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Study of the phase transition in polycrystalline $(Ba_{0.90}Pb_{0.10})(Ti_{0.90}Sn_{0.10})O_3$

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Polycrystalline sample of $(Ba_{0.90}Pb_{0.10})(Ti_{0.90}Sn_{0.10})O_3$ was obtained by means of a conventional ceramic technology. The dielectric measurements were performed depending on temperature and frequency of electric measuring field. The character of the phase transitions of $(Ba_{0.90}Pb_{0.10})(Ti_{0.90}Sn_{0.10})O_3$ ceramics strongly depends on the presence of Pb in the sample. The obtained results pointed out the diffused character of phase transition. The temperature dependence of the dielectric properties showed that the phase transition from the paraelectric phase to ferroelectric one takes place at the same temperature (T_{m} = 367 K). It does not depend on the frequency of the measuring electric field. A change of the value of the parameter γ takes place in the paraelectric phase.

Key words: *dielectric properties, phase transition, polar regions, ceramics*

PACS: *77.84.-s, 81.05.Je, 77.80.B, 77.90.+k*

1. Introduction

Among a number of well-known ferroelectric materials, barium titanate BT (ABO_3-type compounds with perovskite structure) and some of its solid solutions are the most interesting due to their excellent dielectric properties. $BaTiO_3$ in its pure form does not have ideal properties for industrial applications. The one that has such properties is a barium lead stannate titanate solid solution. The Pb-substitution at Ba-site is an effective way to improve dielectric properties. A great attention is focussed on $Ba(Ti_{1-x}Sn_x)O_3$ and $(Ba_{1-x}Pb_x)TiO_3$ solid solutions, which are the most useful material for many applications and have been extensively investigated, particularly their phase transitions [1–8]. It was found that barium stannate titanate ceramics $Ba(Ti_{1-x}Sn_x)O_3$ exhibits many exceptional material properties and has a large range of applications as a ceramic capacitor, PTCR thermistor, piezoelectric transducers and actuators [9, 10]. The paper presents the results of measurements of dielectric properties of $(Ba_{0.90}Pb_{0.10})(Ti_{0.90}Sn_{0.10})O_3$ ceramics.

2. Experimental

The $(Ba_{0.90}Pb_{0.10})(Ti_{0.90}Sn_{0.10})O_3$ (abbreviated to BP10TS10) polycrystalline sample was prepared by a solid state synthesis. The sample was synthesized from analytically pure: BaC_2O_4, PbC_2O_4, TiO_2 and SnO_2. The raw materials in an appropriate molar ratio were ground and mixed in ether, then dried and cold pressed. After the calcination at the temperature of 1250 K and after re-milling, the BP10TS10 sample was sintered at the temperature of 1600 K for 2 hours. A sample in the shape of disc-pellets sized 10 mm (diameter) and 1.50 mm thick was painted with silver electrodes.

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The measurements were performed automatically using a LCR Agilent 4284A meter and a temperature control system Quatro Krio 4.0 with and BDS 1100 cryostat. The research was done in the frequency range from 20 Hz to 1 MHz under cooling process at rate 2 K/min.

3. Results and discussion

The real part of the electric permittivity dependence on temperature $\varepsilon'(T)$ for BP10TS10 sample is presented in figure 1. For all frequencies of the electric field, the maximum value of the electric permittivity ε' decreased, and the temperature of the maximum (T_m) did not change $T_\mathrm{m} = 367$ K.

The broadening of the temperature range of the phase transition was also observed, which is connected with the degree of freezing clusters during the transition from paraelectric to ferroelectric phase in the cooling process. This behavior indicates a diffusive nature of the phase transition.

Figure 2 shows the temperature dependence of dielectric loss $\tan\delta$ during the cooling process. The dielectric loss tangent exhibits a local anomaly in the vicinity of the temperature of 367 K, which corresponds to the temperature T_m. The analysis of figure 2 shows that the local maxima appear for all frequencies tested.

The effective polarization changes, thermally induced and described as the ε' fast increase can be also described by means of an electric modulus M' ($M^* = M' + M''$) dependence on temperature T. The modulus M' is sensitive to the small changes of local polarization.

The minima position in the $M'(T)$ curve can be interpreted as temperature points representing transitions from one phase to another.

Figure 3 presents the temperature dependence of the real part of electric modulus (M'). In the paraelectric phase, the nonlinear dependence was observed, which indicates a diffusive nature of paraelectric-ferroelectric (PE-FE) phase transition.

