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Phase transitions and macroscopic properties of $NaNO_3$ embedded into porous glasses

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ABSTRACT

The crystal structure and dielectric response of nanocomposite materials on base of porous glasses with average pore diameters of 320, 46 and 7 nm with embedding sodium nitrate have been studied by neutron diffraction and dielectric spectroscopy in low and high temperature phases up to melting. In porous glasses with 46 and 7 nm pores $NaNO_3$ forms dendrite nanoclusters with "diffraction" sizes of 50(2.5) and 20(2) nm. Decreasing of particle sizes results in decreasing of T_c (temperature of order–disorder orientational transition) and T_{melt} and in smearing of structure phase transition. The values of critical exponent β for orientational transition are estimated from temperature dependences of intensities of superstructure elastic peaks for these three types of nanocomposite materials.

1. Introduction

The physical macroscopic properties of solids in a restricted geometry are of interest from fundamental and applied points of view. The observed phenomena become especially significant if the characteristic sizes of dispersed particles become comparable with the correlation length of the order parameter critical fluctuations. Development of new nanotechnologies stimulates strongly the studies of various nanostructured and ultra-dispersed substances because these nanocomposite materials (NCM) are very perspective for creation of microelectronic and non-linear optic devices. There are various methods of preparation of such dispersed substances and one of them is an intrusion of materials into artificial or natural porous matrices.

For NCM with embedded ferroelectrics and dielectrics very interesting and sometimes surprising results were obtained during the last years. The most remarkable result was the giant growth of dielectric permittivity ε (up to 10^8 at 100 Hz) upon approaching the bulk melting temperature that was observed for $NaNO_2$ embedded in artificial opals and porous glasses [1,2]. Our studies of the temperature evolution of structure of $NaNO_2$ embedded into porous glasses with different average pore diameters have revealed some interesting experimental facts, i.e.:

- The suppression of the incommensurate phase transition (PT) at decreasing of particle sizes (for large pores) [3] and the crossover of the ferroelectric PT from the first-order PT to the second-order one as a function of pore diameter [4,5] for small particles.
- The formation of specific volume "pre-melted state" above T_c accompanied by increasing of unit cell volume, RMS ion displacements, sodium ions mobility and conductivity [6–8].

It was shown that the rotations of planar nitrite anions play the principal role in formation of unusual properties of paraelectric phase but on cooling the ferroelectric PT essentially restricts these rotations.

Dielectric measurements have shown that nanostructured sodium nitrate ($NaNO_3$) demonstrates very high dielectric permittivity (like sodium nitrite) approaching melting temperature [9]. $NaNO_3$ is an ionic-molecular crystal with planar (as $NaNO_2$) anions NO^-_3 but does not undergo ferroelectric PT.

The melting–freezing transition for sodium nitrate embedded into porous glasses with pore radii of 2.5, 5, 10 and 20 nm has been studied by differential scanning calorimetry (DSC) and Raman spectroscopy [10]. The samples were prepared from water solution of $NaNO_3$. The excess water was removed by heating in an oven for 2–3 days at 120 °C. It was estimated that 40% of the pores were filled with the $NaNO_3$ solid. The results were very surprising. It was shown that melting transition for the confined sodium nitrate exhibits a $1/r_p$ dependence where r_p is the pore radius for $r_p > 5$ nm. For $NaNO_3$ within 2.5 nm pores no melting transition has been observed and the authors have suggested that $NaNO_3$ within these porous glasses exists as disordered aggregates, but within glasses with $2.5 < r_p < 20$ nm $NaNO_3$ exists in a new phase stabilized by surface OH groups of the porous silica.

Later DSC measurements of $NaNO_3$ embedded into porous glasses with average pore diameter 320 (PG320) and 46 (PG46) nm have

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shown that the melting temperature decreases with decreasing of pore diameter. As for the orientational PT it becomes diffuse and $C_p(T)$ maximum shifts to lower temperatures at pore size decreasing [11]. Dielectric measurements of $NaNO_3$ within porous glasses with average pore diameter of 12 nm have shown that dielectric spectra are dominated by conductivity, but also weak dielectric dispersion is observed [12] and relaxation time τ decreases sharply approaching T_c. So it is easy to see that the sodium nitrate in a restricted geometry demonstrates unusual structure and dielectric properties, but the temperature evolution of crystal structure of this NCM has not carried out up to now. The principle goal of this contribution was to perform the complex study an effect of restricted geometry on dielectric properties and structure of confined $NaNO_3$.

