THE FERROELECTRIC PHASE TRANSITION IN THE AMMONIUM IODATE EMBEDDED INTO THE ALUMINA POROUS MATRIX

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The temperature dependences of the linear permittivity ε' and the harmonic coefficient γ of composite materials obtained by embedding the ferroelectric NH_4IO_3 into the porous alumina (Al_2O_3) matrix with a pore diameter of 60 nm have been studied. It was found out that the phase transition was diffused and the Curie temperature shifted to a low-temperature region $T \sim 25$ K. The results obtained were interpreted within the framework of the phenomenological Landau theory and the Ising model. On the basis of these theoretical descriptions, it was shown that the phase transition temperature in a nanocomposite was consequence of dimensional effects. At the same time, the electrical interaction between particles in adjacent pores does not play an important role, due to the low spontaneous polarization of ammonium iodate and significant distances between neighboring pores.

Key words: ferroelectric; dielectric permittivity; nanocomposite; phase transition

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Introduction

The dielectric properties of nanocomposites based on porous matrices filled with ferroelectrics are currently the focus of considerable attention. The physical properties of such structures are affected by the size and geometry of the porous network. The greatest number of studies are dedicated to nanocomposites with sodium nitrite, Rochelle salt, potassium nitrate and triglycine sulfate embedded into the pores (see [1 – 3] and references therein). Exploring the factors governing the changes in the properties of the ferroelectric component of nanocomposites is one of the key goals of modern physics of low-dimensional systems and solid-state electronics.

In this paper, we have studied the dielectric properties of nanocomposites based on ammonium iodate embedded in porous alumina (Al_2O_3) films.

Samples and experimental procedure

Ammonium iodate (NH_4IO_3) consists of colorless crystals of ammonium salt and iodic acid, soluble in water. Japanese researchers Oka, Mitsui, Shiroishi and Sawada discovered the ferroelectric properties of ammonium iodate in 1976 [4]. Ammonium iodate is in the cubic α phase at temperatures above 393 K. Below this temperature, the crystal transforms into the orthorhombic piezoelectric β phase ($Pc2_1n$) with lattice constants a = 6.426 Å, b = 9.104 Å, c = 6.466 Å. A transformation into the ferroelectric γ phase ($Pm2_1b$), which is also orthorhombic with lattice constants a = 6.413 Å, b = 9.156 Å, c = 6.411 Å occurs with a further decrease in temperature in the region of about 358 K. The structural transformation between the nonpolar piezoelectric β phase and the ferroelectric γ phase near 358 K is caused by a change in the tilt of the IO_6^- octahedra in the perovskite-like structure. At the same time, small shifts of the ammonium ion NH_4^+ along the polar axis *b* and spontaneous polarization occur (the magnitude of the spontaneous polarization vector at room temperature is $P_s \approx 1.8$ μC/cm²). Although the space group of the high-temperature β phase is polar, the dipole moment of the cell is equal to zero. The phase transition is of the first-order type with anomalies of the dielectric, the piezoelectric, and the elastic constants.

Porous anodized aluminum oxide films with a cell size of 125 nm and a pore diameter of 60 nm were used in the experiment. The pore depth was about 50 μm. Aluminum oxide films were manufactured by TopMembranes Technology using two-step electrochemical anodizing of aluminum in an aqueous solution of oxalic acid at a voltage of 35 V. The structure of the film is shown in Fig. 1. The porous film was filled with ammonium iodate from a saturated aqueous solution under vacuum at 353 – 363 K. The sample was then slowly cooled, with NH_4IO_3 nanocrystals forming in the pores as a result. The procedure was repeated ten times, the pores were then filled and NH_4IO_3 nanorods were formed within them. The degree of pore filling, determined from the change in the mass of the films, was about 60%. Vacuum drying was used to remove the remaining water.

