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Effect of intensive mechanical activation on dielectric and magnetic properties of barium titanite

© N.A. Tolstykh[1], E.V. Ievleva[1], L.N. Korotkov[1], Ch. Li[2], A.A. Alexandrov[2], K.G. Abdulvakhidov[2]

[1] Voronezh State Technical University, Voronezh, Russia
[2] Southern Federal University, Rostov-on-Don, Russia
E-mail: l_korotkov@mail.ru

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The effect of mechanical action (The effect of mechanical action force action in a combination of shear strain (FASS)) on the dielectric permittivity (ε) and magnetic response of nanocrystalline barium titanate was studied. A noticeable increase in the saturation magnetization of the material as a result of PPS was found, which is associated with an increase in the dislocation density. Annealing at a temperature of 1300 °C of the original and PPS -treated samples leads to a significant increase in ε. However, the dielectric permittivity of the treated sample is lower in comparison with the initial one, which indicates a higher concentration of lattice defects in it.

Keywords: shear deformations, lattice defects, weak magnetism, dielectric properties.

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Ferroelectrics in the form of single crystals, thin films and ceramics are widely used in microwave devices, acoustoelectronics devices, electronic memory instruments etc. [1,2]. One of the most sought-after ferroelectrics in the practical sense is barium titanate ($BaTiO_3$) and solid solutions on its basis. Above Curie temperature, $T_C \approx 120\,^\circ$C $BaTiO_3$ has a simple cubic lattice $Pm\bar{3}m$. Below T_C it changes to ferroelectric phase with a tetragonal crystal lattice ($P4mm$). With further temperature decrease a transition to orthorhombic phase $Amm2$ is implemented at temperature $T_1 \approx 5\,^\circ$C, and then (around $-90\,^\circ$C) into rhombohedral phase $R3m$ [1].

Physical properties $BaTiO_3$ depend on the technology of its manufacturing. In particular, volume barium titanate is a diamagnetic, but in nanocrystalline state it acquires the properties of weak ferromagnetic [3–5]. Magnetism of ultradisperse is related to oxygen vacancies (V_O), localized mostly on the particle surface. They form complexes $Ti^{3+}-V_O$ and $Ti^{3+}-O$ in particles $BaTiO_3$, where Ti^{3+} ions have a non-integer spin n the state d^1 [3–5].

Noticeable impact on physical properties of materials is provided by force action in a combination of shear strain (FASS) [6,7]. The effect is related to development of mechanical stresses in the specimen, and their relaxation causes various defects: dislocations, plastic deformation and disintegration of the substance particles into multiple small ones.

The purpose of this paper — to experimentally research the impact of shear strains on the structure, dielectric and magnetic properties of barium titanate.

Powder $BaTiO_3$ was synthesized using ceramic technology. The initial components were $BaCO_3$ and TiO_2 of AR grade. Solid-phase synthesis was carried out on air at temperature 1300 °C for 2 h. The synthesized material was exposed to prior four-hour grinding in a planetary mill „DECO-PBM-V-OUL“ using sleeves and balls from zirconium oxide.

Some of the isolation powder was subjected to additional mechanical treatment, combining force action and shear strain, using Bridgman anvils from tungsten carbide at pressure 175 MPa for 40 min.

X-ray diffraction analysis done at room temperature using X-ray diffractometer D2 Phaser (Bruker, Germany) (radiation CuK_α, $K_{\alpha1} = 1.54060$ Å, $K_{\alpha2} = 1.54443$ Å, pitch $\Delta 2\theta = 0.01^\circ$, data collection time $\tau = 0.1$ s), showed that the produced material has tetragonal crystalline lattice ($P4mm$). The size of the coherent scattering area determined using Williamson–Hall method, for the initial specimen and specimens subjected to FASS, was around 27 nm, the parameters of tetragonal cell were $a \approx 3.995$ Å and $c \approx 4.027$ Å.

Measurements of dielectric permittivity (ε) and dielectric loss angle tangent (tgδ) were carried out on specimens in the form of a disc with diameter of 10 mm and thickness of around 0.7 mm in the temperature range 20–500 °C at frequency 10 kHz.

