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## PHASE TRANSITIONS IN COMPOSITES BASED ON DIISOPROPYLAMMONIUM CHLORIDE AND LEAD TITANATE

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The paper presents the results of studies in the dielectric properties of  $(\text{DIPAC})_{1-x}/(\text{PbTiO}_3)_x$  composites with the  $x$  volume fraction of lead titanate in composite from 0.10 to 0.40. It has been shown that the addition of lead titanate to diisopropylammonium chloride leads to an increase in the dielectric constant and the appearance of additional phase transitions during heating and cooling. The appearance of a new phase transition was explained in the framework of the Landau–Ginzburg theory, taking into account the dipole-dipole interaction between the components.

**Keywords:** ferroelectric composite, phase transition, dielectric constant, lead titanate, diisopropylammonium chloride

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## ФАЗОВЫЕ ПЕРЕХОДЫ В КОМПОЗИТАХ НА ОСНОВЕ ХЛОРИДА ДИИЗОПРОПИЛАММОНИЯ И ТИТАНАТА СВИНЦА

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В работе представлены результаты исследований диэлектрических свойств композитов  $(\text{DIPAC})_{1-x}/(\text{PbTiO}_3)_x$  с объемной долей  $x$  титаната свинца в композите от 0,10 до 0,40. Показано, что добавка титаната свинца к хлориду диизопропиламмония приводит к увеличению диэлектрической проницаемости и возникновению дополнительного фазового перехода при нагреве и охлаждении. Появление нового фазового перехода объясняется в рамках теории Ландау–Гинзбурга с учетом диполь-дипольного взаимодействия между компонентами.

**Ключевые слова:** сегнетоэлектрический композит, фазовый переход, диэлектрическая проницаемость, титанат свинца, хлорид диизопропиламмония

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## Introduction

Ferroelectrics are multifunctional materials with vast potential for practical applications in various devices, such as nonlinear capacitors, piezoelectric, pyroelectric, and electro-optical devices. Spontaneous polarization switching by an applied electric field makes it possible to use these materials in data storage devices.

Recently, there has been a great focus on novel organic ferroelectrics. For example, diisopropylammonium chloride ( $C_6H_{16}NCl$ , DIPAC), with spontaneous polarization  $P_s \approx 8.9 \mu\text{C}/\text{cm}^2$  and the Curie temperature  $T_c^s = 440 \text{ K}$  [2], was discovered in 2006 [1]. New crystals were obtained several years later by replacing chlorine with bromine and iodine (characterized by larger ionic radii): diisopropylammonium bromide ( $C_6H_{16}NBr$ , DIPAB) with the Curie temperature  $T_c^s = 426 \text{ K}$  and spontaneous polarization  $P_s \approx 23 \mu\text{C}/\text{cm}^2$  [3], as well as diisopropylammonium iodide ( $C_6H_{16}NI$ , DIPAI) with the parameters  $T_c^s = 378 \text{ K}$ ,  $P_s \approx 5.17 \mu\text{C}/\text{cm}^2$  [4].

In particular, DIPAB has a spontaneous polarization value close to that in barium titanate, a high Curie temperature, and exhibits good piezoelectric response. These attributes make ferroelectrics of the diisopropylammonium group an alternative to perovskite-type ferroelectrics. This is the reason for the growing interest in studies of these materials [2–6].

Furthermore, the structures incorporating ferroelectric composites based on such materials may have unusual properties uncharacteristic for homogeneous substances.

The dielectric properties of diisopropylammonium chloride (DIPAC) nanoparticles embedded in opal and MCM-41 silica matrices were considered in [7], where it was found that embedding such a compound into the opal pores shifts the phase transition temperature of the composite towards low temperatures and increases its expansion coefficient compared to the bulk sample. In addition, the thermal hysteresis of the phase transition increases in the opal nanopores. No anomalies of the dielectric constant related to the ferroelectric transition were observed for DIPAC embedded into MCM-41 molecular sieves because this compound is amorphous.