A digital E7-25 LCR meter with a frequency range of 25 Hz – 1 MHz was used for measuring the linear dielectric properties of the samples. The experimental setup for studying the harmonics included a sinusoidal oscillator with an operating frequency of 2 kHz. The field strength was approximately 750 V/cm for the bulk sample and 500 V/cm for the alumina film filled with ammonium iodate. The signal was taken from a resistor that was series-connected with the sample and fed to a digital spectrum analyzer (a computer with a ZET-230 24-bit analog-to-digital converter and ZetLab software). The amplitudes of the second ($U_{2\omega}$) and third ($U_{3\omega}$) harmonics were recorded in the experiment. The harmonic coefficient γ was calculated by the formula

$$\gamma = \frac{\sqrt{U_{2\omega}^2 + U_{3\omega}^2}}{U_\omega^2}.$$

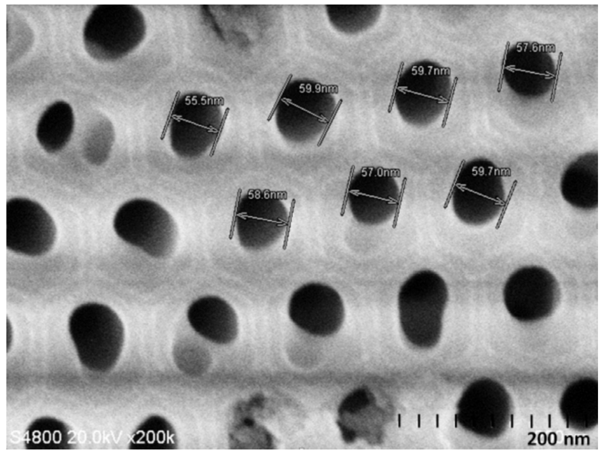

Fig. 1. Surface morphology of the Al_2O_3 film with pore sizes of 60 nm, obtained with an electron microscope

The technique of nonlinear measurements is described in more detail in [5].

The measurements were carried out in the temperature range of 80 – 500 K under continuous heating and cooling at a rate of 1 K/min. The temperature was measured with a digital TC-6621 thermometer with an accuracy of about 0.1 K. The silver paste was used as electrodes.

Experimental results and discussion

The temperature dependence of the dielectric constant for bulk ammonium iodate exhibited low-frequency dispersion (Fig. 2). It is evident from the inset in Fig. 2 that the phase transition temperatures for bulk ammonium iodate determined from the ε'(*T*) and γ(*T*)dependences coincide. It should be borne in mind that the dielectric permittivity reaches its maximum at the Curie point, while the harmonic coefficient value is minimal at this point.

It also follows from the ε'(*T*) dependence for the NH_4IO_3/Al_2O_3 composite (Fig. 3) that the dielectric constant decreases with increasing frequency; however, no anomaly in the behavior of this dependence is observed in the Curie temperature region for NH_4IO_3.

Nevertheless, the studies, which were carried out by nonlinear dielectric spectroscopy, indicate an anomaly in the region of 343 K, which suggests the presence of a phase transition in NH_4IO_3 in nanopores with a diameter of