One of the special properties of ferroelectric ceramics is the diffuseness of the phase transition (diffuse phase transition — DPT). It means that the phase transition does not take place in the whole specimen volume at a strictly determined Curie temperature T_C (point phase transition), but in a certain temperature zone (the so-called the Curie zone). Two structural phases, one with lower and one with higher symmetry, coexist in this zone, namely ferroelectric (low temperature phase) and paraelectric (high temperature phase). The phenomenon of the diffuseness of the ferroelectric phase transition has been discovered in both ceramic materials and crystals and a lot of papers are devoted to this phenomenon including the physical nature, causes, criteria and the evaluation of the degree of diffuseness [11–16].

The following formula describes ferroelectric materials with diffusive phase transition (DPT):

$$\varepsilon^{-1} = \varepsilon_\mathrm{m}^{-1} + A(T - T_\mathrm{m})^{\gamma},$$

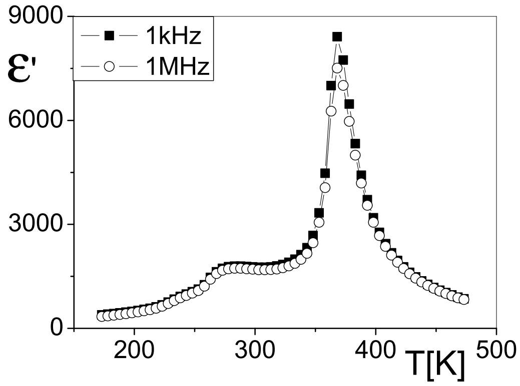

Figure 1. The dependence of the real part of electric permittivity ε' on temperature for the BP10TS10 sample.

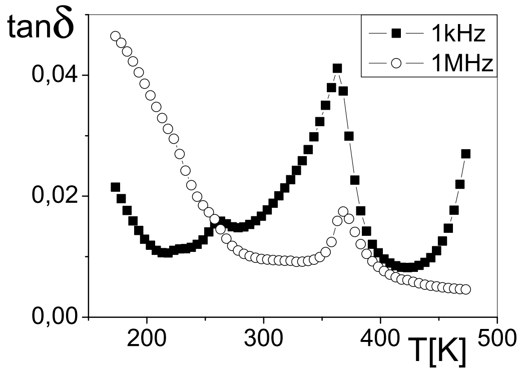

Figure 2. The dependence of the dielectric loss ($\tan\delta$) on temperature for the BP10TS10.

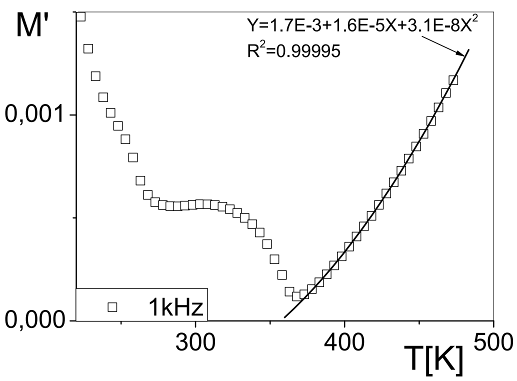

Figure 3. The dependence of the real part of electric modulus (M') on temperature for the BP10TS10 sample.

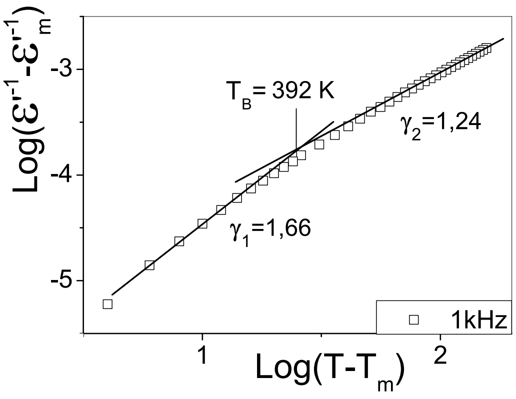

Figure 4. The dependence of $\log(\varepsilon^{-1} - \varepsilon_{\mathrm{m}}^{-1})$ on $\log(T - T_{\mathrm{m}})$ for the BP10TS10 sample.

where: ε_{m} is the maximum value of electric permittivity; T_{m} is the temperature value at ε_{m}; A and γ are constants for the chosen frequency. In DPT, the value of γ is close to 2 while for a sharp transition, this value is close to 1. The values that follow from the above formula are presented in figure 4 as a dependence of $\log(\varepsilon^{-1} - \varepsilon_{\mathrm{m}}^{-1})$ on $\log(T - T_{\mathrm{m}})$.

The analysis of the obtained results indicates two temperature regions with values γ_1 and γ_2. The values of these parameters are 1.66 and 1.24, respectively. The change of the value of γ takes place in the region of the Burns temperature $T_{\mathrm{B}} = 392$ K. This temperature is about 25 K higher than the temperature of phase transition T_{m}. The value of γ_1 is close to 2 and suggests the behaviour of ferroelectrics with DPT. The value of γ_2 is close to unity and indicates a typical behavior for ferroelectrics with a sharp phase transition at temperatures $T > T_{\mathrm{B}}$.

