Sol-gel synthesis of Pb-free thin-film nanomaterials for electrocaloric devices

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Abstract. Lead-free Ba$_x$Ca$_{1-x}$TiO$_3$, BaSn$_y$Ti$_{1-y}$O$_3$ and composite Ba$_x$Ca$_{1-x}$TiO$_3$ / BaSn$_y$Ti$_{1-y}$O$_3$ thin films were synthesized by a sol-gel technique. A large electrocaloric effect is expected in the obtained films. Atomic force microscopy studies revealed that the thin films consists of ellipsoidal objects enclosed by an amorphous matrix. The electrical properties of synthesized nanomaterials were investigated by impedance spectroscopy.

1. Introduction.
Recently the development of nanoscale electronic devices has posed a problem of heat removal from very small surface area. There is a great interest in the design of miniature solid-state cooling systems having low power consumption and maximum temperature drop. To date, devices based on thermoelectric effects, in particular, the electrocaloric [1-3] are the most promising for the study and creation.

The electrocaloric effect is described as a reversible temperature change of the material under applied electric field at adiabatic conditions. The physical reason for the effect is the reorientation of the electric dipoles in the presence of an electric field and a decrease in entropy of the sample and increasing its temperature under adiabatic conditions. When removing the electric field dipoles acquire random orientation, entropy increases and the temperature decreases [2]. Thus, the presence of electric dipoles in the material is a prerequisite for obtaining the electrocaloric effect.

Perovskite-like lead-containing materials are generally used to produce cooling devices based on electrocaloric effect [1]. Lead is a heavy metal, well known to be extremely toxic to all life forms.

It is known that electrocaloric effect in ferroelectrics is strong near the Curie temperature. Therefore, the development of materials with phase transition at operating temperature is an important task. Table 1 shows phase transition temperatures and maximum values of temperature change in some materials under adiabatic conditions driven by the change in the electric field. [2].

Another problem in the production of miniature cooling devices is to achieve high electric field intensity while minimizing the applied voltage. This effect can be realized by the reduction in thickness of the active material. Thin-film nanomaterials best meet these requirements. Sol-gel process is one of the most suitable techniques to obtain such materials because of its economical efficiency, ease equipment, the ability to easily control the composition of resulting products and a wide range of precursors [4-6]. Sol-gel process has already become a well-established technique for the synthesis of functional layers used as gas sensors, inorganic adsorbents, catalysts and catalyst supports, synthetic zeolites, ceramics with special thermal, optical, magnetic and electrical properties, glass ceramics, transparent conductive coatings etc. [7-9].
Table 1. Maximum values of electrocaloric cooling (ΔT) and respective electric field changes (ΔE). T_{ph} - phase transition temperatures.

| Material | T_{ph}, K | ΔT, K | ΔE, V/cm |
|----------|-----------|-------|----------|
| Pb_{0.99}Nb_{0.02} [(ZrSn_{0.27})_{0.93}Ti_{0.07}]_{0.98}O_3 (ceramics, 250 nm) | 420 | 2 | 20 |
| PbZr_{0.95}Ti_{0.05}O_3 (film, 300 nm) | 500 | 12 | 480 |
| PbSc_{1/2}Ta_{1/2}O_3 | 291 | 1.8 | 25 |
| PbSc_{1/2}Ta_{1/2}O_3 (16-layers ceramic film, 16×100 μm) | 273 | 2.4 | 138 |
| 0.85PbMg_{1/3}Nb_{2/3}O_3−0.15PbTiO_3 (ceramics, 100 μm) | 291 | 1.6 | 16 |
| 0.9PbMg_{1/3}Nb_{2/3}O_3−0.1PbTiO_3 (film, 260 nm) | 350 | 5 | 895 |

The objective of this work was to develop an alternative lead-free material having large electrocaloric effect. The composites of Ba_{x}Ca_{(1−x)}TiO_3 and BaSn_{y}Ti_{(1−y)}O_3 at various ratios near the phase transition point were chosen for the study. The development of such complex materials requires the strict control of synthesis parameters having considerable influence on the structure and properties of composites. The choice of these composite materials is determined by their physical-chemical properties such as phase transition temperature, crystal lattice structure, the possibility to obtain electrocaloric effect [3].

2. Experiment.
Barium acetate, calcium acetate monohydrate, tin acetate and titanium isopropoxide were used as precursors in the synthesis process. Titanium isopropoxide was chosen as a gelation agent. Ethylene glycol monomethyl ether and acetic acid were used as a solvent and a reaction activator. Additional reagents provided the complete dissolution, the desired viscosity of solutions and structure of thin films. The solutions with different precursor concentrations were prepared and cast onto glass and silicon substrates. The resulting layers were spin-coated (3000 rpm) during 15 s and then annealed at different temperatures in the range 100 °C-600 °C.

The surface morphology of thin-film nanomaterials was studied by tapping mode atomic force microscopy (AFM) using a scanning probe nanolaboratory NTegra Therma (NT-MDT, Russia). Composite thin films were characterized by impedance spectroscopy (Z-500P, Elins, Russia). Measurements were done in the frequency range from 1 Hz to 500 MHz at 25 °C.

3. Results and Discussion.
AFM analysis showed that sphere-like aggregates form as a result of nucleofilic growth during sol ageing. Processes of aggregation and growth depend on precursor ratio of solutions. The grains have an ellipsoidal shape. The estimated sizes of the long and short diameters of grains are 160 nm and 130 nm, respectively (Fig. 1a, 1b). From a macroscopic point of view, the films are dense and uniform. It was observed that the layer completely covers the surface substrates. Thus, the films have good adhesion to glass and silicon which are commonly used to produce electronic devices.

Fractal dimension of the films was calculated by decomposition method using a free program Gwyddion for characterization of the surface. Value of fractal dimension was 2.57, 2.51, and 2.56, for Figures 1a, 1b, 1c respectively.
The typical impedance spectrum of composite thin film presented as Nyquist plot is shown in fig. 4. Two regions corresponding to different relaxation processes are observed in Nyquist plot.

Impedance spectrum in the low-frequency range (region I – from 1 Hz to 10 kHz) can be approximated by a straight line and can be fitted to an equivalent circuit containing constant phase element (CPE). The impedance of a constant phase element is described by the equation [13]:

$$Z = 1 / A(\omega)^n,$$

where $A$ is a frequency-independent constant, $n$ is an exponential index.
In the high frequency range (region II – from 10 kHz to 500 kHz) can be approximated by a circle segment with the center below the x axis and equivalent circuit of composite film consists of a CPE connected in parallel with a resistor. The changing view of the curve indicates that electrical barriers are exist in films. They are responsible an additional mechanism of dielectric polarization and the presence of polar regions [13]. In high-frequency range the processes of dipole relaxation and elastic dipole polarization contribute to electric properties [14, 15]. Thus, dipole structures that can cause electrocaloric effect are observed in the composite films.

Our further research will be aimed at experimental confirmation of electrocaloric effects in the obtained composite films.

4. Conclusion

In this study sol-gel technique was developed to synthesize lead-free thin-films of the composition $\text{Ba}_x\text{Ca}_{1-x}\text{TiO}_3 / \text{BaSn}_y\text{Ti}_{1-y}\text{O}_3$. A high electrocaloric effect is expected in such structures. It was found that the structure consists of sphere-like aggregates in an amorphous matrix. It was also shown that the processes of dipole relaxation and elastic dipole polarization occur in the obtained films that make them promising for electrocaloric devices.

5. References

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