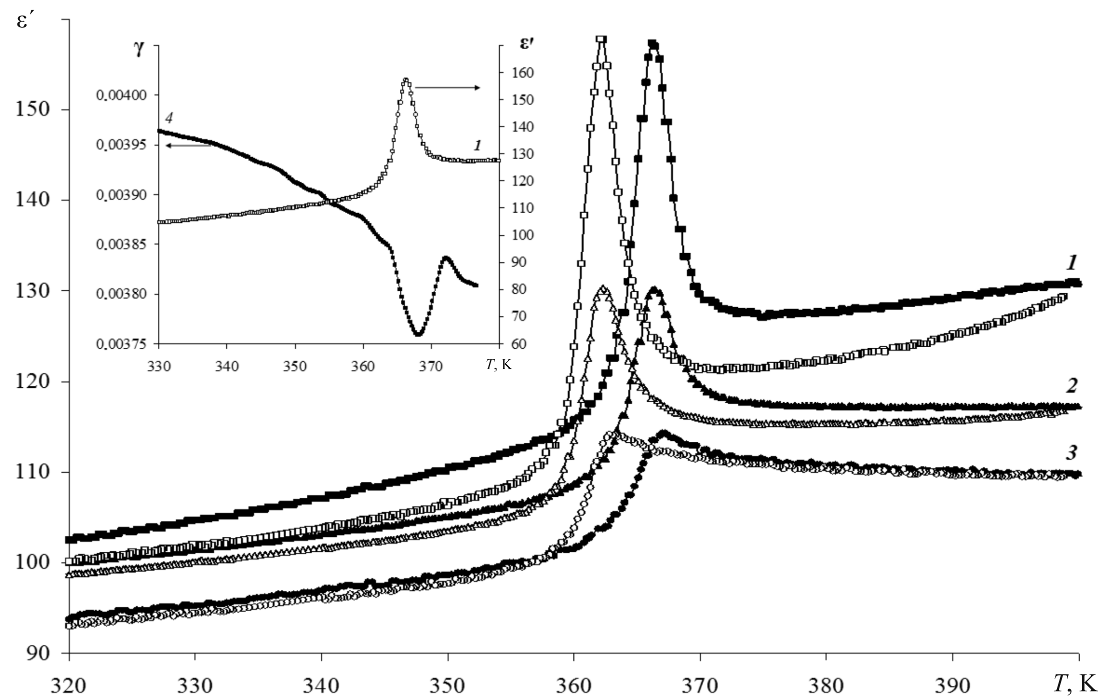

Fig. 2. Temperature dependences of the dielectric constant of bulk NH_4IO_3 at different frequencies, kHz: 1 (curve *1*), 100 (*2*), 1000 (*3*); obtained under sample heating (shaded symbols) and cooling (open symbols).
The inset shows the ε'(*T*) (*1*) and γ(*T*) (*4*) dependences at a frequency of 1 kHz

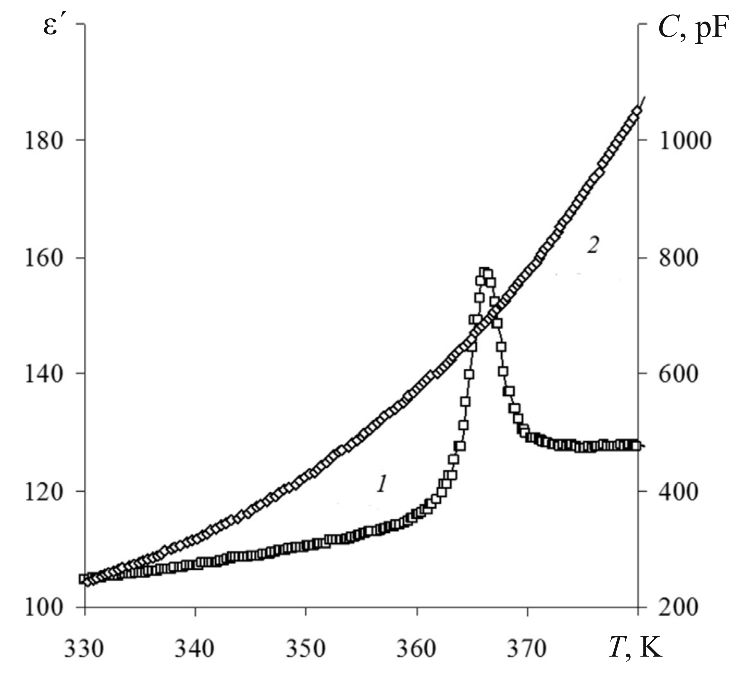

Fig. 3. Temperature dependences of the dielectric permittivity (*1*) and the capacitance (*2*) of the NH_4IO_3/Al_2O_3 composite at a frequency of 1 kHz, obtained under sample cooling

