Ferroelectric phase transitions in sodium nitrite nanocomposites

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Abstract The structure and dielectric properties of sodium nitrite and its solid solutions confined in porous glasses have been studied. The temperature dependences of the order parameter and the unit cell volume for $NaNO_2$ embedded into porous glasses with different pore sizes were studied by neutron diffraction in the ferro- and paraelectric phases. The characteristic sizes of nanoparticles are determined. It is shown that at a size of nanoparticles smaller than ~50 nm a crossover of the phase transition from first order to second order is observed. The effect of doping of sodium nitrite with potassium nitrite on the dielectric properties of the nanocomposite materials was studied and a strong lowering of the dielectric losses was observed.

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1 Introduction

During the last years studies of confined materials are strongly stimulated by the development of new nano-technologies because these materials demonstrate unique physical properties especially in materials undergoing phase transitions when the characteristic size of dispersed particles becomes comparable with the correlation length of the critical fluctuations of the order parameter. Sodium nitrite can be considered as a model object for studying the physical properties of confined ferroelectric materials (CFM). The properties and structure of bulk $NaNO_2$ in the ferro- and paraphrases are well known and it facilitates a comprehension of microscopic mechanisms leading to the formation of unusual physical properties of CFM. Due to high wetting ability it is possible to produce nanocomposite sodium nitrite on the basis of different porous media with various topology and dimensionality: 3D random dendrite-type (porous glasses) and regular (opals) interconnected nanocaverns, quasi-1D parallel nanochannels (chrysotile asbestos and mobile crystalline material (MCM)-41) etc. Such nanocomposites have been extensively studied by different experimental methods including calorimetry [1], nuclear magnetic resonance (NMR) [2–4], ultrasonic [5, 6] and dielectric [3, 7–10] measurements, Raman [11], X-ray and neutron diffraction [12–15] etc, and very intriguing and surprising results were obtained. In particular it was shown that sodium nitrite ($NaNO_2$) within artificial opals demonstrates a giant growth of ε (up to 10^8 at 100 Hz) at approaching the bulk melting temperature [7]. The structure

refinement of sodium nitrite within porous glasses with average pore diameter 7 nm has shown that in this CFM a specific volume pre-melted state was formed above ~380 K [13, 15]. This pre-melted state has manifested itself in the "softening" of the lattice accompanied by a steep growth of the unit cell volume and the amplitudes of thermal motions of the constituent ions. The "softening" of the lattice and the formation of a pre-melted state were confirmed by NMR measurements of the ^{23}Na spin-lattice relaxation time [4] and measurements of the direct current and alternating current conductivity in this CFM [10, 16].

2 Sample preparation and experimental procedure

Bulk sodium nitrite undergoes a first order phase transition at $T_c \approx 437$ K due to the ordering of the dipole moments of the NO_2 groups along the b-axis accompanied by a displacement of the sodium ions. In the ferroelectric phase $NaNO_2$ has a body centered orthorhombic lattice ($a=$ 3.57 Å, $b=5.578$ Å, $c=5.39$ Å at room temperature) with two molecules per unit cell and belongs to the space group $Im2m$. Between the ferroelectric and paraelectric phases there is a very narrow (~1.5 K) incommensurate phase [17, 18]. Above ~438.5 K a mirror plane perpendicular to the b-axis appears and the space group changes to $Immm$. The melting point of bulk sodium nitrite is 554.1 K.

The samples with nanostructured $NaNO_2$ were produced by immersion of empty vacuum dried porous glasses in the melted $NaNO_2$ for several hours. Due to its high wetting ability, sodium nitrite penetrates the pores and fills about 22–25% of their volume. For the present study we have used porous glasses with three different pore sizes. The pore sizes were tested by mercury intrusion porosimetry and the average pore diameter was found to be of 3±0.5, 7±1 and 20±2 nm. For the dielectric measurements the $Na_{1−x}K_xNO_2$ solid solutions were embedded in the porous glass with 7 nm nominal pore diameter. The samples for dielectric studies were in the shape of flat plates of about $10 \times 10 \times 1$ mm^3 with sputtered gold electrodes.

