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FERROELECTRIC PROPERTIES OF COMPOSITES BASED ON DIISOPROPYLAMMONIUM BROMIDE AND LEAD TITANATE

S.V. Baryshnikov[1], *E.V. Stukova*[2], *T.A. Meredelina*[1]

[1]Blagoveshchensk State Pedagogical University, Blagoveshchensk, Russian Federation;

[2]Amur State University, Blagoveshchensk, Russian Federation

The results of a study of linear and nonlinear dielectric properties, as well as calorimetric measurements of a ferroelectric composite $(C_6H_{16}NBr)_{1-x}/(PbTiO_3)_x$ with a volume fraction x = 0.1, 0.2, 0.3 of lead titanate particles are presented. It has been shown that the addition of lead titanate particles to diisopropylammonium bromide leads to a change in the sequence of structural phase transitions in the diisopropylammonium bromide, an increase in the effective dielectric constant and tanδ values. In a temperature range of 150–138°C, there were two $C_6H_{16}NBr$ phases (ferroelectric $P2_1$ and nonferroelectric $P2_12_12_1$). The proportion among these phases depended on the fraction of lead titanate particles in the composite.

Keywords: ferroelectric, dielectric constant, composite, phase transition

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СЕГНЕТОЭЛЕКТРИЧЕСКИЕ СВОЙСТВА КОМПОЗИТОВ НА ОСНОВЕ БРОМИДА ДИИЗОПРОПИЛАММОНИЯ И ТИТАНАТА СВИНЦА

С.В. Барышников[1], *Е.В. Стукова*[2], *Т.А. Мероделина*[1]

[1]Благовещенский государственный педагогический университет, г. Благовещенск, Российская Федерация;

[2]Амурский государственный университет, г. Благовещенск, Российская Федерация

В работе приведены результаты исследований линейных и нелинейных диэлектрических свойств, а также калориметрических измерений сегнетоэлектрического композита $(C_6H_{16}NBr)_{1-x}/(PbTiO_3)_x$ с объемной долей частиц титаната свинца в композите x = 0,1; 0,2; 0,3. Показано, что добавка частиц титаната свинца к бромиду диизопропиламмония приводит к изменению последовательности структурных фазовых переходов в бромиде диизопропиламмония, увеличению эффективной диэлектрической проницаемости и значений tgδ композита. В температурном интервал138 – 150°С присутствуют две фазы $C_6H_{16}NBr$ (сегнетоэлектрическая $P2_1$ и несегнетоэлектрическая $P2_12_12_1$), соотношение между которыми зависит от доли частиц титаната свинца в композите.

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

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Introduction

Ferroelectric composites are the focus of considerable attention because heterogeneous materials can exhibit unusual properties compared to homogeneous substances. According to theoretical models, the ferroelectric state is induced by dipole-dipole interaction, allowing to explain the domain structure and the effect of polar impurities on the properties of crystals [1–3]. It was established in [2, 3] that introducing polar impurities to highly polarized matrices can cause the ferroelectric state to appear. In contrast to crystals and solid solutions, polar particles in composites are located at distances of the order of several microns; this brings the question how electrical interactions manifest in such structures.

A number of studies considered the mutual influence of components in ferroelectric composites (see, for example, [4–7] and the references therein), finding that such influence is possible for these objects. An extended temperature range was observed for the ferroelectric phase of potassium nitrate in composites such as $(KNO_3)_{1-x}/(BaTiO_3)_x$, $(KNO_3)_{1-x}/(KNbO_3)_x$ [4, 5]. The interaction effect led to extended temperature range of incommensurate phase of sodium nitrite in the $(NaNO_2)_{1-x}/(BaTiO_3)_x$ composite [6]. A substantial shift in the Curie temperature was found in [7] for the $AgNa(NO_2)_2$ compound in the $[AgNa(NO_2)_2]_{0.9}/[BaTiO_3]_{0.1}$ composite.