To measure the dependence of magnetization M on magnetization of magnetic field H, around 6 mg powder $BaTiO_3$ were placed on special film PARAFILM „M“ and folded to form a sphere (a ball). The ball was fixed in a cylindrical cuvette, which was screwed to the rod of vibration magnetometer LakeShore 7404. Magnetometer sensitivity was 0.1 μemu, which enabled confident reception of the signal from the specimen.

Measurements were performed at room temperature using vibration magnetometer LakeShore 7404 in the fields with intensity of up to ± 10 kOe.

Magnetization curves $M(H)$ for the studied materials are shown in insert to fig. 1. Dependences $M(H)$ may be presented as superposition of contributions of ferro-

magnetic and diamagnetic components of magnetization. Loops $M(H)$, produced after isolation of the diamagnetic contribution, for all studied specimens are shown in fig. 1. They have the typical form of ferromagnetic hysteresis loops observed previously for barium titanate nanoparticles [3–5].

The produced loops of magnetic hysteresis indicate the defects containing complexes $Ti^{3+}-V_O$ and $Ti^{3+}-O$ both in the initial specimen and specimen subjected to FASS.

Coercive force (H_c) for both specimens is nearly identical (see fig. 1 and table). However, magnetization of saturation (M_s) and residual magnetization (M_r) of barium titanate subjected to FASS, is twice higher that in the initial powder, which indicates higher concentration of „magnetic ions“ therein, provided that according to the X-ray diffraction experiment the average dimensions of the coherent scattering are approximately the same. This allows to assume that in process of FASS the complexes of $Ti^{3+}-V_O$ and $Ti^{3+}-O$ type are formed both on the surface of nanocrystallites and inside them, probably on dislocations [5], the density of which increases substantially during FASS-treatment [6].

For dielectric measurements, sintering was done at temperatures 1000 and 1300 °C for the powder materials in the form of a disc with diameter 10 mm and thickness 0.7 mm. Dielectric permittivity (ε) was measured using an LCR meter E7-20 at frequency 10 kHz in the heating mode in the interval of 20–500 °C.

Dependences $\varepsilon(T)$ have the appearance specific for $BaTiO_3$ (fig. 2). As temperature decreases, quick growth of dielectric permittivity is observed, with the latter reaching the maximum in the near vicinity of T_C, below which in a certain temperature interval the ε collapse is observed down to temperatures close to $T_1 \approx 5$ °C.

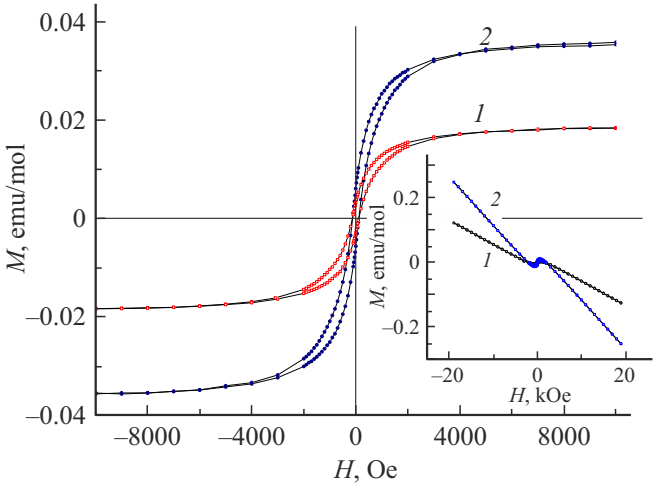


Figure 1. Dependences $M(H)$ for the initial powder $BaTiO_3$ (*1*) and powder subjected to FASS (*2*) after subtracting the diamagnetic response. In insert — full dependences $M(H)$.