The structure of CFM was studied using neutron powder diffraction technique with the multidetector powder diffractometer installed on the reactor WWR-M (Petersburg Nuclear Physics Institute, Gathina, Russia) at $\lambda=1.38$ Å and with the diffractometer E9 (Hein-Meitner Institute, Berlin, Germany) at $\lambda=1.796$ Å. The temperature stability was about of ±1.5 K. The diffraction patterns were treated by the FullProf program. The coordinates of atoms, lattice parameters a, b, c, the parameters of thermal motions, etc. were determined. All Bragg peaks were fitted by the pseudo-Voigt function, which is a convolution of Lorenzian and Gaussian.

The low frequency dielectric measurements were carried out with the computer controlled LCR -meter (LCR-819, GoodWill Corp.) in the frequency range 12 Hz–100 kHz. The samples were kept in vacuum to decrease the possible effect of water. The temperature stability was better than 0.5 K.

3 Results and discussion

Typical diffraction patterns for the bulk (a) and $NaNO_2$ embedded into 3 nm porous glasses (b) are presented in Fig. 1. Vertical bars in Fig. 1 (a) indicate the positions of Bragg peaks for the bulk. As one can see, the structure of CFM corresponds to the bulk one but the peaks are visibly broadened due to the size effect. An additional diffuse background due to scattering from porous silica glass is observed. From this background we have determined the nearest Si–O (~1.67 Å) and O−O (~2.37 Å) distances, which are found to be equal to those for the glass silicate tetrahedron SiO_4 and are practically temperature independent up to high temperatures [16].

The broadening of Bragg peaks gives a possibility to extract information about the characteristic size of nanoparticles and of possible elastic stresses. These two contributions have different angular dependences. Having a large enough number of reflections one can determine the contribution of both effects. In our samples we did not observed any broadening due to stresses up to 480 K. The temperature dependences of the average cluster sizes for all CFM are presented in Fig. 2. These values are practically temperature independent up to 480 K. It should be
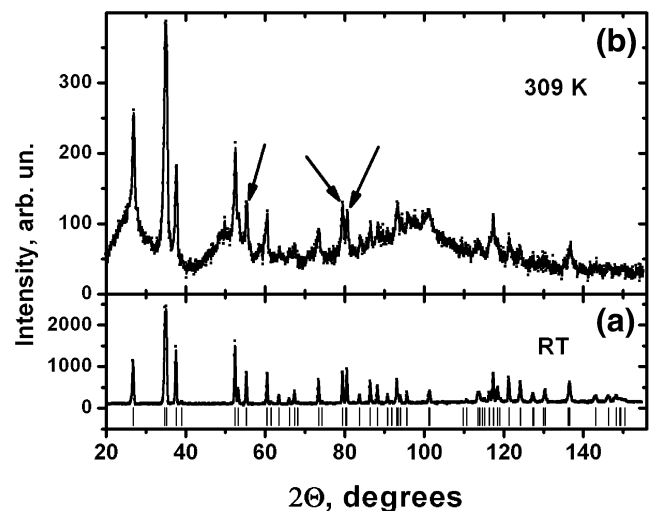

Fig. 1 Neutron diffraction patterns at room temperature for bulk (**a**) and at 309 K for sodium nitrite confined within 3 nm porous glasses (**b**). The arrows indicate the positions of (022), (123) and (132) Bragg peaks
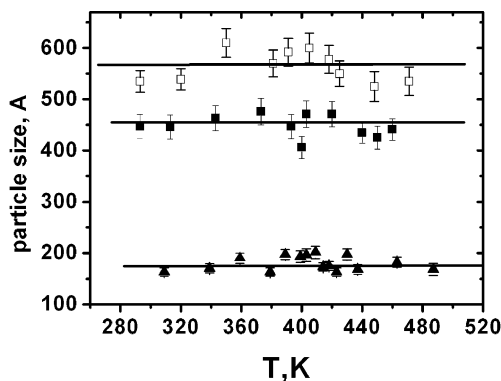
Fig. 2 Temperature dependences of nanoparticle sizes for 30 Å (*black triangles*), 70 Å (*black squares*) and 200 Å (*open squares*) porous glasses

emphasized that in all cases the "diffraction" cluster size is much larger than the pore diameter, i.e. the confined material forms a kind of the "dendrite" clusters. However the increase of the pore diameter from 3 to 7 nm results in a proportional increase of the cluster size, while a further increase of the pore diameter from 7 to 20 nm gives very little effect on the cluster size, i.e. the clusters become more "compact."