Ref. [8] reports on the studies of linear and nonlinear dielectric properties, accompanied by calorimetric measurements, for a ferroelectric composite

$(\text{DIPAB})_{1-x}/(\text{PbTiO}_3)_x$  with the volume fraction of lead titanate particles  $x = 0.1, 0.2$  and  $0.3$ . It was established that adding lead titanate particles to diisopropylammonium bromide leads to a change in the sequence of structural phase transitions, an increase in the effective dielectric constant and dielectric loss tangent ( $\text{tg}\delta$ ) of the composite. Two phases are observed in  $C_6H_{16}NBr$  in the temperature range from  $423$  to  $411 \text{ K}$  (the ferroelectric phase  $P2_1$  and the non-ferroelectric one  $P2_12_12_1$ ); the ratio between the phases depends on the fraction of lead titanate particles in the composite.

The goal of this study consists in establishing the effect of lead titanate particles on the properties of diisopropylammonium chloride in the  $(\text{DIPAC})_{1-x}/(\text{PbTiO}_3)_x$  composite.

## Samples and experimental procedure

Diisopropylammonium chloride was obtained by reacting diisopropylamine with a 30% aqueous solution of HCl followed by recrystallization from methyl alcohol. According to X-ray spectroscopy data, the obtained diisopropylammonium chloride was in the polar phase  $P2_1$  at room temperature, which corresponds to ICDD card 00-009-0589. A non-polar crystal structure is observed in DIPAC at temperatures above  $T_c \approx 440 \text{ K}$ ; it belongs to space group  $2/m$ . The phase transition in DIPAC is classified as a first-order transition because there is a thermal hysteresis of about  $4 \text{ K}$ .

Lead titanate is a classical perovskite-type ferroelectric with the Curie temperature  $T_c = 763 \text{ K}$ .  $\text{PbTiO}_3$  is in a tetragonal ferroelectric phase at room temperature, with  $P_s \approx 60 \mu\text{C}/\text{cm}^2$  [9].

Diisopropylammonium chloride powder with an average particle size of about  $10 \mu\text{m}$  and lead titanate powder with an average particle size of about  $1 \mu\text{m}$  were used to prepare the  $(\text{DIPAC})_{1-x}/(\text{PbTiO}_3)_x$  samples. The  $\text{PbTiO}_3$  content was varied from  $x = 0.10$  to  $0.40$  ( $x$  is the volume fraction of lead titanate). Samples for measurement were prepared by thorough mixing, followed by molding under a pressure of about  $10^4 \text{ kg}/\text{cm}^2$  into disks  $10 \text{ mm}$  in diameter and  $1.5 \text{ mm}$  thick. Silver electrodes were deposited on the surface of the samples to conduct dielectric measurements. An electron micrograph of the surface of a composite sample without electrodes is shown in Fig. 1.