A series of organic compounds with a polar point group at room temperature and relatively high melting point (around 177°C) were discovered recently. Such ferroelectrics include diisopropylammonium chloride ($C_6H_{16}NCl$, DIPAC) with $P_s \approx 8.2$ μC/cm^2, $T_c = 167$°C [8]; diisopropylammonium bromide ($C_6H_{16}NBr$, DIPAB) with $P_s \approx 23$ μC/cm^2, $T_c = 153$°C [9]; diisopropylammonium iodide ($C_6H_{16}NI$, DIPAI) with $P_s \approx 5.17$ μC/cm^2, $T_c = 105$°C [10]. In particular, DIPAB has spontaneous polarization close to barium titanate, a high Curie temperature and exhibits good piezoelectric response. These properties make it an alternative to perovskite-like ferroelectrics and ferroelectric polymers.

This study considers the effect of $PbTiO_3$ particles on the temperatures of phase transitions and dielectric properties of the $(C_6H_{16}NBr)_{1-x}/(PbTiO_3)_x$ composite.

Samples and experimental procedure

The $C_6H_{16}NBr$ compound can exist at room temperature in two different polymorphic phases: with spatial symmetry $P2_1$ or $P2_12_12_1$, depending on the conditions in which it was obtained and the thermal history [10]. Monoclinic phase $P2_1$ is ferroelectric, transforming into the nonpolar phase $P2_1/m$ at temperatures above $T_c \approx 152$°C. The ferroelectric transition in $C_6H_{16}NBr$ is a transition of the first kind. The second phase, stable at room temperature, has orthorhombic symmetry with space group $P2_12_12_1$and is not an active ferroelectric phase; it is also transformed to nonpolar monoclinic phase $P2_1/m$ under heating, but with an intermediate polar structure with symmetry $P2_1$, existing in the range from about 148 to 152°C. The structure of $C_6H_{16}NBr$ changes immediately from $P2_1/m$ to $P2_1$ under cooling at 145°C, and the rhombic phase no longer forms.

Diisopropylammonium bromide in our study was obtained as a product of diisopropylammonium reacting with 48% aqueous solution of HBr (1:1 molar ratio) by the technique described in [11], followed by recrystallization from methanol at room temperature. The largest crystals were 2–3 mm in size.

Lead titanate has a tetragonal phase below 490°C, isomorphic to barium titanate, and is a ferroelectric of the first kind. Spontaneous polarization of $PbTiO_3$ at room temperature is approximately $P_s \approx 70$ μC/cm^2, which is significantly higher than for $BaTiO_3$ ($P_s \approx 22$ μC/cm^2). The values of the dielectric constant ε′ along the polar axis lie in the range of $(1.5–2.2)\cdot 10^2$ for $PbTiO_3$ at room temperature, while it is $(2– 4)\cdot 10^3$ for $BaTiO_3$ [12].

We used composite samples of $(C_6H_{16}NBr)_{1-x}/(PbTiO_3)_x$, where x was 10, 20 and 30 wt%, for the experiments. The samples were thoroughly mixed and pressed under about 10^4 kg/cm^2. Average particle size in the composite ranged from 3 to 10 μm. The samples were disc-shaped, with a diameter 10 of mm and a thickness of 1.5 mm; silver electrodes were deposited on their surface.

The characteristics of the given samples were measured automatically using a computer, under heating and subsequent cooling at a rate of 1 deg/min in the temperature range 30–170°C.

The E7-25 immittance meter was used to determine the dielectric properties. The measurements were carried out at frequencies of 10^3, 10^4 и 10^5 Hz at a voltage of 0.7 V. The error in measuring the capacitance of the samples did not exceed 5%. Temperatures were recorded by a TS-6621 digital thermometer with a chromel-alumel thermocouple. The error in measuring the temperature did not exceed 0.1°C.