In Fig. 3 the temperature dependences of the unit cell volume for all types of CFM and for the bulk are presented. These curves for CFM are visibly different from that for the bulk. The onset of the fast increase of the volume for all CFM is observed at ~380 K, i.e. below T_C, and at high temperature these values exceed the unit cell volume of bulk sodium nitrite in the vicinity of the melting point. Such a behavior can be considered as an evidence of lattice "softening" in CFMs with 3 and 20 nm pores as it was proved earlier for sodium nitrite within 7 nm glasses [4, 14–16]. One
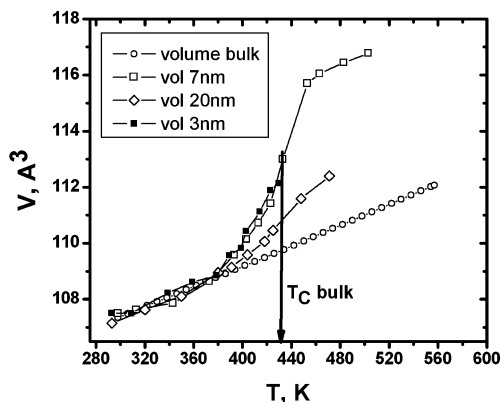
can note that the effect is less pronounced in the case of 20 nm CFM.

It is known [19] that the dependence of the intensity of diffraction peaks on the structure factor for sodium nitrite can be written in the following form

$$|F|^2 = F_{\text{real}}^2 + \eta^2(T) \times F_{\text{im}}^2,$$

where F_{real} and F_{im} are the real and imaginary parts of the structure factor F and η is the order parameter for the ferroelectric phase. For sodium nitrite there are two families of reflections with different dependence on η: the first ones where $F_{\text{im}} \approx 0$ or $F_{\text{im}}^2 \ll F_{\text{real}}^2$ (for example (110), (011), (101) and (200)) are independent from the order parameter, and the second ones (the part of them marked by arrows on Fig. 1 (b)) where $F_{\text{im}}^2 \gg F_{\text{real}}^2$ ((022), (123), (132)). The values of F_{im}^2 and F_{real}^2 for different reflections in the ferroelectric phase are presented in the Table 1. It is easy to see that the intensities of these peaks are practically proportional to $\eta^{\mathbf{2}}$. The obtained temperature dependences of η are presented in Fig. 4. The curves $\eta(T)$ for CFM can be well fitted by a power law $(1 - T/T_c)^\beta$ with $T_C=418.5\pm 3.5$ and 423.6 ± 2.1 K for the 3 and 7 nm porous glasses correspondingly. The critical exponent β is equal to 0.33 ± 0.04 for both CFM. This value of β is in a good agreement with the value (0.362 ± 0.004) obtained for the 3D-Ising model [20], by computer simulation of finite-size scaling for a second order PT. The curve $\eta(T)$ for CFM for the 20 nm porous glass differs principally from those for nanocomposites with 3 and 7 nm pores and looks similar to the dependence obtained for the bulk [19]. Keeping in mind the results of the dielectric study of sodium nitrite within opal [7], where two types of nanocaverns exist with characteristic sizes from 70 nm up to 120 nm (and in which the authors observed a temperature hysteresis of the

Fig. 3 Temperature dependences of the unit cell volume for 30 Å (*black squares*), 70 Å (*open squares*) and 200 Å (*open rhombuses*) porous glasses and the massive sodium nitrite (http://GPEengineeringSoft.com)

Table 1 Real and imaginary parts of the structure factor for sodium nitrite in the ferroelectric phase for different reflections.

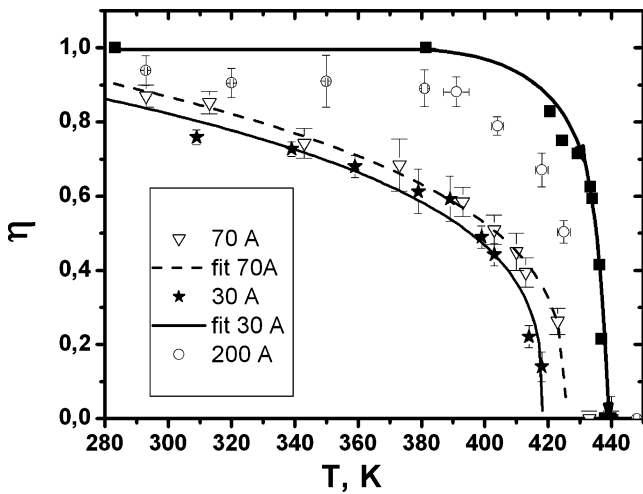| H K L	F^2real	F^2im
0 1 1	2.83	0.02
1 1 0	6.74	0.07
1 0 1	8.17	0
2 0 0	8.18	0
0 2 0	10.82	0.009
1 1 2	0.006	0.687
0 2 2	0.254	3.864
0 1 3	0.01	1.065
1 3 0	0.36	0.266
2 2 0	3.81	0.054
1 3 2	0.054	2.762
1 2 3	0.3	2.718
0 4 2	0.028	5.128

