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STABILIZATION OF THE FERROELECTRIC PHASE OF POTASSIUM NITRATE IN COMPOSITES CONTAINING METALLIC MICROPARTICLES

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Abstract. In the paper, the temperature dependences of the differential thermal analysis signal, permittivity, and amplitude of the third harmonic of the $(KNO_3)_{1-x}/Sn_x$ composites have been studied. It was shown that the temperature of the α → β phase transition decreased by 2 − 3 K in the potassium nitrates being parts of the composites, and the temperature of the γ → α phase transition decreased up to 360 K. This result can be explained within the framework of the Landau − Ginzburg theory, taking into account the shielding of potassium nitrate particles by tin metal particles.

Keywords: ferroelectric, composite, permittivity, phase transition

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СТАБИЛИЗАЦИЯ СЕГНЕТОЭЛЕКТРИЧЕСКОЙ ФАЗЫ НИТРАТА КАЛИЯ В КОМПОЗИТАХ, СОДЕРЖАЩИХ МЕТАЛЛИЧЕСКИЕ МИКРОЧАСТИЦЫ

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Аннотация. Исследованы температурные зависимости сигнала дифференциального термического анализа, диэлектрической проницаемости и амплитуды третьей гармоники композитов $(KNO_3)_{1-x}/Sn_x$. Показано, что у нитрата калия в этих соединениях происходит понижение температуры фазового перехода α → β на 3 − 2 K, а температура фазового перехода γ → α понижается вплоть до 360 K. Полученный результат можно объяснить в рамках теории Ландау − Гинзбурга с учетом экранирования частиц нитрата калия металлическими частицами олова.

Ключевые слова: сегнетоэлектрик, композит, диэлектрическая проницаемость, фазовый переход

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Introduction

Ferroelectrics are the focus of much attention as materials for producing ultra-high density non-volatile memory, due to high values of the dielectric constant, their capability to change the polarization direction and store energy [1]. Research efforts are currently concentrated both on synthesizing new ferroelectric compounds [2] and improving the polar properties of existing materials. One of the approaches to modifying the ferroelectric properties of substances is producing composites based on them [3–5]. Ferroelectric composites can have different structures (depending on the nature and compatibility of components), formed in the polar matrix by different particles: polar, non-polar, metal, etc.

A promising ferroelectric for applications in microelectronic devices is potassium nitrate Kno_3, since it has a sufficiently high value of spontaneous polarization $P_s \approx 10$ μC/cm²[6]. However, potassium nitrate has several drawbacks, limiting its applications for these purposes: it does not have spontaneous polarization at room temperature, and the polar phase of this compound is stable only in a narrow temperature range, under cooling from 397 to ~373 K [6]. Numerous studies have been dedicated to attempts to expand the temperature range where the ferroelectric phase of KNO_3 exists to room temperature [7–10]. Thin films [7], composites [8] and nanocomposites [9,10] were prepared from potassium nitrate. An expansion of the domain where the polar phase exists in KNO_3 was detected in all of these studies.

This paper reports on the study of thermal and dielectric properties of $(KNO_3)_{1-x}/Sn_x$ composites ($x = 0$, 0.10 and 0.20), obtained upon mixing of potassium nitrate powder and tin microbeads with a size of 20–38 μm.

Samples and experimental procedure

Potassium nitrate KNO_3 is in paraelectric state under standard conditions and has the space group *Pmcn* [6]. This phase is customarily denoted by α. As potassium nitrate is heated to 401 K, a structural phase transition occurs to another, paraelectric β-phase, which has the $R\bar{3}m$ structure. Upon subsequent cooling from 453 K, phase I is transformed into an intermediate, ferroelectric γ-phase with the three-dimensional $R\bar{3}m$ symmetry, and, finally, this γ-phase is transformed into the α-phase near 373K. Spontaneous polarization P_s of the γ-phase is approximately 1–2 μC/cm² at 393 K [6]. It was established in [11] that the temperature range for stability of the polar state in potassium nitrate depends on the thermal history and cooling rate.