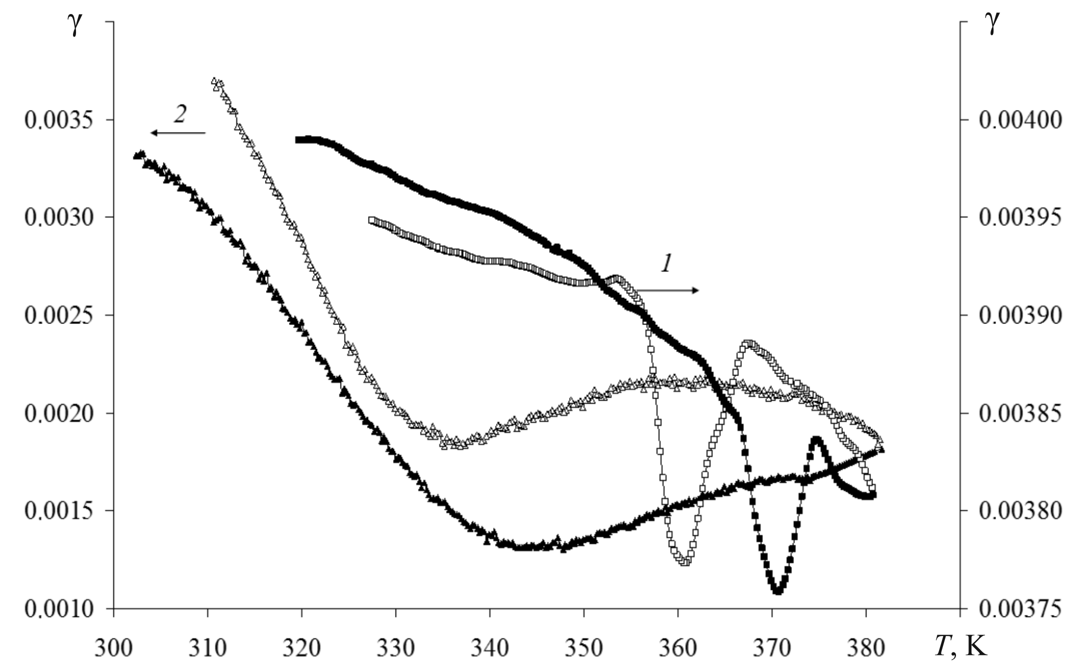

Fig. 4. Temperature dependences of the harmonic coefficient for a bulk NH_4IO_3 sample (*1*) and a NH_4IO_3/Al_2O_3 composite (*2*); obtained under heating (shaded symbols) и under cooling (open symbols)

60 nm. Fig. 4 shows the temperature dependences of the harmonic coefficient for the bulk sample and for the NH_4IO_3/Al_2O_3 composite, pointing to a diffused phase transition and to a shift of the Curie temperature toward the low temperature region by $\Delta T \approx 25$ K.

The decrease in the phase transition temperature in ammonium iodate embedded into alumina pores agrees with the conclusions of theoretical models developed on the basis of Landau's phenomenological theory and the Ising model [6 – 8]. These models predict that the structural phase transition temperature for small isolated particles of spherical or cylindrical shapes shifts deeper into the ferroelectric phase as the particle size decreases. The conclusions of these models were also confirmed experimentally for individual small particles of ferroelectrics such as barium titanate (see [9] and references therein). Theoretical analysis [10] established that the interaction between ferroelectric particles in the pores, which is electrical in nature, can significantly weaken the dimensional effects. The interaction with the walls of the pores can play an additional role for small particles in porous matrices, leading to a change in the sign of the phase transition shift [11]. A significant decrease in the ferroelectric transition temperature in ammonium iodate embedded into alumina pores indicates that the size effects are predominant for such a nanocomposite. The electrical interaction between particles in adjacent pores does not play a substantial role, due to low spontaneous polarization of ammonium iodate and significant distances between adjacent pores.

The issue of diffused phase transition in ferroelectrics embedded into nanoscale matrices is not new: it was discussed from a theoretical standpoint in a number of studies [12, 13]. Some reasons that can lead to this effect are that the deformation of the particles in the pores and the values of the effective internal electric field are distributed non-uniformly. A similar picture is observed both in bulk disordered ferroelectric structures and in solid solutions. These substances are characterized by a gradual diffused transition from the paraelectric to the ferroelectric phase (observed in a wide temperature range, usually called the Curie region), instead of a sharp structural one. The ferroelectric properties, such as spontaneous polarization, piezoelectric coefficients, anomalous specific heat capacity and others change gradually within the Curie region.

Conclusion

This study has revealed a decrease in the temperature of the ferroelectric phase transition in nanostructured ammonium iodate embedded into the pores of aluminum oxide. The temperature of the phase transition has been found to decrease by 25 K. The shift of the phase transition to the region of lower temperatures for nanostructured ammonium iodate agrees with the theoretical descriptions of the Landau and Ising models for isolated small particles.

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