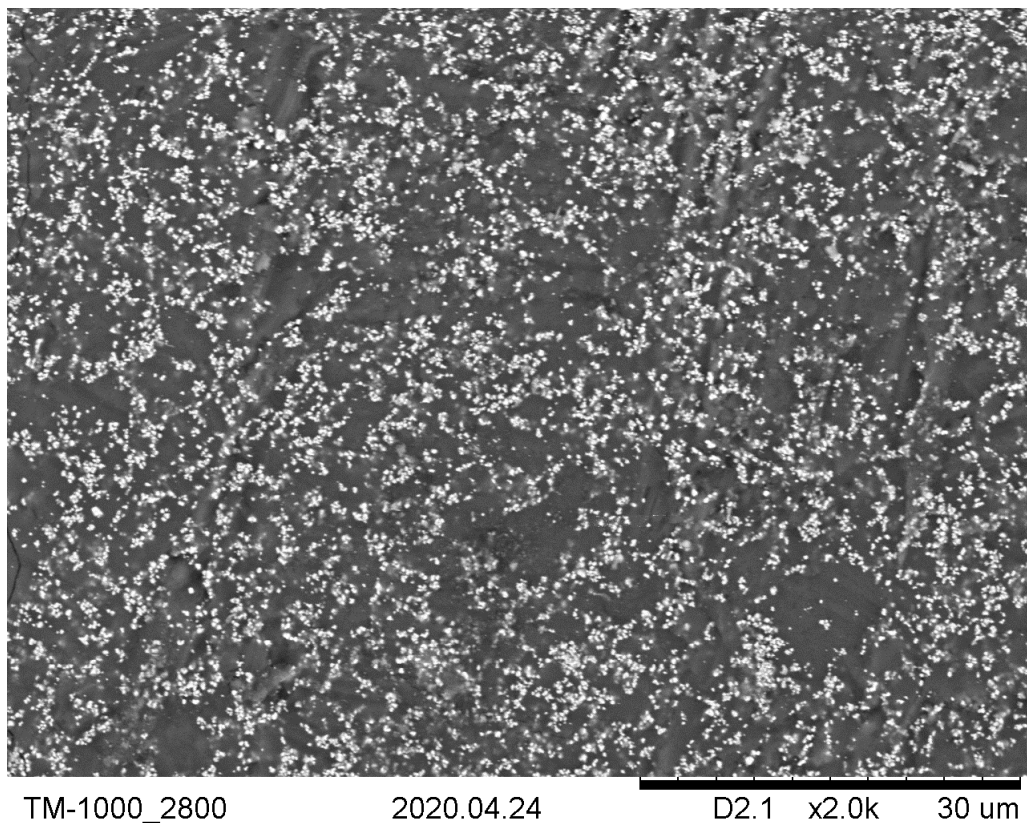


Fig. 1. Electron micrograph for surface of  $(\text{DIPAC})_{0.90}/(\text{PbTiO}_3)_{0.10}$  composite sample at a magnification of 2,000 times (dark matrix corresponds to diisopropylammonium chloride particles, light inclusions to lead titanate particles)

Analysis of dielectric properties of the  $(\text{DIPAC})_{1-x}/(\text{PbTiO}_3)_x$  composite samples was carried out using an E7-25 digital LCR meter with a frequency range of  $25-10^6$  Hz and an operating voltage of 0.7 V. A TC-6621 thermometer with a chromel-alumel thermocouple was used to measure the temperature. The temperature was determined with an accuracy of 0.1 K. The studies were carried during successive heating-cooling cycles at a rate of 1 K/min in the temperature range from 290 to 450 K in computer-controlled automatic mode.

### Experimental results and discussion

The results of studies on the dielectric properties of polycrystalline DIPAC samples and  $(\text{DIPAC})_{1-x}/(\text{PbTiO}_3)_x$  composites at  $x = 0.10$ , 0.20 and 0.25 are shown in Fig. 2. Analysis of the dependences for  $\epsilon'(T)$  indicates that an additional peak appears on the curves in the composite with  $x = 0.10$  both upon heating and upon cooling; the peak is also observed for composites with a volume fraction of  $\text{PbTiO}_3$  up to 0.30.

If  $x > 0.30$ , the temperature peaks of the phase transition are smoothed out with a further increase in the volume fraction of inclusion particles in pure DIPAC upon heating ( $T_1$ ) and upon cooling ( $T_2$ ). At the same time, the amplitudes of additional peaks on the temperature dependences of the dielectric constant upon heating ( $T_3$ ) and upon cooling ( $T_4$ ) increase with increasing volume fraction of lead titanate particles.

The temperature value of the main phase transition in composite samples with the volume fraction of inclusions up to 0.30 does not change significantly compared to the pure DIPAC sample (Fig. 3). The temperature of the additional peak in composite samples with  $x$  ranging from 0.10 to 0.30 is virtually independent of the fraction of inclusions, and decreases slightly (by about 5 K) for the sample with  $x = 0.40$ .

To explain the appearance of new phase transitions in the composite, let us consider a system of interacting particles. According to phenomenological theory, the