The $(KNO_3)_{1-x}/Sn_x$ $(KNO_3)_{1-x}/Sn_x$ composites were prepared from chemically pure KNO_3 and Sn microbeads 20–38 μm in size. Potassium nitrate powder was mixed with Sn microbeads indifferent ratios (x=0.1 and 0.2 (x is the volume fraction)) in an agate mortar for 10minutes. Next, the samples were pressed from the obtained powder into disks with a thickness of 1 mm and a radius of 5 mm under 7500 kg/cm². Fig. 1 shows a micrograph of the sample prepared from a mixture of potassium nitrate powder and tin microbeads with a volume fraction of $x = 0.2$.

Indium-gallium paste was applied to the samples as electrodes to measure the electrophysical characteristics.

The temperature dependences of dielectric permittivity ε′ were obtained with an E7-25 meter. Nonlinear dielectric measurements of $(KNO_3)_{1-x}/Sn_x$ composites were carried out with the setup described in [12]. The electric field strength in the sample was about 100 V/mm during the temperature measurements of the coefficient $\gamma_{3\omega} = U_{3\omega}/U_{1\omega}$. The temperature was determined with an accuracy up to 0.1 K using a Chromel/Alumel thermocouple and a TS-6621 thermometer.

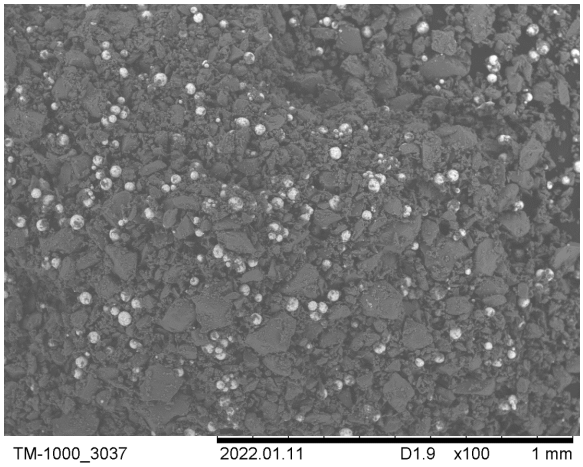

Fig. 1. SEM micrograph of $(KNO_3)_{0.8}/Sn_{0.2}$ mixture

Differential thermal analysis (DTA) was conducted for the$((KNO_3)_{1-x}/Sn_x$ samples using a Linseis STA PT 1600 simultaneous thermal analyzer (Linseis, USA), enabling combined gravimetry and DTA.

Measurements of the quantities ε' and $\gamma_{3\omega}$ were carried out in the temperature range from 300 to 453 K at a rate of 2 K/min. The maximum heating temperature of 453 K is chosen because the ferroelectric phase is not formed in bulk potassium nitrate heated to lower temperatures.

Experimental results

Fig. 2 shows the $\varepsilon'(T)$ dependences for $(KNO_3)_{1-x}/Sn_x$ (x = 0, 0.10, 0.20) composites obtained under heating and cooling. A sharp increase in the $\varepsilon'(T)$ dependence is observed in pure KNO_3 (x = 0) under heating to 401–410 K, induced by the $\alpha \rightarrow \beta$ phase transition. An additional step is detected in the curve upon cooling, suggesting that an intermediate ferroelectric γ-phase emerges [6].

The $\varepsilon'(T)$ dependences for $(KNO_3)_{1-x}/Sn_x$ (x = 0.10, 0.20) composites are strongly smeared (see Fig. 2). The$\alpha \rightarrow \beta$ phase transition between 1 and 2 K is the same as the phase transition in pure potassium nitrate. Upon cooling, the $\varepsilon'(T)$ curve obtained during heating starts coinciding with the corresponding curve obtained during cooling at lower temperatures than for pure potassium nitrate. This indirectly points to a decrease in the temperature of the $\gamma \rightarrow \alpha$ structural transition. Aside from this, the values of dielectric permittivity ε' increase with increasing volume fraction of tin microparticles.