The setup for studying the nonlinear properties of the composites included an oscillator with a frequency of 2 kHz. The electric field applied to $C_6H_{16}NBr$ samples and $(C_6H_{16}NBr)_{1-x}/(PbTiO_3)_x$ composites was about 10 V/mm. The signal was taken from the resistor series-connected to the sample and fed to the spectrum analyzer. The coefficients of the second and third harmonics were found as the ratio of the harmonic amplitude to the capacitive component of the main signal:

$$\gamma_{2\omega} = u_{2\omega}/u_{\omega},\ \gamma_{3\omega} = u_{3\omega}/u_{\omega}.$$

The technique for nonlinear measurements is described in more detail in [13, 14].Differential scanning calorimetry with the thermoelectric power of about 5 μV was used to measure the heat capacity. The heating and cooling rate was 2 deg/min. The error in measuring the temperature did not exceed 0.1°C.

Experimental results and discussion

The dielectric properties obtained for polycrystalline samples of C 6 $H_{16}NBr$ and $(C_6H_{16}NBr)_{1-x}/(PbTiO_3)_x$ composites with x = 0.1; 0.2 and 0.3 are shown in Fig. 1.

It follows from the $\varepsilon'(T)$ dependences that, firstly, the maximum dielectric constant ε'_{max} increases with increasing lead titanate content, and, secondly, an additional anomaly appears on the $\varepsilon'(T)$ curve for the composites under cooling in the range from 133–137°C; this anomaly is absent in the respective curve for pure $C_6H_{16}NBr$.

The table shows the maximum values of the dielectric constant ε'_{max} of the composites with different volume fractions of lead titanate inclusions, at frequencies of 10^3 and 10^5 Hz.

