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Dielectric investigation of the composites based on thiourea

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Abstract

The composites of thiourea and lithium niobate as well as lead titanate and barium titanate (thiourea fraction was 0.90 for all cases) have been studied by dielectric spectroscopy close to structural phase transitions in thiourea. It was found that the hysteresis increased and the temperature of ferroelectric phase transition from phase I to phase II decreased for all compositions investigated in comparison with the same properties of polycrystalline thiourea. The largest lowering of the phase transition temperature was observed for the thiourea and barium titanate composite. The results are analyzed within the framework of Landau–Ginzburg theory.

Keywords: Ferroelectrics; Dielectric permittivity; Composite; Phase transition; Spontaneous polarization.

1. Introduction

Multicomponent materials combining diverse substances are called composites. Recently, the development of composite materials based on ferroelectrics has become one of the priority directions of research. These structures are being considered as smart materials, the properties of which depend on the environment.

Ferroelectric composites can be of various structures which are formed by polar particles in different matrixes: in weakly or strongly polarizable ones, polar ones, etc. The variation of matrix and filler composition, weight fractions as well as dispersion degree allows production of a wide spectrum of materials with required property set. It was revealed [1–7] that the interference of component properties is possible for these systems. Thus, it was shown that for the ferroelectric composites $(KNO_3)_{1-x}/(BaTiO_3)_x$, $(KNO_3)_{1-x}/(KNbO_3)_x$, $(KNO_3)_{1-x}/(PbTiO_3)_x$, $(KNO_3)_{1-x}/(LiNbO_3)_x$ the broadening of the ferroelectric phase existence interval was observed for potassium nitrate [1–4]. For the composites $(NaNO_2)_{1-x}/(BaTiO_3)_x$, the interaction effect leads to the substantial growth of both real and imaginary parts of dielectric permittivity as well as to the widening of disproportionate phase temperature range. The real part of dielectric permittivity ε' when cooled from the paraphase to 273 K turns out to be less than when heated, whereas the tangent of dielectric loss angle demonstrates the inverse dependence [5]. The research carried out [6,7] of dielectric permittivity and the third harmonic for composites $(TGS)_{1-x}(BaTiO_3)_x$ и

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$(TGS)_{1-x}(PbTiO_3)_x$ showed that the inclusions of small $BaTiO_3$ and $PbTiO_3$ particles in the objects discussed lead to the increase in the phase transition temperature of TGS, and the addition of barium titanate leads to the rise of the $\varepsilon'(T)$ maximum of 5 K, whereas the addition of the same amount of lead titanate leads to the rise of only 3 K.

The influence of $BaTiO_3$, $PbTiO_3$ and $LiNbO_3$ (particle size was from 5 to 30 μm) inclusion on the dielectric properties and phase transition temperatures in the polycrystalline samples of thiourea has been studied in the paper presented.

2. Samples and experimental technique

Thiourea crystals $SC(NH_2)_2$ demonstrate a complicated sequence of structural phase transitions. At room temperature the crystal belongs to the centrosymmetric group *Pnma* (D_{2h}^{16}) with cell parameters $a = 7.65$ Å, $b = 8.53$ Å, $c = 5.52$ Å (phase V). When temperature is reduced, nonpolar phase (IV) appears in the temperature range from 202 to 180 K; polar phase (III) is formed between 180 and 176 K with the spontaneous polarization value being $P_s = 2.5$ μC/cm^2; nonpolar phase (II) exists between 176 and 169 K, and polar phase (I) is formed below 169 K with spontaneous polarization along the *a* axis being equal to $P_s = 3$ μC/cm^2. The dielectric permittivity values ε_b and ε_c virtually do not depend on temperature, whereas ε_a at low temperatures demonstrates the diversity of abnormalities [8].

In $BaTiO_3$ crystals, three phase transitions of displacive type are observed being accompanied with structure and properties changes. Barium titanate has several equivalent directions of polarization and presents an example of a multiaxial ferroelectric. At the temperature higher than 293 K, barium titanate has cubical crystalline structure of perovskite type. This paraelectric modification belongs to the space group *Pm*3*m*. Below the transition temperature $T_0 = 293$ K, phase transition takes place, and to the temperature as low as 278 K $BaTiO_3$ is ferroelectric with tetragonal symmetry of *P*4*mm* class. Below 293 K, when cubical cell is distorted, the spontaneous polarization P_s appears abruptly, the value of which smoothly increases from 18 μC/cm^2 near T_0 to 26 μC/cm^2 at near-room temperature. At temperatures below 278 K, the second phase transition takes place and the crystal becomes rhombic. In the temperature range from 203 to 183 K, barium titanate undergoes the third phase transition and at temperatures lower than these it is of rhombohedral structure. Temperature hysteresis takes place for all phase transitions [9].

Lead titanate provides a classical example of displacement-type ferroelectric. The crystal in paraelectric phase belongs to the space group *Pm*3*m*. At a temperature of 763 K $PbTiO_3$ undergoes the first-kind phase transition from the cubic perovskite phase into the tetragonal ferroelectric phase which is isomorphic to tetragonal one of $BaTiO_3$. The properties of $PbTiO_3$ in cubic and tetragonal phases are similar to those of $BaTiO_3$. $PbTiO_3$ cell parameters at room temperature are as follows: $a = 3.904$ Å, $c = 4.150$ Å, $c/a = 1.063$, which indicates larger tetragonal lattice distortion than in the case of $BaTiO_3$, where $c/a = 1.01$. This significant distortion causes substantial change of the lattice when the ferroelectric transition occurs. $PbTiO_3$ spontaneous polarization at room temperature is about 70 μC/cm^2, which is almost three times larger than this value for $BaTiO_3$. However, dielectric permittivity value, measured along the polar axis for $BaTiO_3$ at room temperature, lies within the limits of $(2–4)\cdot10^3$, whereas for $PbTiO_3$ it is equal to $(1{,}5–2{,}2)\cdot10^2$ according to Refs. [10,11].

Lithium niobate $LiNbO_3$ is uniaxial ferroelectric with rhombohedral structure ($a = 5.47$ Å, $\alpha = 53.72°$, space group *R*3*c*) and Curie temperature of 1483 K. Though $LiNbO_3$ crystals are not of perovskite structure, they possess the ABO_3 lattice with oxygen octahedrons. The sequence of distorted oxygen octahedrons connected with their faces along the third-order axis *c* is typical for these crystals at room temperature. Unlike perovskite ferroelectrics, the relative displacement of cations from the possible nonpolar sites is very large, which leads to high values of spontaneous polarization (app. 70 μC/cm^2 at room temperature [12,13]).

Thiourea, barium titanate, lead titanate and lithium niobate powders were used for making samples. Powders taken in corresponding volume parts were mixed thoroughly, and samples in the form of tablets (12 mm in diameter, app. 1 mm thick) were pressed under the pressure of 6 t/cm^2. Silver paste was used for electrode deposition. Dielectric measurements were carried out under heating and cooling rate of 1 K/min in the temperature range from 77 to 300 K and frequency from 0.1 Hz to 10 MHz by means of wide-band dielectric spectrometer Novocontrol BDS-80.

3. Experimental data

Dielectric permittivity temperature dependences for thiourea monocrystal and polycrystalline samples are shown in Fig. 1. From the graphs it follows that three phase transitions are observed for the monocrystal: two of them (at 169 K and 176 K) are ferroelectric, and the third one at 202 K is structural. Only two transitions are observed for the polycrystalline sample. There is no maximum at 176 K corresponding to the