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LETTER TO THE EDITOR

The giant dielectric constant of opal containing sodium nitrate nanoparticles

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Abstract. The temperature dependence of the dielectric constant of opal containing dispersed sodium nitrate (α - NaNO_2) was measured in the temperature interval from 370 to 600 K. Features associated with the ferroelectric and melting–freezing phase transitions in sodium nitrite particles were observed. A low-temperature shift (~ 10 K) of the Curie point of α - NaNO_2 compared to that of the bulk NaNO_2 was found on cooling, and significant broadening (up to ~ 100 K) of the melting–freezing phase transition was observed. A giant enhancement of the dielectric constant (up to $\sim 10^8$ at 100 Hz) of α - NaNO_2 was found at high temperatures, when the sodium nitrite particles melt, transforming to electrolytic drops.

In the last decade many studies have been devoted to different nanostructures. A number of interesting size effects has been found and new materials based on arrays of nanostructures (mainly semiconducting) have been fabricated. Ferroelectric nanostructures are also interesting, because their polarization, coercive field, Curie temperature and other properties depend on the characteristic sizes of the nanostructures [1–5]. Regular arrays of ferroelectric particles are especially attractive, because they are interesting not only for studying new physical phenomena, but also for potential applications in ferroelectric memories [2].

Recently good progress in preparation and investigation of nanostructures using nanoporous media, namely, zeolites [6], asbestos [7], opal [8] etc has been achieved. In this work we have prepared and studied a regular array of ferroelectric sodium nitrite nanoparticles in a porous opal matrix. The dielectric properties against temperature for this system are presented.

We used synthetic opals which consist of closely packed silica spheres with diameters ~ 200 nm. The structure of opal is described in [8]. α - NaNO_2 (opal containing NaNO_2) was prepared by imbibition of plane-parallel opal specimens (~ 5 mm \times 5 mm \times 1 mm) in the NaNO_2 melt at 550–560 K for 3–6 h. The characterizing size of the particles in the pores of opal is determined by the pore size. The free space of the cubic face-centred opal lattice is a three-dimensional lattice of tetrahedral and octahedral cavities joined through windows [8], the total free space volume fraction being ~ 0.26 . For the cubic face-centred opal lattice consisting of ideal spheres with diameters ~ 200 nm, the linear size of NaNO_2 particles is expected to be ~ 45 nm in the tetrahedral cavities and ~ 80 nm in the octahedral cavities, the window size being ~ 30 nm. The real sizes of the particles should be slightly smaller than the estimated ones because of silica sphere deformation leading to a reduction of the opal free space [8]. The windows are large enough for contacts between the particles from

the neighbouring cavities. Our data on the conductivity of o-NaNO₂ confirm the existence of this kind of contact.

The sample surface was cleaned mechanically from bulk sodium nitrite and washed with ethanol. The capacitance of the sample with graphite electrodes was measured by ZK 4800 or E7-13 RLC meters at 1 kHz or 100 Hz (at 100 Hz the sensitivity of this instrument was not high, and so we could obtain reliable data only for the temperature interval corresponding to high capacitance of the sample). At low temperatures the sample capacitance was also measured by the resonance method (a *Q*-meter type IDN-1 was used). At high temperatures the rate of decay of charging current through the sample was also measured to calculate its capacitance. There was a good agreement between the experimental results obtained by different methods, other conditions being equal. The measurements were performed in atmospheric conditions, and so at temperatures lower than ~370 K a quantity of absorbed water did not allow us to obtain the correct results. At temperatures higher than 370 K, the data have been found to be reliable. The heating or cooling rate in the temperature interval from 370 to 600 K was about 1 K min⁻¹.

The temperature dependences of the dielectric constant of the host opal matrix, ϵ_h , and the guest substance NaNO₂, ϵ_g , are shown in figure 1. The matrix dielectric constant $\epsilon_h \sim 6$ does not depend on the temperature in the investigated interval. ϵ_g displays a peak due to the ferroelectric–paraelectric transition at a temperature ~440 K, the peak value of ϵ_g being $\sim 10^3$.