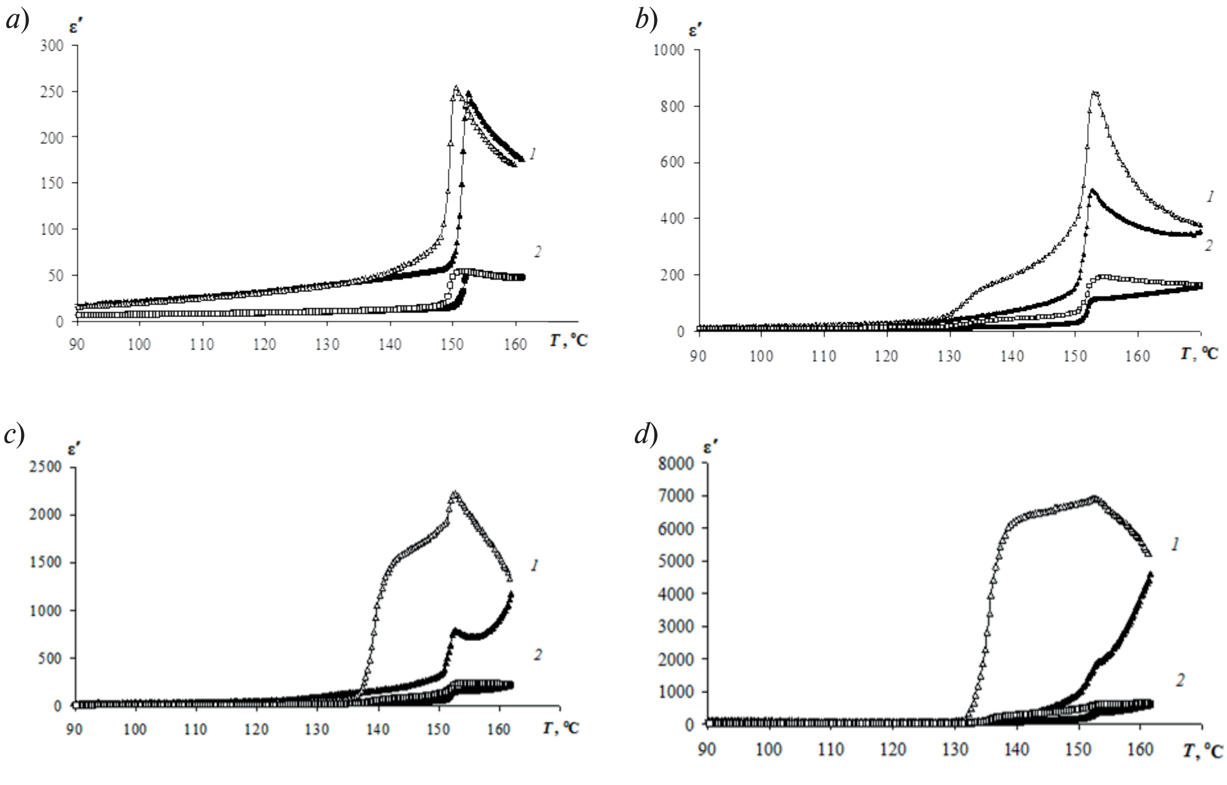

Fig. 1. Temperature evolution of dielectric constant in $(C_6H_{16}NBr)_{1-x}/(PbTiO_3)_x$ composite with x = 0 (*a*), 0.1 (*b*), 0.2 (*c*), 0.3 (*d*), obtained at frequencies of 1 kHz (*1*) and 100 kHz (*2*) under heating (dark symbols) and cooling (light markers)

Calorimetric studies (Fig. 2) indicate that adding lead titanate induces an additional phase transition under cooling. The nature of this phase transition is not yet fully understood. Signal intensity for this additional transition increases with an increase in the proportion of lead titanate particles in the composite.

Nonlinear dielectric spectroscopy (NDS) was used to analyze the structure forming between two phase transition under cooling. Fig. 3 shows the temperature dependences of the main signal at a frequency of 2 kHz and the coefficients of the second (4 kHz) and third (6 kHz) harmonics. It was confirmed in [13] for ferroelectrics with the phase transition of the first kind that nonlinear dielectric permittivities are expressed as

$$\varepsilon_2 = -\left(3\beta + 10\gamma P_s^2\right) P \chi_1^3; \quad (1)$$

$$\varepsilon_3 = \left[-\beta - P_s^2\left(10\gamma + 18\beta^2\chi_1 + 120\chi_1\beta\gamma P_s^2\right) + 200\chi_1\gamma^2 P_s^4\right]\chi_1^4, \quad (2)$$

where χ_1 is the electric susceptibility; P_s is the spontaneous polarization; β, γ are the Landau coefficients.

It can be seen from (2) that third-order permittivity is significantly increased in polar phase due to spontaneous polarization and has a minimum at the phase transition point. Thus, study of temperature dependence of third harmonic generation is a direct method for detecting the ferroelectric state.

