Investigation of lead-free thin films based on barium titanate for electrocaloric devices

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Abstract. Lead-free thin films were synthesized by sol-gel for possible use in solid-state coolers. Surface morphology of the layers was obtained by atomic force microscopy (AFM). Electrophysical properties were investigated by impedance spectroscopy.

1. Introduction
Due to the rapidly deteriorating global environment problem of eliminating the use of refrigerants is relevant world over. Devices based on solid-state cooling elements are alternative solution of using compression and evaporative coolers. Using such elements is especially important for miniature devices. Solid-state coolers, which are based on thermoelectric effects, in particular, the electrocaloric are the most perspective for diverting large heat flux from small surfaces of modern devices. Currently, elements which are controlled by an electric field are developed and investigated actively [1].

Electrocaloric effect is manifested in increasing the temperature of the substance when creating therein an electric field E and reduction of the temperature when switching off the field under adiabatic conditions. This effect is strongly pronounced in ferroelectric materials due to the possibility of domain reorientation. Electrical domains have a random direction and the polarization vector of the total sample P is equal to zero when no electric field. If you turn on a constant electric field, the dielectric is polarized, and the dipole moments of molecules or domains are reoriented. Main line of domains appears, entropy decreases and the temperature of the sample increases. When you turn off the external field, the dipoles get random orientation again. Due to this internal energy is reduced and the temperature decrease under adiabatic conditions [2]. It is obvious that high electric field determines maximum effect. These conditions are achieved in thin films easier.

Found that the maximum electrocaloric effect in ferroelectrics observed near their phase transition. Ferroelectric-paraelectric transition does not occur abruptly, but in a certain temperature range to not single crystals. In this case percolation cluster is formed for the ferroelectric phase. Ferroelectric effect is an especially strong upon reaching the percolation threshold [3]. Thus, a material having a phase
transition temperature close to the operating temperature does not require special heating of the active substance.

Currently ferroelectrics with a perovskite structure with a lead content [4-6], known for its toxic effects, are the most commonly used electrocaloric materials. The authors [5] reported about achieving of the giant electrocaloric effect $\Delta T = 12$ K on the films PbZrO$_{0.95}$Ti$_{0.05}$O$_3$ thickness of 350 nm near the phase transition temperature of 242 °C, as well as in films 0.9*PbMg$_{1/3}$Nb$_{2/3}$O$_3$-0.1*PbTiO$_3$ temperature change is $\Delta T = 5$ K at a voltage of 25 V at 260 nm thick films near the phase transition temperature of 60 °C [6]. Therefore, the problem of finding an alternative lead-free materials having the electrocaloric properties is very actual.

Among the promising materials for considered purposes can be distinguished, for example, NH$_4$HSO$_4$ [7]. Another promising material is known ferroelectric material - barium titanate. Currently working on the development of optimal design of cooling elements on the basis of electrocaloric effect are conducted actively [8,9].

2. Purpose

The main purpose of this work was obtaining thin lead-free electrocaloric films. For this aim, the composition of compounds based on barium titanate (Ba$_x$Ca$_{1-x}$)TiO$_3$ and Ba(Sn$_y$Ti$_{1-y}$)O$_3$ in different ratios, known for its ferroelectric properties was selected. Analysis of T-X- diagrams of ternary systems determined the choice of material [10]. Sol-gel method to obtain the investigated structures was chosen because it is relatively economical, affordable for a wide selection of components, precision calculation of the composition, as well as it allows for obtaining enough homogeneous thin films. This method is widely used to produce gas-sensitive layers [11,12], functional transparent, protective and adsorption coatings [13,14], etc.

3. Experiment

As a precursor to obtain the desired material were used barium acetate, calcium acetate, tin acetate and titanium isopropoxide. The dipole structure was formed by using acetyl acetone molecules in combination with titanium isopropoxide. Ethylene glycol and 2-methoxyethanol were used to obtain a specific viscosity and stability of the solution. Sol matured at room temperature. Sol solution with a different maturation time (from 2 to 300 hours) has been applied by the dispenser on glass substrates and annealed after centrifugation at 600 ºC from 30 minutes to 1 hour.

Surface morphology was investigated by atomic force microscopy (AFM) in tapping mode (NTEGRA, NT-MDT, Zelenograd, Russia). Electrophysical properties were obtained using impedancemeter "Z-500 P" (ELINS) in the frequency range from 1 Hz to 500 kHz.

4. Results

Homogeneous by visual inspection, transparent, colorless thin films were obtained in the experiment. Analysis of the morphology of the surface with AFM showed that the film surface formed objects with elliptical shape. Their average diameter is about of 120-150 nm (Figure 1). The sample had a fractal structure with a fractal dimension of 2.50, calculated by triangulation with program Gwyddion. Supposedly, such a structure was formed on the basis polymerization centers of titanium compounds, in the initial stage of forming the sol solution. Perhaps this process step leads to the production dipole structure of the sample, which will determine the electrical properties of thin films.
Study electrical properties of the films of the composition \((\text{Ba}_{x}\text{Ca}_{1-x})\text{TiO}_3\) and \(\text{Ba}(\text{Sn}_{y}\text{Ti}_{1-y})\text{O}_3\) confirmed the existence of dipolar relaxation processes (Fig. 2). They are manifested on the graph of the complex part of impedance of the structure \(\text{Im}\) from its real part \(\text{Re}\), at high frequencies (section II), which can be approximated by a circle segment, unlike section I, can be approximated by a straight line.

The changing in the character of these curves was revealed at different temperatures. At temperatures down to 220 °C character of the curve determined by the influence constant phase element (CPE), while at temperatures above 250 °C distributed capacitance affects on the dependence stronger. Moreover phase transition point of the compound in question lies in the same temperature range.
Fig. 3. Dependence of the complex part of impedance of the structure $\text{Im}$ from its real part $\text{Re}$ at different temperatures.

For samples with different relative content of Ba and Ca was revealed (Fig. 4) that at higher relative content of Ba (composition number 2) the nature of the curves changes at lower temperatures. Probably because that barium compounds are more active than calcium compounds. Thus, addition of calcium compounds improves the thermal stability properties of the films, but based on its physical characteristics, increases the Curie temperature and reduces the dielectric constant of the composition. Knowing that the influence of CPE is defined by ions and the diffusion coefficient, it is logical to assume that the calcium compounds bind free ions in the material.

5. Conclusion.
The study revealed that the morphology of investigated films had a fractal structure consisting of objects in the form of an ellipse having a linear dimension of about 120-150nm.

Availability dipole relaxation processes required to use this material in electrocaloric devices was discovered during the investigation of the electrophysical properties of the material by impedance spectroscopy.

It was found that the introduction of calcium compounds stabilizes the electrical properties of the investigated compositions with increasing temperature.
Fig. 4. Dependence of the complex part of impedance of the structure \( \text{Im} \) from its real part \( \text{Re} \) samples composition (\( \text{Ba}_x \text{Ca}_{1-x} \text{TiO}_3 \) and \( \text{Ba}(\text{Sn}_y \text{Ti}_{1-y})\text{O}_3 \)) with different relative proportions \( \text{Ba} \) and \( \text{Ca} \) (1: \( x = 0.2 \); 2: \( x = 0.3 \)) at different temperatures: a) \( T = 310^\circ \text{C} \), b) \( T = 250^\circ \text{C} \), c) \( T = 220^\circ \text{C} \).
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