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INFLUENCE OF Sn AND Pb IONS SUBSTITUTIONS ON DIELECTRIC PROPERTIES OF BARIUM TITANATE

The results of the microstructural and dielectric measurements of $(Ba_{1-x}Pb_x)(Ti_{1-x}Sn_x)O_3$ (BPTS*x*) (x = 0, 0.05, 0.10, 0.30) polycrystalline samples are presented. The samples were obtained by means of a high temperature synthesis and their expected stoichiometry was confirmed by energy dispersive spectroscopy (EDS) measurements. The dielectric properties of BPTS*x* were studied with the use of broadband dielectric spectroscopy. The measurements over a wide range of temperature (from 140 K to 600 K) and frequency (from 0.1 Hz to 10 MHz) were performed. The experimental results indicate an influence of Pb ions in a sublattice A and Sn ions in a sublattice B substitution on paraelectric – ferroelectric phase transition parameters. Diffused phase transitions from a paraelectric to ferroelectric state (for x = 0.10 and x = 0.30) were observed. From the electric modulus measurements in the frequency domain the relaxation times and the activation energy were determined.

*Keyword*s: barium titanate ceramics, dielectric properties, phase transition

1. Introduction

Barium titanate $BaTiO_3$ (BT) and lead titanate $PbTiO_3$ (PT) are the most common perovskite ferroelectric materials. The biggest advantage of these materials is a wide possibility of modification their physical properties by ferroactive and nonferoroactive ions substitutions in the perovskite A and/or B sublattices [1-6]. The popularity of solid solutions based on BT and PT are growing due to their good parameters, which gives a possibility of their wide technical applications, especially in electronics and optoelectronics. The strong modifications of the physical properties were obtained by a substitution of Sn ions in a sublattice B in BT [7-9]. The previous publications, concerning the investigation of physical properties of perovskite structure solutions with Sn ions substitutions, point out a possibility of their applications in actuators, capacitors, small sized devices, and multilayer ceramic capacitors [10-12]. An influence of Pb ions substitutions in a sublattice A and Sn ions in a sublattice B on the dielectric properties and the phase transition characters in barium titanate was investigated. The aim of these studies was to obtain a functional material of appropriate microstructure and diffusion of paraelectric-ferroelectric phase transition. This material should have stable electrical characteristics over a wide temperature range.

2. Experimental

The polycrystalline samples of $(Ba_{1-x}Pb_x)(Ti_{1-x}Sn_x)O_3$ for x = 0, 0.05, 0.10 and 0.30 (abbreviated to BPTS5, BPTS10 and BPTS30) were obtained by mean of a high temperature synthesis (1300 K) and sintering (1700 K). Barium oxalate, lead oxalate, titanium oxide and tin oxide were used as starting materials. A quality of the obtained material was checked by means of a scanning electron microscope (SEM), and the designed composition was confirmed by an EDS spectroscopy method.

Dielectric measurements were carried out with the use of a broadband dielectric spectroscopy at the temperature ranging from 140 K to 600 K and at frequency ranging from 0.1 Hz to 10 MHz. The Quatro Cryosystem temperature controller together with an Alpha-AN High Performance Frequency Analyzer system WinDETA Novocontrol software was used.

3. Results and discussion

The images of the fractures of the investigated samples at 1000× magnification are shown in Fig. 1. The surface of the fracture goes along the grains as well as along the boundaries between the grains. In the grains a tendency to the formation of crystalline structure is observed. A good homogeneity of the microstructures and a small degree of porosity were noted. The pores had an irregular shape without curvings and narrowings. The growth terraces of grains are clearly seen. They indicate that the growth of grains proceeds according to a layer mechanism with a screw dislocations [13].