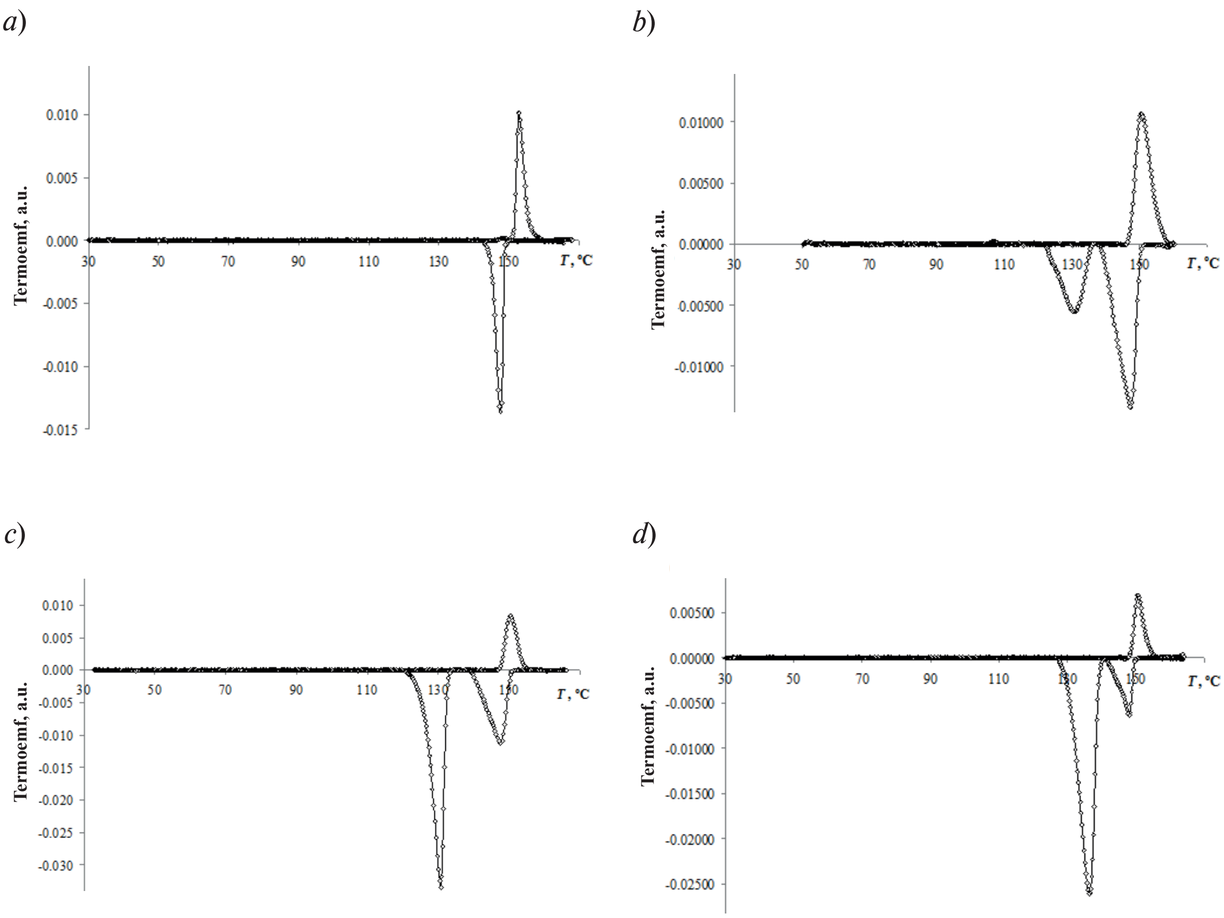

Fig. 2. Relative variation of thermopower for samples of $(C_6H_{16}NBr)_{1-x}/(PbTiO_3)_x$ composite with x = 0 (*a*), 0.1 (*b*), 0.2 (*c*), 0.3 mm (*d*);
positive signal corresponds to heating, negative signal to cooling