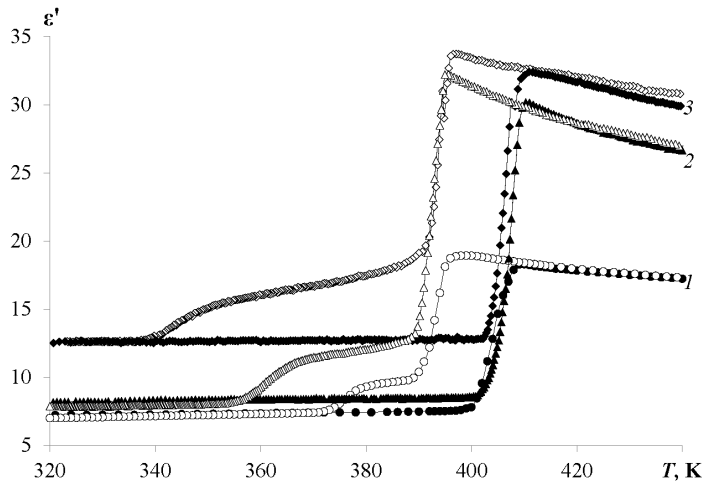

Fig. 2. Temperature dependences of $\varepsilon'(T)$ for the $(KNO_3)_{1-x}/Sn_x$ composite for different values of x: 0 (*1*), 0.1 (*2*), 0.2 (*3*); shaded symbols correspond to heating, empty symbols to cooling

According to DTA for pure KNO_3 (Fig. 3), one phase transition is observed in the heating mode: β → α around 407 K. Two phase transitions detected during cooling: the first one, α → γ, is observed at about 394 K, and the second one, γ → β, at about 371 K, which corresponds to the data known from the literature [6].

Measurements of the DTA signal in$(KNO_3)_{1-x}/Sn_x$ composites (see Fig. 3) indicate the presence of one phase transition during heating at 406 and 405 K for $x = 0.10$ and 0.20 respectively. The temperatures of the α → γ transition during cooling are 392 and 391 K, and temperatures of the γ → β transition are 368 and 361 K for $x = 0.10$ and 0.20, respectively.

To determine the boundaries within which the ferroelectric phase exists in $(KNO_3)_{1-x}/Sn_x$ ($x = 0$, 0.10, 0.20) samples, we examined the temperature dependence of the third harmonic coefficient $\gamma_{3\omega}$. An increase in the third harmonic coefficient $\gamma_{3\omega}$ was observed under cooling for $(KNO_3)_{1-x}/Sn_x$ samples in the temperature ranges of 397–373 K, 394–362 K and 394–353 K (Fig. 4).

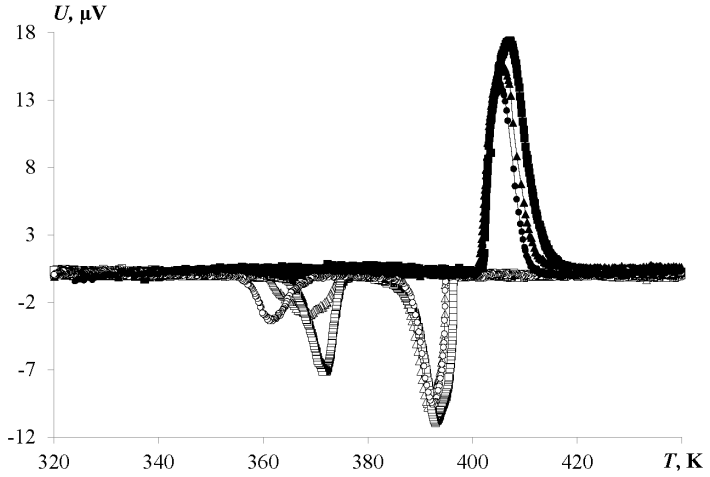

Fig. 3. Temperature dependences of DTA signal for $(KNO_3)_{1-x}/Sn_x$ composite for $x = 0$ (■), 0.1 (▲) and 0.2 (●); shaded symbols correspond to heating, empty symbols to cooling