Parameters of magnetic hysteresis loops $BaTiO_3$

Sample	H_c, Oe	M_r, emu/mol	M_s, emu/mol
Initial	127.2	0.0032	0.019
Subjected to FASS	122.2	0.006	0.036

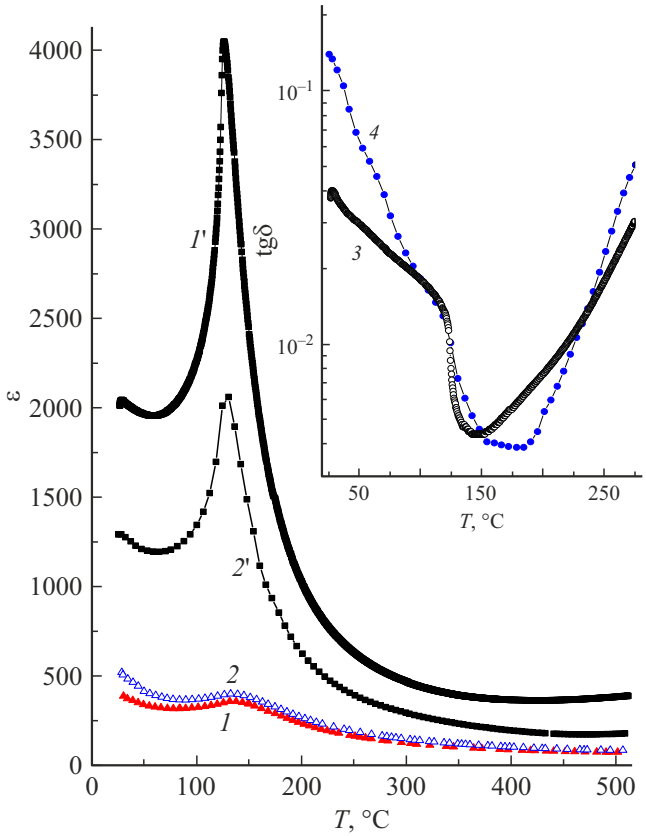


Figure 2. Temperature dependences ε for the initial ceramic specimen $BaTiO_3$ (*1*, *1′*) and ceramic specimen subjected to FASS (*2*, *2′*) sintered at temperatures 1000 (*1*, *2*) and 1300°C (*1′*, *2′*). In insert — temperature dependences tgδ for initial specimen (*3*) and specimen subjected to FASS (*4*) sintered at temperature 1300 °C.

Curves $\varepsilon(T)$, obtained for the specimens sintered at temperature of 1000 °C, match each other to a large extent. Both specimens are characterized by relatively low dielectric permittivity and weak smeared maximum ε in the near vicinity of $T_C \approx 133$ °C. It is natural to relate the comparatively low dielectric permittivity of both specimens to their substantial porosity, and also high defect rate and residual mechanical stresses. The presence of the latter is indicated by substantially smeared maxima ε near T_C, which are somewhat displaced towards high temperatures compared to the ones observed for regular ceramics $BaTiO_3$ [1]. The causes for such displacement have not been found yet, however, one may assume that it may be caused by residual elastic stresses as it happens in epitaxial ferroelectric films [8].

This assumption is supported by the fact that annealing of specimens at 1300 °C causes reduction of Curie temperature to ~ 127 °C. At the same time ε of both materials increases substantially, and a clear peak of ε is formed near T_C.

Dielectric permittivity of the specimen subjected to FASS after annealing at temperature 1300 °C is noticeably lower than in the initial one (compare curves *1′* and *2′* in fig. 2), and dielectric losses in the ferroelectric phase, where they are mostly due to interaction of domain boundaries with the lattice defects [9], are on the contrary higher (insert to fig. 2). This indicates that the specimen subjected to FASS contains higher concentration of defects, which persist even after high-temperature thermal annealing.

It seems that dislocations are such defects, which may be responsible for the increased magnetization of saturation in the specimen subjected to FASS.

Therefore, the experiment showed that both the initial powder of barium titanate and the powder subjected to FASS-treatment have weak magnetism at room temperature. FASS caused noticeable increase in saturation magnetization. With account of the FASS action nature, the assumption was made that increased M_s of $BaTiO_3$ particles is due to the growth of dislocation density therein, where due-to disturbed chemical bonds, one may expect appearance of Ti^{3+} ions with a non-compensated magnetic torque.

It is found that the lattice defects caused by intense shear strain have high resistance to high-temperature thermal annealing, which is reflected in a weaker dielectric response of the treated specimen compared to the initial one after their thermal annealing at temperature 1300 °C.

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Conflict of interest

The authors declare that they have no conflict of interest.

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