Dielectric and thermal studies of rubidium nitrate embedded in the aluminum oxide pores

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The properties of particles in pores can differ significantly from the properties of the corresponding bulk materials due to the influence of size effects and the interaction of the embedded materials with the walls of the pores. The largest number of publications on this topic was devoted to nanocomposites with sodium nitrite, Rochelle salt, potassium nitrate, and triglycine sulphate, embedded into pores. The experimental data obtained show that the most pronounced influence of restricted geometry is near structural phase transitions. The temperatures of ferroelectric transitions, as a rule, shift relative to the Curie points for bulk materials. Usually, the phase transitions also diffuse.

In this work, we present the results of studies of nanocomposites based on rubidium nitrate $RbNO_3$ embedded in porous Al_2O_3 film with a pore size of 300 nm.

Rubidium nitrate is known to have four stable structures at different temperatures. At room temperature, $RbNO_3$ has a trigonal symmetry (phase IV). This phase is stable up to 437 K and according to is pyroelectric with the formation of 180-degree pyroelectric domains. Within the temperature range from 437 to 492 K, rubidium nitrate occurs in the cubic paraelectric phase (phase III), at 437 K, the conductivity of $RbNO_3$ increases by two orders in magnitude, and this phase is superionic. Within the range from 492 to 558 K, $RbNO_3$ is in the rhombohedral phase (phase II). This phase is defined as antiferroelectric. Above the phase transition of 558 K, $RbNO_3$ again transfers into a cubic phase (phase I), which exists up to a melting point of 587 K.

To obtain nanocomposites, we used chemically pure $RbNO_3$ and porous Al_2O_3 films, manufactured by TopMembranes Technology with a cell size of 450 nm, a pore diameter of 300 nm, and a thickness of 50 μm. A SEM image of the porous Al_2O_3 film is shown in Figure 1.

The embedding of rubidium nitrate into the pores was carried out from a heated saturated aqueous solution of $RbNO_3$, after that the samples were dried. The remaining water was removed by heating the samples at a temperature of 420 K during two hours. After repeating the described procedure three times, the degree of pore filling, determined from the change in the weight of the films after filling pores, was no less than 50%. An AND BM-252G balance was used to weigh the samples. Polycrystalline $RbNO_3$ was used as a reference in the form of pellets with a diameter of 10 mm and a thickness of 1.5 mm, obtained by a pressure of 8×10^3 kg/cm^2.

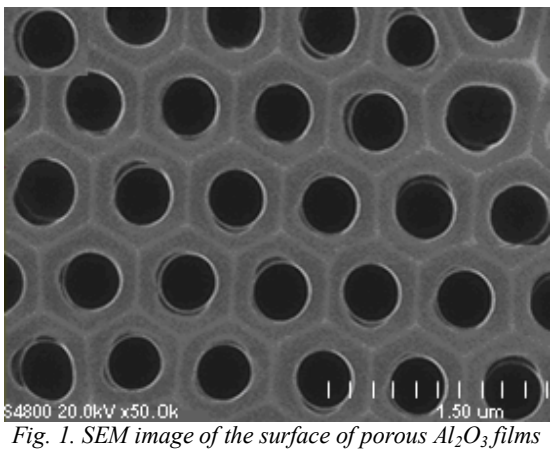

Fig. 1. SEM image of the surface of porous Al_2O_3 films

To measure the complex permittivity, an E7-25 digital immitance meter was used. A Linseis STA PT 1600 thermal analyzer was used to record the DTA signal. The possible emergence of the $RbNO_3$ ferroelectric phase was demonstrated by monitoring the generation of the third and second harmonics when an electric field with a frequency of 2 kHz and strength of 50 V/mm was applied to the sample.

The temperature dependences of the permittivity ε'(T) and the third harmonic coefficient $\gamma_{3\omega}$(T) for polycrystalline rubidium nitrate are shown in Figure 2. The clear anomalies of linear permittivity and abrupt change of the third harmonic coefficient are seen at the phase transition with noticeable thermal of 437 K upon heating and at 422 K upon cooling. The hysteresis.

The phase transition is observed at a temperature third harmonic coefficient has a value of the order of 1%.

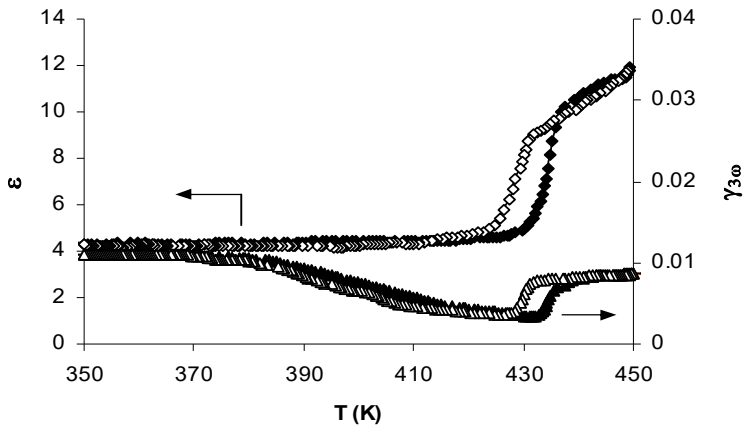

Fig. 2. Dependences of ε'(T) at a frequency of 20 kHz (diamonds) and the third harmonic coefficient $\gamma_{3\omega}$ (triangles) for $RbNO_3$ at a field strength of 50 V/mm. Closed symbols – heating, open symbols – cooling.