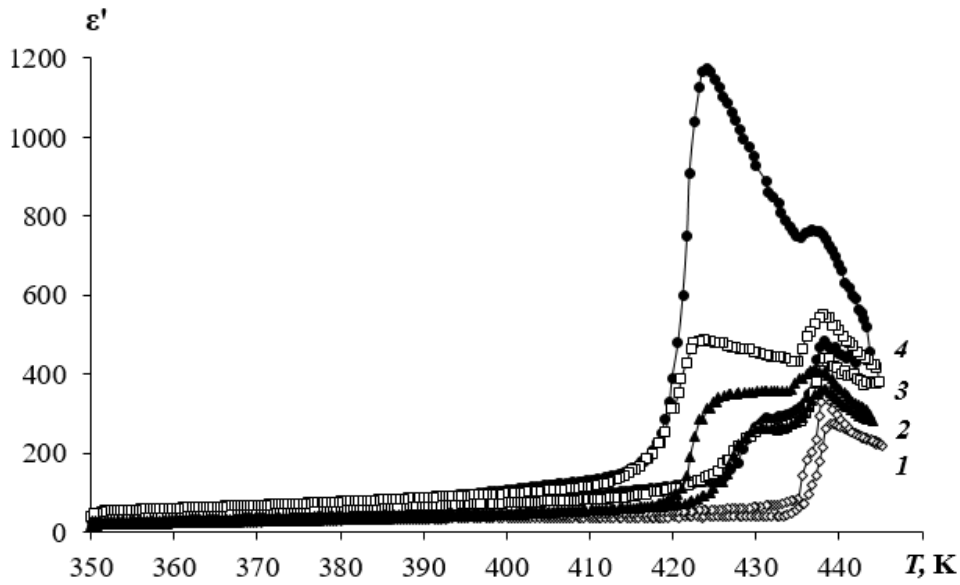


Fig. 2. Temperature dependences for dielectric constant of  $(\text{DIPAC})_{1-x}/(\text{PbTiO}_3)_x$  composite, recorded at a frequency of 10 kHz in a heating-cooling cycle;  $x = 0$  (1), 0.10 (2), 0.20 (3), 0.25 (4)

Landau–Ginzburg expansion in terms of the degree of polarization, serving as the order parameter, is used to describe the phase transition in a homogeneous ferroelectric [10]. The free energy for composites that are a mixture of ferroelectric powders is the sum of the energy of the particles included in the composite and the energy of their interaction. In view of these considerations, the free energy can be written in the following form:

$$\begin{aligned}
 F = & \\
 = & \sum_i \int_{V_i} \left( F_{0i} + \frac{1}{2} \alpha_i P_i^2 + \frac{1}{4} \beta_i P_i^4 + \dots \right) dv_i + \\
 + & \sum_j \int_{V_j} \left( F_{0j} + \frac{1}{2} \alpha_j P_j^2 + \frac{1}{4} \beta_j P_j^4 + \dots \right) dv_j + \\
 & + \Delta F_{ij}.
 \end{aligned} \quad (1)$$

where  $P_i$ ,  $P_j$  are the polarization values for particles of the first kind (for example, DIPAC) and particles of the second kind (for example,  $\text{PbTiO}_3$ ), respectively;  $\Delta F_{ij}$  is the interaction energy between particles, which is mainly electrical in nature in case of composites.

The strength of the electric field generated by a single-domain particle 1  $\mu\text{m}$  in diameter at a distance of 50  $\mu\text{m}$  from it in the direction of polarization can be estimated as approximately  $5 \cdot 10^6$  V/cm for lead titanate and  $7 \cdot 10^5$  V/cm for DIPAC.

The energy of electrical interaction between dipole particles is the sum of the Keesom and Debye energies. The maximum interaction energy of two dipole particles can be written as

$$\Delta F_{ij} \approx \frac{1}{4\pi\epsilon_0} \left[ \frac{2p_1 p_2}{R^3} + \frac{\epsilon_1 p_2^2}{\pi R^6} + \frac{\epsilon_2 p_1^2}{\pi R^6} \right], \quad (2)$$

where the first term is the Keesom energy (describing the interaction of particles with complete dipole moments), and the second and the third are the Debye energy (the interaction of dipole and non-dipole particles due to induced polarization);  $p_1$ ,  $p_2$  are the dipole moments of particles.

The energy  $\Delta F_{ij}$  for a system of dipole particles has the form

$$\begin{aligned}
 \Delta F_{ij} = & \frac{1}{4\pi\epsilon_0} \sum_{i,j} \left[ \iint_{V_i V_j} \left( \frac{2(P_i P_j)}{R_{ij}^3} \right) dv_i dv_j + \right. \\
 & + \iint_{V_i V_j} \left( \frac{\epsilon_i P_j^2}{\pi R_{ij}^6} \right) dv_i dv_j + \\
 & \left. + \iint_{V_i V_j} \left( \frac{\epsilon_j P_i^2}{\pi R_{ij}^6} \right) dv_i dv_j \right],
 \end{aligned} \quad (3)$$

where  $P_i$  and  $P_j$  refer to some average values of particle polarization; this is due to the scatter in the values of dipole moments of particles both in magnitude and in direction.