Fig. 4 Temperature dependences of the order parameter for the bulk (*black squares*, a curve draws by eyes) [18] and NaNO$_2$ embedded into porous glasses with average pore diameters 30 Å (*stars*), 70 Å (*open triangles*) and 200 Å (*open circles*)

dielectric permittivity), and our results for the size of nanoparticles and their temperature dependence of the order parameter, one can conclude that at nanoparticle sizes smaller than 50 nm a crossover from a first order PT to a second order one takes place.

Fig. 6 Temperature dependences of tgδ at 12 Hz for three confined samples: pure NaNO$_2$, and NaNO$_2$ with 5 and 10 mol% KNO$_2$

3.1 Dielectric data

The experimental temperature dependences of the real and imaginary parts of the dielectric permittivity of sodium nitrite embedded in 7 nm porous glass are given in Fig. 5. The huge growth of the dielectric response at low frequencies with temperature increase, apparently, is related

Fig. 5 Temperature dependences of the real and imaginary parts of the dielectric permittivity of sodium nitrite confined in 70 Å porous glasses
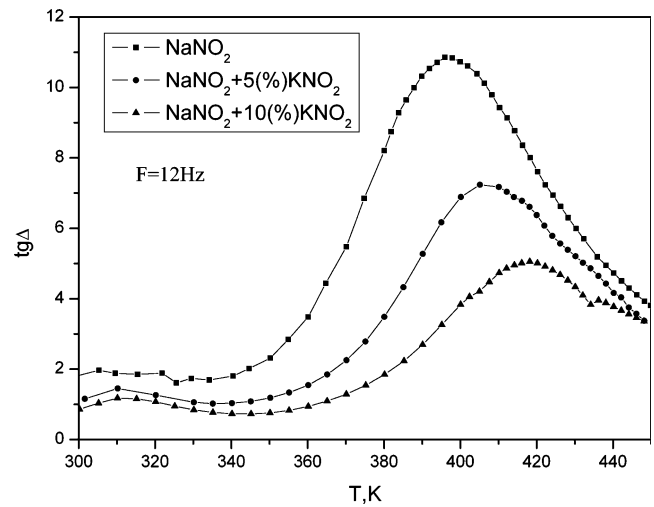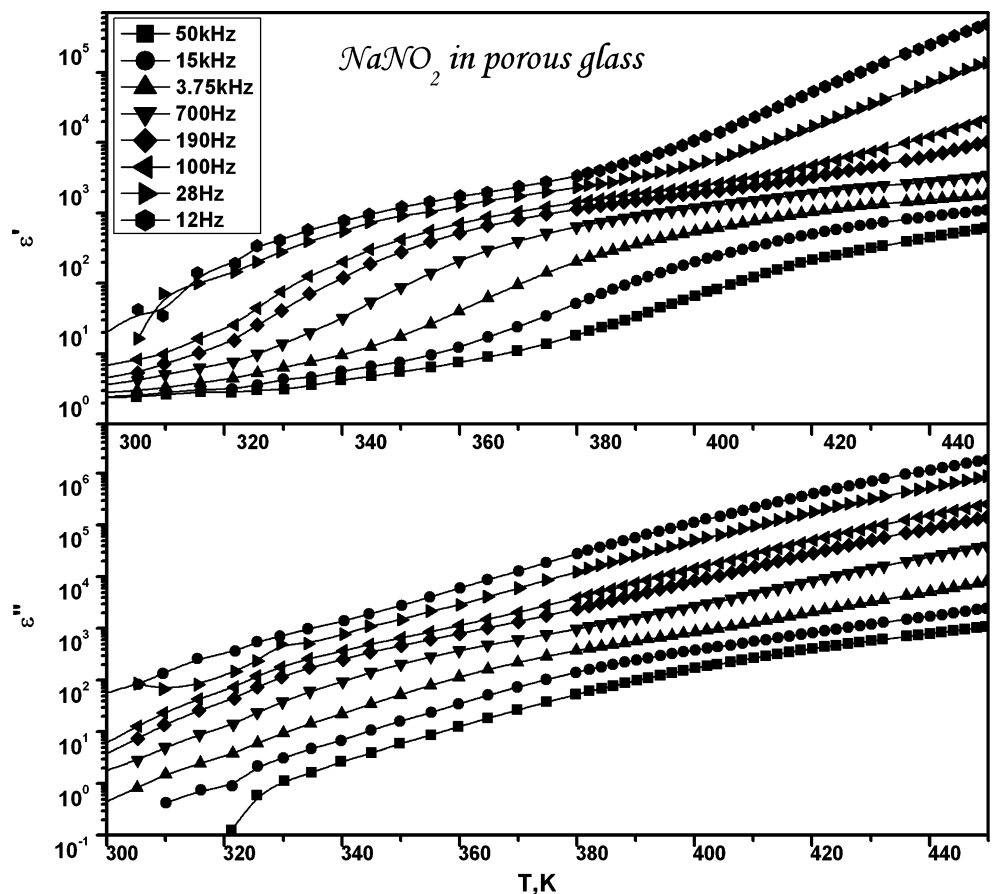
to the nonuniform conductivity of nanocomposites (sharp growth of conductivity in nanoparticles of sodium nitrite in a premelting state and low conductivity of the glass). Unfortunately, because of the complex dendrite system of the glass channels, unlike MCM and opals, until now no exact theoretical model exists for the effective permittivity of such materials. It is possible to perform an analysis of the dielectric spectra using empirical functions [21]. In our frequency and temperature ranges the shape of the dielectric loss spectrum can be well enough described by the sum of two components—the $1/\omega^n$ term related to the conductivity, and the Cole–Cole type term, related to the relaxation contribution. With the increase of temperature the parameter n grows from 0.7 up to 0.9 and tends to 1. That is to a slope which we would have in case of through conductivity. Such behavior is in agreement with the assumption about the formation of a premelting state above 380 K.