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a) b)

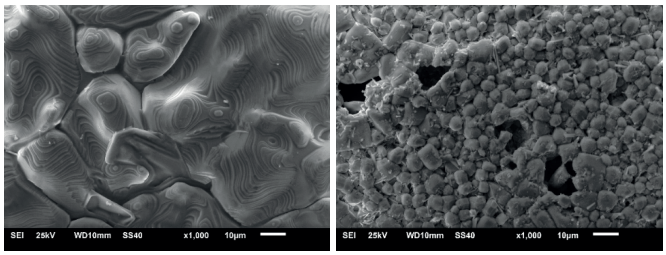

Fig. 1. SEM micrograph for BT (*a*) and BPTS30 (*b*) samples

The temperature dependences of the real part of the dielectric permittivity (ε') are shown in Fig. 2. The Pb and Sn ions substitutions in BPTS*x* solid solution cause the paraelectric-ferroelectric (PE-FE) phase transition temperature decrease.

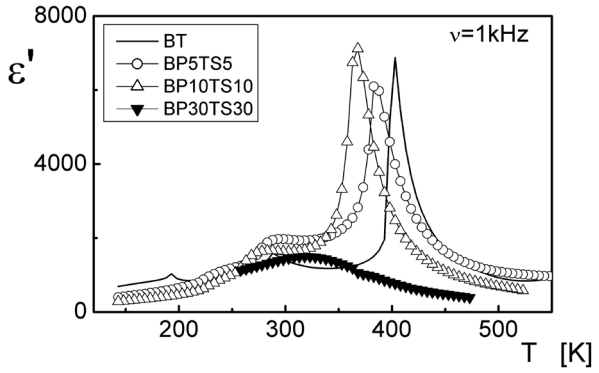

Fig. 2 Temperature dependence of the real part of dielectric permittivity ε' for BT, BPTS5, BPTS10 and BPTS30 samples

One can see a slightly diffused PE-FE phase transitions for x = 0, 0.05 and 0.10. For BPTS30 sample (Fig. 3.) all structural transitions "overlap" to form a strong diffuse of PE-FE phase transition [14].

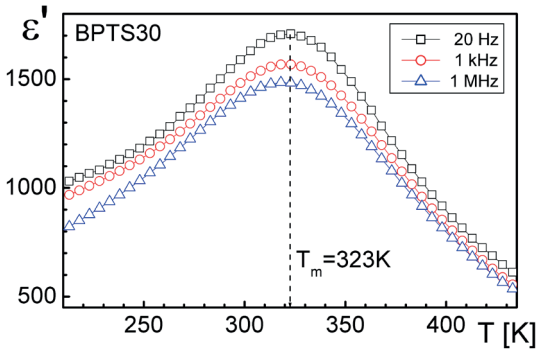

Fig. 3. Temperature dependence of the real part of dielectric permittivity ε' for BPTS30 at the frequency of 20 Hz, 1 kHz and 1 MHz

The temperature T_m = 323 K corresponding to the maximum of the ε'_m depending on the electric field frequency for this sample was constant. The increase of Pb and Sn ions concentration (up to x = 0.30) in BPTSx solid solution did not change the nature of the phase transition from a diffuse transition to a transition of relaxor type. The characteristic feature of relaxor behavior is the dependence of the temperature T_m on electric field frequency and the shift of ε'_m to higher temperatures with increasing frequency. The (Eq.1) describes ferroelectric materials with diffuse phase transition:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m} + A(T - T_m)^{\gamma} \qquad (1)$$

The γ parameter values obtained from the Curie-Weiss law are presented in Fig. 4. The value close to 1 (BPTS5) indicates a very weak diffusion of the PE-FE phase transition. For BPTS30 sample the value of γ is 2.00. This indicates an increase in the diffusion of the phase transition with the increasing Pb and Sn ions concentration.