The phase transition temperatures of DIPAC particles in the composite are found from the condition of minimum free energy, taking into account the interaction:

$$\frac{dF_i}{dP_i} = \frac{d}{dP_i} \left[ \sum_i \int_{V_i} \left( \frac{1}{2} \alpha_i P_i^2 + \frac{1}{4} \beta_i P_i^4 + \dots \right) dv_i + \Delta F_{ij} \right] = 0. \quad (4)$$

According to expressions (3) and (4), the interaction energy of particles and, consequently, the phase transition temperatures for DIPAC in the composite differ from the phase transition temperatures of homogeneous DIPAC. The temperature shift of the phase transition depends on several quantities:

- concentration and size of inclusion particles,
- the values of spontaneous polarization of these particles,
- the degree of their polarization,
- the dielectric constant of these particles.

Analyzing the dependence of phase transition temperatures of the composite on the volume fraction of lead titanate (see Fig. 3), we can assume that the mixture contains two states of DIPAC particles:

the first is particles with no  $\text{PbTiO}_3$  particles in their immediate vicinity; their phase transitions correspond to phase transitions in isotropic DIPAC ( $T_1$  and  $T_2$ );

the second is the particles adjacent to dipole

$\text{PbTiO}_3$  particles; their phase transition temperatures are determined taking into account the interaction energy ( $T_3$  and  $T_4$ ), as follows from relations (3) and (4).

This is confirmed by the fact that the amplitudes of the curves  $\varepsilon'(T)$  (Fig. 3) increase with increasing concentration of  $\text{PbTiO}_3$  for particles of the second type, and the number of particles of the first kind is negligible with  $x > 0.30$ . The phase transition temperatures  $T_3$  and  $T_4$  are virtually independent of the concentration of lead titanate particles in the range of  $x$  values from 0.10 to 0.30, which may point to some anomalies in the thermodynamic potential of DIPAC at these temperatures, while a small change in the interaction energy leads to phase transitions.

### Conclusion

We have carried out studies on the dielectric properties of polycrystalline DIPAC samples and  $(\text{DIPAC})_{1-x}/(\text{PbTiO}_3)_x$  composites at  $x = 0.10, 0.20$  and  $0.25$ . Analysis of the obtained data indicates that an increase in the volume fraction  $x$  ( $\text{PbTiO}_3$  content) from 0.10 to 0.30 produces additional phase transitions for composites based on diisopropylammonium chloride and lead titanate. The main transition peak was practically indistinguishable at  $x > 0.30$ . The appearance of an additional phase transition can be explained by the dipole-dipole interaction of the components of the composite.

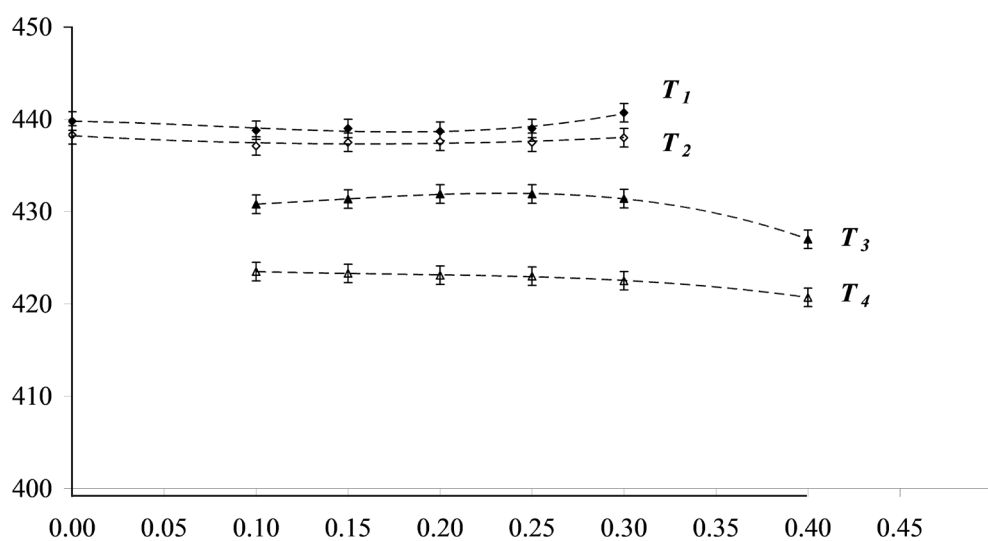


Fig. 3. Positions of temperature peaks depending on volume fraction of inclusions in  $(\text{DIPAC})_{1-x}/(\text{PbTiO}_3)_x$  composite samples:

$T_1, T_2$  are the temperatures of the main peak during heating and cooling, respectively;  
 $T_3, T_4$  are the temperatures of the additional peak during heating and cooling, respectively



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