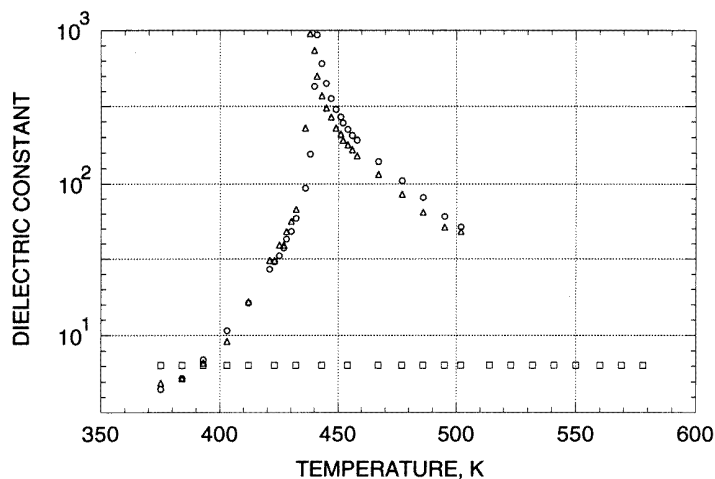


Figure 1. The dielectric constant of the NaNO₂ single crystal along the *b*-axis (○, heating; △, cooling) and opal (□) temperature dependences at the frequency $f = 1$ kHz.

The dielectric constant of the composite material o-NaNO₂, ϵ_c , displays a temperature dependence (figure 2) different from those of $\epsilon_h(T)$ and $\epsilon_g(T)$. A giant enhancement of ϵ_c is observed when the temperature increases. Its value reaches $\sim 10^8$ at low frequencies. Similar enhancement (but only up to $\sim 10^6$ – 10^7) had been observed for electrolyte-saturated porous ceramics and natural rocks. This effect is basically explained in terms of a double electrochemical layer on the surface of dielectric particles immersed in the electrolyte [9, 10], the role of multipolar interaction between neighbouring pores also being important [11]. The mechanism of the giant increase of the dielectric constant of o-NaNO₂ is probably the same as that of ceramics and rocks, and the increase of ϵ_c in the region 450–550 K is associated

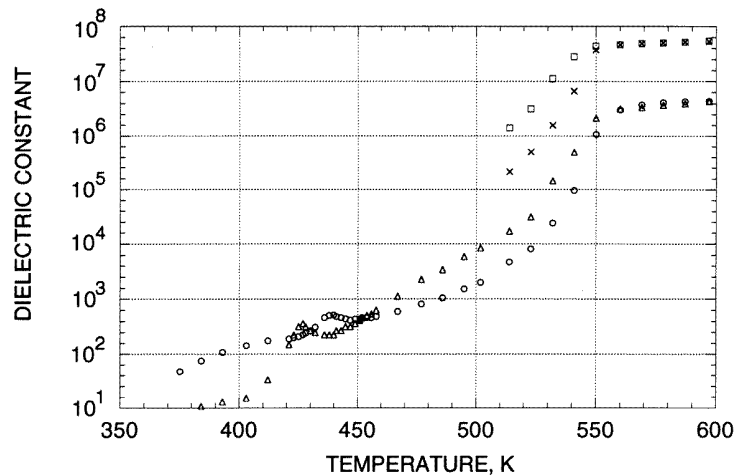


Figure 2. The dielectric constant of *o*-NaNO₂ temperature dependences: ○, heating; △, cooling at the frequency $f = 1$ kHz; ×, heating; □, cooling at $f = 100$ Hz.

with the melting of the dispersed guest substance in the host dielectric matrix, sodium nitrite particles transforming to electrolytic drops.

A broad region between ~ 450 and ~ 550 K (figure 2) should be attributed to the melting–freezing transition of sodium nitrite particles (the bulk NaNO₂ melting temperature is 544 K). The features in the region 420–440 K are due to the ferroelectric transition in sodium nitrite particles. Both phase transitions display a low-temperature shift compared to the corresponding transitions in bulk sodium nitrite and thermal hysteresis between heating and cooling curves. According to our data, the *o*-NaNO₂ dielectric constant displays a peak at 440 K on heating and at 427 K on cooling, corresponding values for the bulk NaNO₂ being 441 and 438 K, respectively. The increase of the thermal hysteresis in *o*-NaNO₂ is quite significant. This increase can be associated with a variety of effects including interphase influence between NaNO₂ and opal and it will be a subject of special study. The significant broadening of the melting–freezing phase transition of NaNO₂ particles which we observe is due to the specific size effects of small particles. This broadening has been discussed in a number of works [12–14] and can be associated with the coexistence of liquid and solid states of a particle in a certain temperature range [13], with quasimolten states [14] and with some other size effects.

To summarize, opal containing a regular three-dimensional array of nanosized sodium nitrite particles displays a number of interesting dielectric properties. Some of them are associated with the occurrence of size effects in the phase transitions of sodium nitrite nanoparticles. The most interesting effect of the giant enhancement of the dielectric constant is associated with the interaction of liquid sodium nitrite particles with each other and with silica spheres of the opal matrix. The resulting value of the dielectric constant of the system $\sim 10^8$ is probably associated also with the regularity of the opal structure. Moreover, this regularity is helpful for the quantitative theoretical consideration of the dielectric properties of the system, which will be presented in future works.

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