The electric modulus M^* and complex permittivity ε^* are related by the following formula: $M^*=1/\varepsilon^*=M'+iM''$. The dependence of imaginary part of the electric modulus (M'') on frequency at selected temperature for BPTS5 sample is presented in Fig. 5

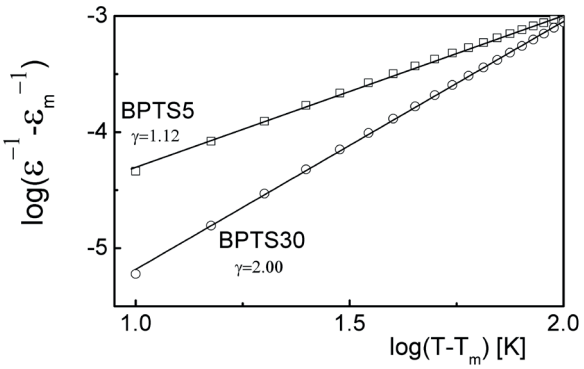

Fig. 4. The dependences of $\log\left(\varepsilon^{-1} - \varepsilon_m^{-1}\right)$ vs. $\log\left(T - T_m\right)$ at 1 MHz for BPTS5 and BPTS30 samples

The increase in temperature cause the increase of the M'' peak values and the shift of the curves towards higher frequencies. On the basis of the data presented in Fig. 5 the relaxations times were calculated using the $\omega\tau = 2\pi\nu_m\tau = 1$ equation, where ν_m – value of frequency for the M'' peaks at fixed temperature.

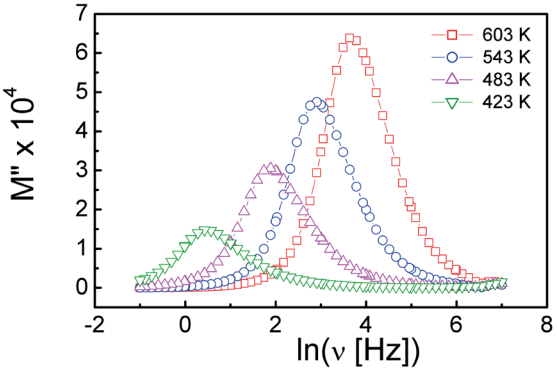

Fig. 5 The imaginary part of electric modulus M'' as a function of frequency for different temperatures for BPTS5 sample

The collected results are presented in the form of $\tau(1000/T)$ plots (Fig. 6).The thermal activation energies in the paraelectric phase for BPTS5 and BPTS10 samples are similar. The increase in the concentration of Pb and Sn ions in the BPTSx samples causes the increase of the relaxation time which may be related to transport of electric charge both in grains and grain boundaries.

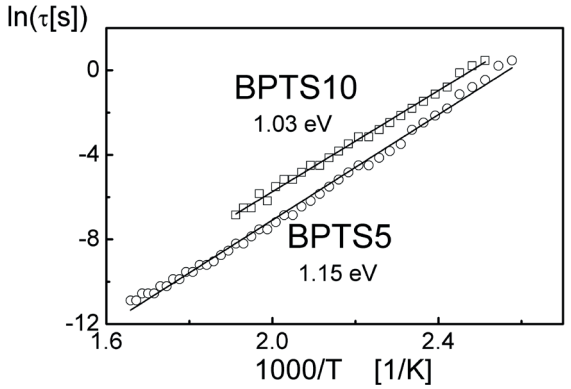

Fig. 6 The relaxation times as a function of 1000/*T* for BPTS5 and BPTS10 samples

4. Conclusions

The simultaneous substitutions of Pb ions (sublattice A) and Sn ions (sublattice B) cause both a decrease in the temperature of paraelectric-ferroelectric phase transition and the increase in its diffusion. The change of nature of PE-FE phase transition generally depends on the cationic sublattice in which ions are substituted and on these ions concentration. The temperature dependences of the electric permittivity for BPTSx samples (for $x = 0$ and $x = 0.05$) indicate the occurrence of slightly diffused PE-FE phase transition whereas for $x = 0.10$ and $x = 0.30$ DPT are observed . The strong phase transition diffusion for BPTS30 sample in the range of temperatures close to room temperature makes this material very attractive for various technical applications. The imaginary part of electric modulus measurements made it possible to estimate the relaxation times τ and the thermal activation energy of the paraelectric phase. The values of these energies are typical for electron transport in semiconducting materials.

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