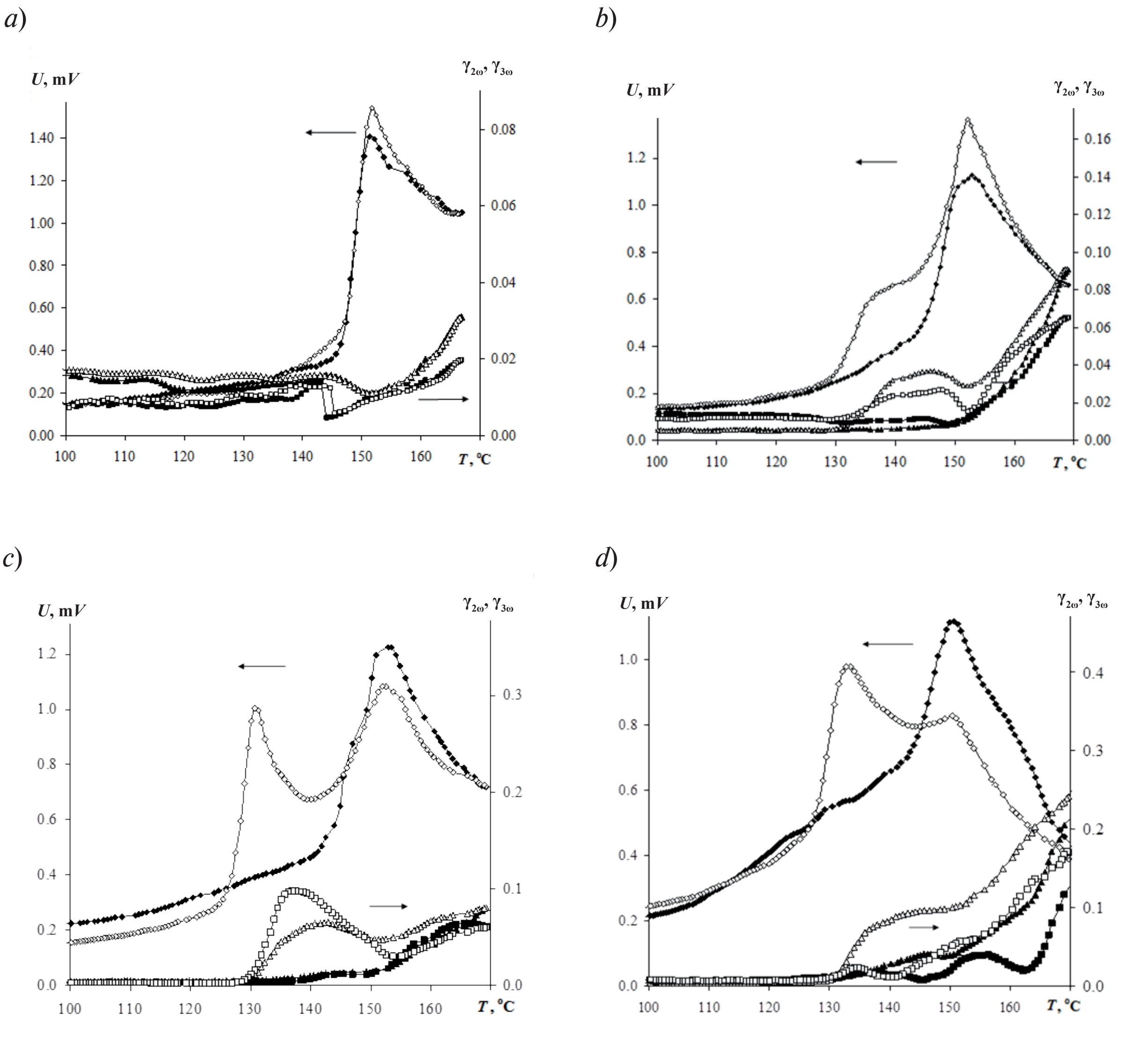

Fig. 3. Temperature dependences for capacitive component of signal at fundamental frequency ω (left axes) and coefficients of second ($\gamma_{2\omega}$) and third ($\gamma_{3\omega}$) harmonics (right axes) for $(C_6H_{16}NBr)_{1-x}/(PbTiO_3)_x$ composites with $x = 0$ (*a*), 0.1 (*b*), 0.2 (*c*), 0.3 (*d*); dark symbols correspond to heating, light symbols correspond to cooling

It follows from the curves in Fig. 3 that a certain anomaly is observed in the behavior of $\gamma_{3\omega}$ for pure $C_6H_{16}NBr$; it is approximately 1.5% near the ferroelectric phase transition. The value of $\gamma_{3\omega}$ for the $(C_6H_{16}NBr)_{0.9}/(PbTiO_3)_{0.1}$ composite under cooling in the temperature range of 133–137°C is about 2.5%, and that of $\gamma_{2\omega}$ is approximately 7.5% The value of $\gamma_{3\omega}$ for the $(C_6H_{16}NBr)_{0.8}/(PbTiO_3)_{0.2}$ composite is about 30% in the temperature range of 133–137 °C, and that of $\gamma_{2\omega}$ is approximately 5%. The value of $\gamma_{3\omega}$ decreases to about 5% with a further increase in lead titanate content in the $(C_6H_{16}NBr)_{0.7}/(PbTiO_3)_{0.3}$ composite, while $\gamma_{2\omega}$ increases to 20%.