Figure 5 presents the temperature changes of the real part of electric conductivity σ'. The $(\ln\sigma')(1/T)$ curve shows that the local maximum of a.c. conductivity occurs at the temperature T_{m}. Moreover, in the phase transition region, a PTCR effect is observed.

The low values of phase angle ϕ in the investigated temperature range (figure 6) suggest the existence of polar regions [17, 18], which contribute to the dipolar polarization [19].

The changes of cluster configuration leads to their liability and sensitivity to the applied electric field. An increase of the value of the phase angle at higher temperatures testifies to freeing the charges [6, 10, 18] and leads to an increase of electric conductivity.

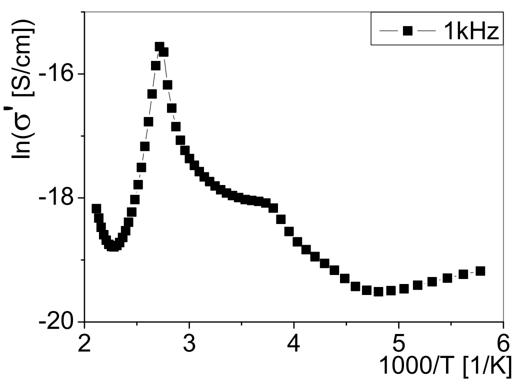

Figure 5. The ac-conductivity (σ') dependence on reciprocal temperature ($1000/T$) for the BP10TS10 sample.

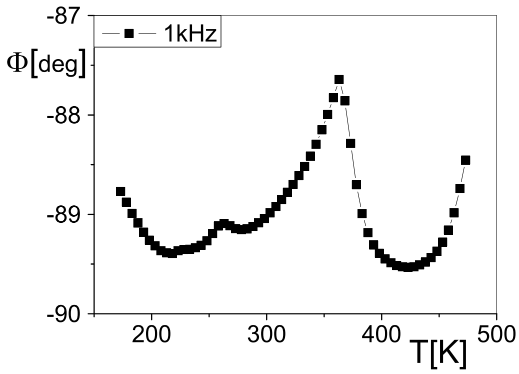

Figure 6. The dependence of phase angle (ϕ) on temperature for the BP10TS10 sample.

4. Conclusions

The dielectric studies show that the value of electric permittivity of $(Ba_{0.90}Pb_{0.10})(Ti_{0.90}Sn_{0.10})O_3$ decreases with an increase of frequency in the whole investigated temperature range. The maximum of electric permittivity ε' is observed in the cooling process at a temperature of 367 K (T_m). It was confirmed that the T_m does not depend on the frequency of the measuring electric field. The obtained dielectric data suggest a diffuse character of the phase transition. The substitution of lead for barium in the amount of 10% in the BP10TS10 ceramics compensates the effect of tin on the temperature of the PE-FE phase transition and provides high values of electric permittivity ε'. The occurrence of a Pb positional fluctuation in the paraelectric phase is typically considered as a formation of polar regions. The substitution of Pb for Ba causes a local distortion of the lattice structure, resulting in a change of the electrostatic forces (the long and short range). The change of the value of the parameter γ in the paraelectric phase suggests a typical behavior for ferroelectrics with a sharp phase transition at temperatures $T > T_B$. The effect of differences in the values of ionic radii and the deformation of a unit cell are reduced at these temperatures.

Due to the existence of a PTCR effect in this compound, it can be used as a material for thermistors. The obtained material is expected to be a promising candidate for electronic ceramics.

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Вивчення фазового переходу в полікристалітах $(Ba_{0.90}Pb_{0.10})(Ti_{0.90}Sn_{0.10})O_3$

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Полікристалічний зразок $(Ba_{0.90}Pb_{0.10})(Ti_{0.90}Sn_{0.10})O_3$ отриманий за допомогою стандартної керамічної технології. Діелектричні вимірювання здійснені в залежності від температури і частоти електричного вимірюючого поля. Характер фазових переходів керамік $(Ba_{0.90}Pb_{0.10})(Ti_{0.90}Sn_{0.10})O_3$ сильно залежить від присутності Pb в зразку. Отримані результати вказують на дифузійний характер фазового переходу. Температурна залежність діелектричних властивостей показала, що фазовий перехід з параелектричної до сегнетоелектричної фази має місце при тій самій температурі ($T_{\mathrm{m}} = 367$ K). Вона не залежить від частоти вимірюючого електричного поля. Зміна значення параметра γ має місце в параелектричній фазі.

Ключові слова: *діелектричні властивості, фазовий перехід, полярні області, кераміка*