Figure 3 shows the temperature dependences of the effective permittivity ε*(T) and the third harmonic coefficient $\gamma_{3\omega}(T)$ for $RbNO_3/Al_2O_3$ composite. As it follows from the graphs, the effective permittivity increases for the composite. The third harmonic coefficient also increases by an order of magnitude. In the cooling mode, two phase transitions are observed on the ε*(T) curve.

The increase of the third harmonic coefficient for the $RbNO_3/Al_2O_3$ nanocomposite indicates indirectly that limiting the size of $RbNO_3$ particles to the nanometer range leads to the rubidium nitrate transition from the pyroelectric to the ferroelectric state.

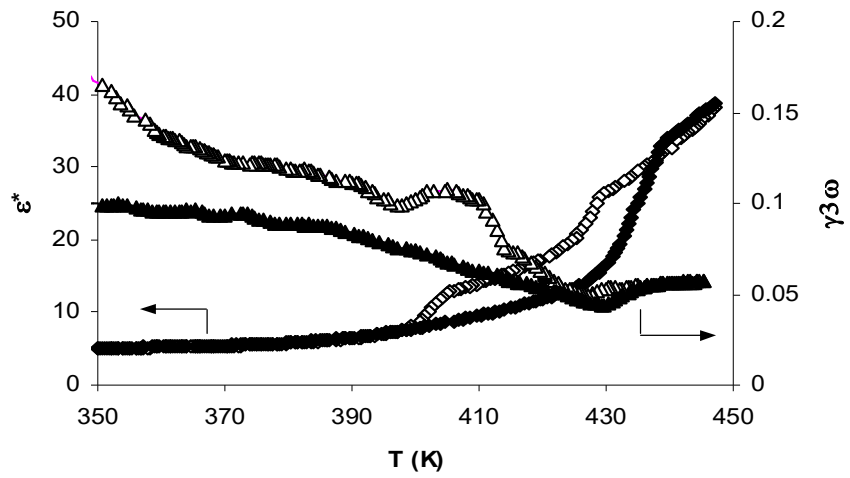

Fig. 3. Dependences of ε(T) at a frequency of 20 kHz (diamonds) and the third harmonic coefficient $\gamma_{3\omega}$ (triangles) for an Al_2O_3 film, filled with $RbNO_3$ at a field strength of 50 V/mm. Closed symbols – heating, open symbols – cooling.*

The DTA data for polycrystalline $RbNO_3$ and $RbNO_3/Al_2O_3$ composite are shown in Figure 4. For a rubidium nitrate polycrystal, the phase transition is observed at 437 K upon heating and at 423 K upon cooling.

The DTA curves for the $RbNO_3/Al_2O_3$ composite clearly show two phase transitions during heating and cooling. This is apparently due to the fact that part of $RbNO_3$ was not embedded into pores of the alumina film and is located on the surface. Phase transitions at about 437 K upon heating and 423 K upon cooling correspond to rubidium nitrate that was not embedded into pores. For $RbNO_3$ in Al_2O_3 pores, the transition temperature decreases down to 434 K upon heating and down to 401 K upon cooling.

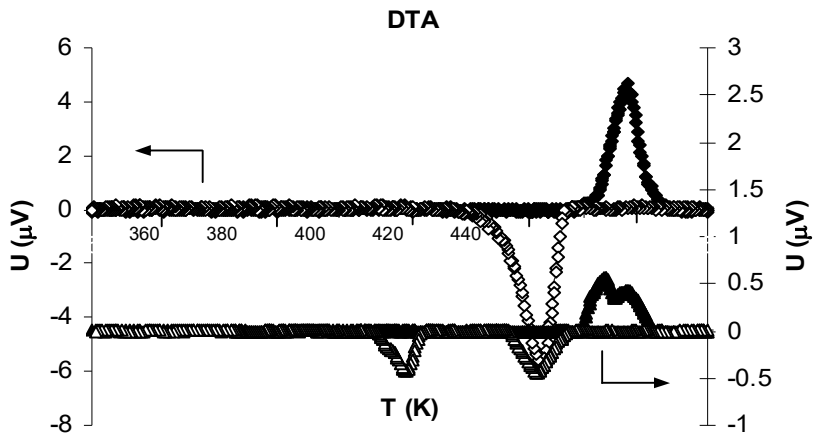

Fig. 4. A DTA signal for polycrystalline $RbNO_3$ (diamonds) and Al_2O_3 film, filled with $RbNO_3$ (triangles). Closed symbols – heating, open symbols – cooling.

To treat the temperature shift of the polymorph phase transition for nanoparticles under nanoconfinement, as a rule, size effect models developed for isolated particles on the base of the phenomenological Landau theory and the Ising model, are used. These models predict the reduction of the polymorph phase transition temperature with decreasing the particle size if the order parameter (for the Landau theory) or the value of the exchange integral (for the Ising model) at the particle boundaries is smaller than in the bulk.

Conclusions

In conclusion, the studies of the temperature dependences of the dielectric permittivity, the third harmonic coefficient, and the DTA signal show that for nanoporous Al_2O_3 matrices with a channel-pore size of 300 nm filled with rubidium nitrate, the polymorph phase transition at T_c≈437 K in bulk shifts by 3 K to low temperatures and the thermal hysteresis loop increases from 14 K (for polycrystalline $RbNO_3$) to 33 K (for $RbNO_3$ in nanoporous Al_2O_3 film).