2. Samples and experiment

Porous glass was obtained by an etching of sodium borosilicate glass with a phase separation. Rectangular glass plates of the size of $10\times10\times0.5$ mm^3 were cut out from the original glass. The obtained porous glasses contained about 90% of SiO_2. The average pore diameters were determined by the adsorption poroscopy and the mercury porosimetry and were 320 nm for PG320, 46 nm for PG46 and 7 nm for PG7. The porosities determined by the mass decrement after leaching were 45% (PG320), 50% (PG46) and 23% (PG7). Sodium nitrate undergoes orientational order–disorder phase transition (not ferroelectric) at 549 K and melts at ~580 K. At low temperature it crystallizes in the order calcite structure (R-3c) with two formula units per unit cell. On heating the structure undergoes a broaden transition (temperature range of nearly 100 K) in R-3m structure. This transition manifests itself as the disappearance of superstructure reflections at the Z points of reciprocal space, i.e. at the (0 0 1.5) point indexed using the hexagonal setting of R-3m. The intensity of superstructure peaks follow the power law $\mathbf{I=I_0\tau^{2\beta}}$, where τ is reduced temperature $\tau=(T_c-T)/T_c$, β is critical exponent. At high temperature the nitrate groups are disordered with respect to 60° reorientations about their threefold axis. $NaNO_3$ was introduced into porous glass from the melt. After filling the surfaces of plates were polished mechanically to remove the remnant of massive $NaNO_3$. In our samples we have avoided the influence of absorbed OH radicals and study the "pure" confined material. The temperature evolution of crystal structure was studied by neutron diffraction on diffractometers E2 and E9 in Helmholtz Zentrum Berlin (HZB) at neutron wavelengths of 2.39 Å and 1.79 Å respectively in temperature diapason of 293–550 K. The dielectric response was studied at frequencies of 0.1 Hz–10 MHz and temperature diapason of 293–570 K using Novocontrol BDS80. The samples with thin gold electrodes are used. Possible remnant water was removed by drying at 380 K into a nitrogen atmosphere.

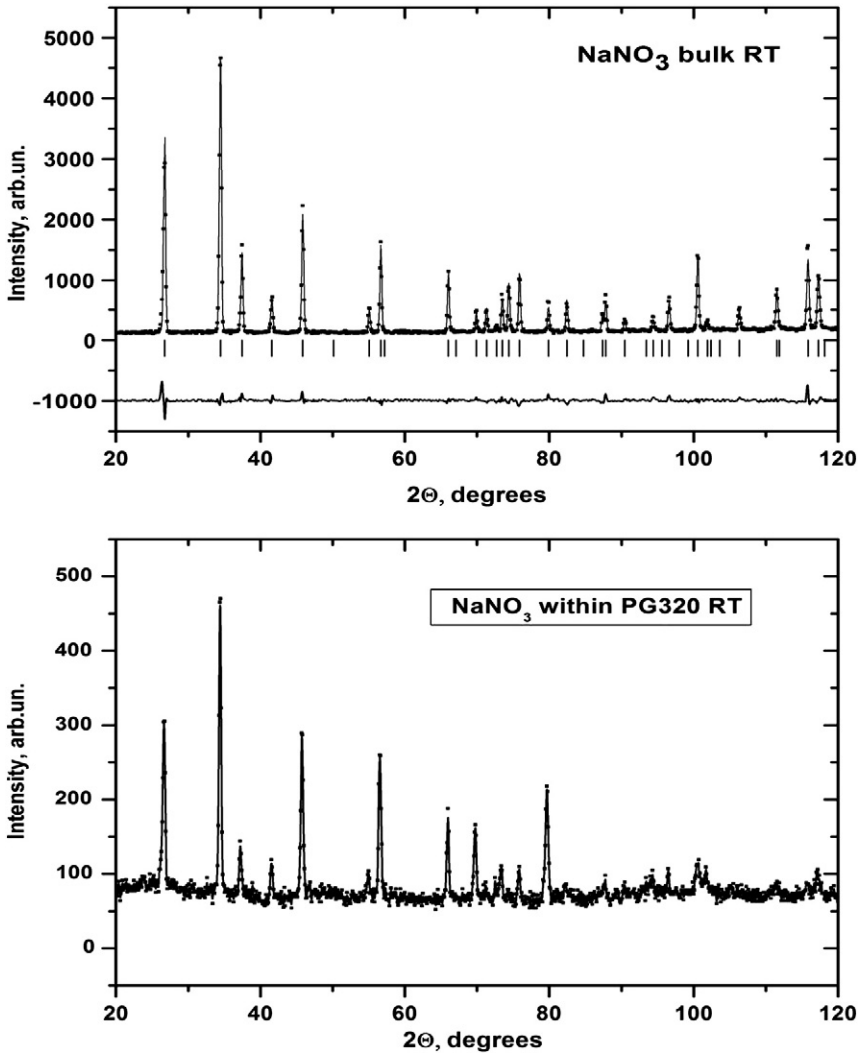

Fig. 1. Diffraction patterns for bulk (upper) and $NaNO_3$ within PG320 (bottom) at room temperature. The vertical bars indicate the positions of reflections.