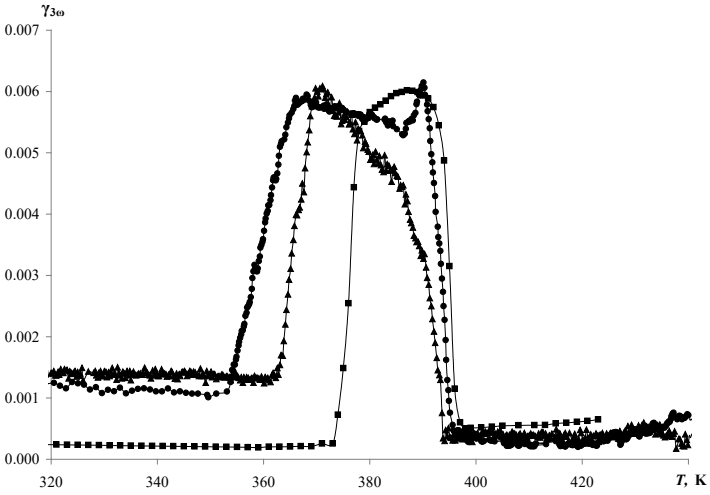

Fig. 4. Temperature dependences of $\gamma_{3\omega}$ for the $(KNO_3)_{1-x}/Sn_x$ composite for $x = 0$ (■), 0.1 (▲) and 0.2 (●); shaded symbols correspond to heating, empty symbols to cooling

Results and discussion

To interpret the results obtained, in particular, the decrease in the Curie temperature of potassium nitrate, which is part of the $(KNO_3)_{1-x}/Sn_x$ composite, let us consider an array of particles located at a certain distance from each other. We write the free energy F of the composite as the sum of the energy of KNO_3 particles and the interaction energy between KNO_3 and Sn particles:

$$F = \sum_i \left(F_{0i} + \frac{1}{2}\alpha P_i^2 + \frac{1}{4}\beta P_i^4 + \frac{1}{2}\delta(\nabla P_i)^2) \right) dv_i + \sum_i \int_{S_i} \Delta F_{S_i} dS_i, \quad (1)$$

where P_i is the polarization of KNO_3 particles, which is a function of temperature and coordinates; α, β, δ are the decomposition coefficients, generally dependent on temperature; v_i, S_i are the volume and surface areas of the ith particle, respectively; ΔF_{Si} is the surface free energy.

Integration of surface free energy over the area S_i takes the form

$$\sum_i \int_{S_i} \Delta F_{S_i} dS_i = \int_{S_i} \sigma_i dS_i + \int_{S_i} \varphi_i dS_i + \int_{S_i} \mu_i dN_i,$$

where σ_i is the surface tension, φ_i is the electrical potential, δ_i is the surface charge density, μ_i is the chemical potential, N_i is the number of particles.

The first term in expression (1) takes into account the so-called baric effect. It can manifest as either an increase or a decrease in the temperature of the structural transition, depending on the sign of the baric coefficient and the ratio of thermal expansion coefficients characterizing the composite components. The second term accounts for the energy from shielding of KNO_3 particles by Sn metal particles. The third term accounts for the energy of the electric field resulting from different electron work functions from KNO_3 and from Sn metal particles.

The phase boundaries in$(KNO_3)_{1-x}/Sn_x$ have a large surface, making a substantial contribution to the composite energy and to a decrease in the effective field of KNO_3particles. This can lead to a change in the Curie temperature and spontaneous polarization. According to Landau–Ginsburg theory, the change in the Curie temperature accounting for ΔF_s is expressed as

$$\tilde{T}_C = T_C - \frac{1}{\alpha_0} \int_{AS} \Delta F_{S_i} dS.$$

The greatest contribution to the temperature shift of the ferroelectric phase transition can be made by shielding fields, inducing a rearrangement in the domain structure and production of oppositely oriented domains.

As established in [13, 14], the presence of free charge carriers in ferroelectrics tends tomodify the dielectric properties, Curie temperature, spontaneous polarization, etc. It was reported in [14] that the additional energy generated by excitation of non-equilibrium charge carriers leads to a decrease in the temperature of ferroelectric phase transition by ΔT_s:

$$\Delta T_C = \Delta E_g Cn/\pi P_s^2,$$

where ΔE_g is the variation in the bandgap width upon a first-order phase transition, is the Curie–Weiss constant.

Conclusion

We can conclude from analysis of dielectric measurements and differential thermal analysis that a decrease by 2–3 K is observed in the temperature of the $\alpha \rightarrow \beta$ phase transition in $(KNO_3)_{1-x}/Sn_x$ composites, while the temperature of the phase transition $\gamma \rightarrow \alpha$ decreases up to 360 K. The result can be explained within the Landau-Ginsburg theory, taking into account the shielding of potassium nitrate particles by tin metal particles.

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