The experimental data obtained by NDS confirm that two phases of the $C_6H_{16}NBr$ compound are found in the range of 137–133°C under cooling: ferroelectric $P2_1$and nonferroelectric $P2_1/m$. The anomalies in phase transitions for the capacitive component of the signal through the sample are more pronounced in comparison with the ε′(*T*) dependence, which is due to barrier transitions forming in the composite at the interfaces of $C_6H_{16}NBr$ and $PbTiO_3$ compounds, acting as capacities at low supplied voltages and making a noticeable contribution to the effective dielectric constant. This mechanism does not work with measuring voltages above 3 V, and the effective dielectric constant decreases.

Table

Variation in dielectric properties of composites with increasing lead titanate contents

Composition	ε'_{max}	$(tg\delta)_{max}$	ε'_{max}	$(tg\delta)_{max}$
	10^3 Hz		10^5 Hz	
$C_6H_{16}NBr$	~250	~8	~55	~0.9
$(C_6H_{16}NBr)_{0.9}/(PbTiO_3)_{0.1}$	~900	~30	~190	~2.6
$(C_6H_{16}NBr)_{0.8}/(PbTiO_3)_{0.2}$	~2200	~40	~230	~3.5
$(C_6H_{16}NBr)_{0.7}/(PbTiO_3)_{0.3}$	~7000	~90	~550	~6.0

Conclusion

Studying the dielectric properties of the $(C_6H_{16}NBr)_{1-x}/(PbTiO_3)$ composite, we have found that increasing x leads to smeared phase transitions and increased values of ε′ and tgδ′ (see Table). The increase in permeability may be due to barrier mechanisms, which is confirmed by the dependence of dielectric properties on the amplitude of the measuring field and its frequency. Analyzing the data obtained by calorimetric measurements, we have discovered an additional phase transition whose specific heat capacity increases with increasing x. The additional phase transition can be explained by electrical interaction of diisopropylammonium bromide and lead titanate particles in the composite.

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THE AUTHORS

BARYSHNIKOV Sergey V.
Blagoveschensk State Pedagogical University
104 Lenina St., Blagoveshchensk, 675000, Russian Federation
svbar2003@list.ru

STUKOVA Elena V.
Amur State University
21 Ignatievskoe Ave., Blagoveshchensk, 675027, Russian Federation
lenast@bk.ru

MEREDELINA Tatiana A.
Blagoveshchensk State Pedagogical University
104 Lenina St., Blagoveshchensk, 675000, Russian Federation
biofirm@mail.ru

СПИСОК ЛИТЕРАТУРЫ

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СВЕДЕНИЯ ОБ АВТОРАХ

БАРЫШНИКОВ Сергей Васильевич – *доктор физико-математических наук, профессор кафедры физического и математического образования Благовещенского государственного педагогического университета.*

675000, Российская Федерация, Амурская область, г. Благовещенск, ул. Ленина, 104
svbar2003@list.ru

СТУКОВА Елена Владимировна – *доктор физико-математических наук, профессор кафедры физики Амурского государственного университета.*

675027, Российская Федерация, Амурская область, г. Благовещенск, Игнатьевское шоссе, 21
lenast@bk.ru

МЕРЕДЕЛИНА Татьяна Александровна – *кандидат физико-математических наук, доцент кафедры физического и математического образования Благовещенского государственного педагогического университета.*

675000, Российская Федерация, Амурская область, г. Благовещенск, ул. Ленина, 104
biofirm@mail.ru