechanical activation are stabilized and those of point defects grow. As a result, the integrated intensities decrease and the diffraction profile half-width is enlarged (the lower curve in Fig. 2).

Thus, mechanical activation implemented with the aid of Bridgman anvils makes it possible to create nanostructured powder samples existing in different metastable states. A difference between which signifies different initial conditions for $Pb(Zr_{0.58}Ti_{0.42})O_3$ ceramics sintered under identical temperature–time conditions.

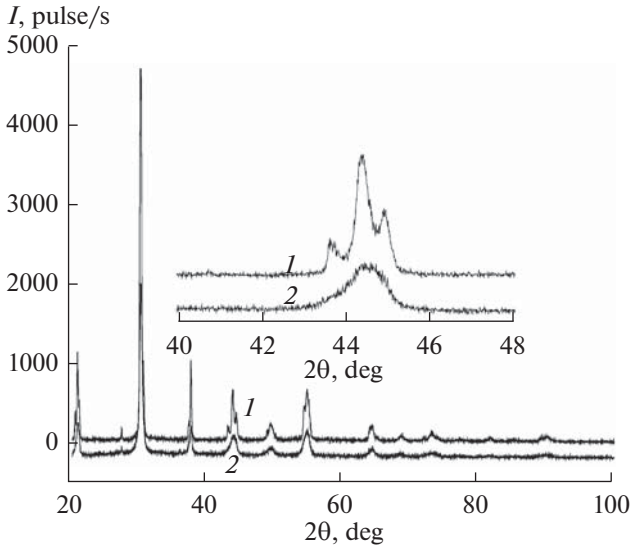

Fig. 2. Diffraction profiles of the (*1*) reference and (*2*) activated (P = 200 MPa) ceramic samples of the $Pb(Zr_{0.58}Ti_{0.42})O_3$ powder.

Figure 3 illustrates variations in the permittivity $\varepsilon/\varepsilon_0$ of the reference and working ceramic samples treated at different pressures. As is seen from Fig. 3, the permittivity $\varepsilon/\varepsilon_0$ of the ceramics obtained via the mechanical activation of synthesized powders is severalfold higher than that of the reference sample. In the solid-phase method, ceramics with large permittivities are generally fabricated using different pore-generating materials and doping agents. In this case, the necessity of their application loses significance.

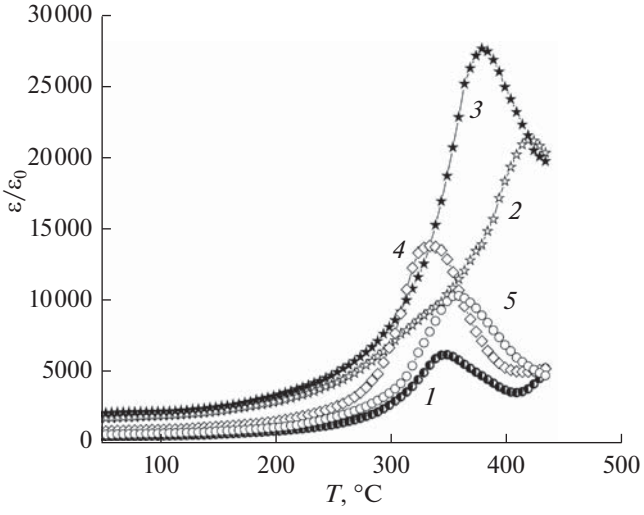

Fig. 3. Variations in the temperature-dependent permittivity of the (*1*) reference and working samples of the $Pb(Zr_{0.58}Ti_{0.42})O_3$ powder. In the latter case, activation was performed at (*2*) 120, (*3*) 160, (*4*) 280, and (*5*) 320 MPa.

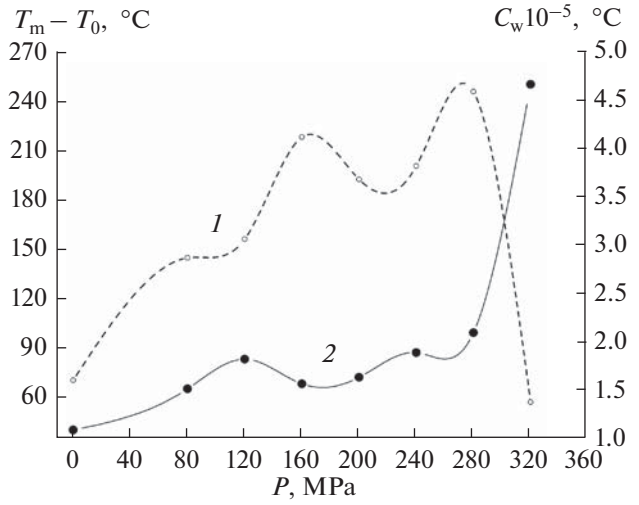

Fig. 4. Variations in (*1*) the Curie–Weiss constant C_w and temperature difference corresponding to the permittivity maximum and (*2*) Curie–Weiss temperature of the $Pb(Zr_{0.58}Ti_{0.42})O_3$ ceramics vs. the applied pressure under mechanical activation.

Let us consider how mechanical activation affects the Curie–Weiss constant C_w and temperature difference $T_m - T_0$, where T_m is the temperature corresponding to the permittivity maximum and T_0 is the Curie–Weiss temperature obtained when $1/\varepsilon(T)$ is extrapolated from the paraelectric region before intersection with the temperature axis. Since the applied pressure varies in steps, C_w and $T_m - T_0$ can be expected to exhibit stepwise steady changes as well. The dependences between these parameters and the applied pressure, which were constructed under the action of mechanical activation, are depicted in Fig. 4. Contrary to expectations, the dependence $C_w(P)$ is nonmonotonic.

The difference $T_m - T_0$ indicates that the phase transition is close to second-kind phase transitions and is zero at the phase transition. As is obvious from Fig. 4, $T_m - T_0$ grows with increasing treatment pressure. The exception is the pressure $P = 160$ MPa at which an insignificant decrease in this difference is observed. However, it can be said that the phase transition in the $Pb(Zr_{0.58}Ti_{0.42})O_3$ ceramics becomes more similar to the second-kind phase transitions upon the termination of mechanical activation.

Thus, in this work, it was demonstrated by the example of $Pb(Zr_{0.58}Ti_{0.42})O_3$ that, due to the mechanical activation of preliminarily synthesized powders, the physical properties of the corresponding ceramic samples can purposefully be controlled over a wide range.

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Translated by S. Rodikov

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