For possible applications of such materials, the ratio of the dielectric losses to the real part of ε, i.e. tgδ, is very important. In confined $NaNO_2$ in the region of anomalous high values of ε, tgδ can be more than 10. This essentially decreases the appeal of such confined materials for possible practical applications. Considering that the growth of conductivity in confined sodium nitrite is related to the fast increase of the sodium ion mobility, we have supposed, that the introduction of less mobile ions of potassium into the system could lower the losses, not influencing essentially the structure of the material. It is known, that sodium nitrite forms solid solution with potassium nitrite at all concentrations [22]. We have studied the dielectric response of confined (within 7 nm porous glasses) solid solutions $(NaNO_2)_{1-x}$–$(KNO_2)_x$ with concentrations of potassium 5 and 10 mol%. In general such mixed materials show a temperature and frequency dependences of the real and imaginary parts of the dielectric susceptibility quite similar to those of pure confined sodium nitrite. However, as we have expected, the introduction of potassium has reduced considerably the value of tgδ (Fig. 6) in confined geometry. As a next step, we plan in the near future to produce mixed materials embedded in glasses with smaller pore diameters. We expect that by lowering the pore diameter we will create more "weak links" between the conducting nanoclusters and will suppress the conductivity contribution to the dielectric response.

4 Conclusion

The temperature dependences of the order parameter of nanoparticles of $NaNO_2$ embedded in porous glass with average pore diameters 3, 7 and 20 nm were obtained from a structure refinement of neutron diffraction patterns in the temperature region from room temperature to 480 K, i.e. in the ferro- and paraelectric phases. In all cases the structure of confined sodium nitrite at room temperature corresponds to the bulk $NaNO_2$, but the temperature dependences of the order parameter $\eta(T)$ differ considerably from those observed for the bulk material. For sodium nitrite confined within 3 and 7 nm porous glasses, $\eta(T)$ follows the power law $(1 - T/T_C)^\beta$ with T_C=418.5±3.5 and 423.6±2.1 K, respectively, and with β=0.33±0.04 for both CFM. For $NaNO_2$ within 20 nm porous glass the temperature dependence of the order parameter is very similar to that observed for the bulk and cannot be fitted by a power law. So, the obtained results permit to conclude, that for cluster sizes smaller than ~50 nm (pore diameter 7 nm or less) a crossover from a first order PT to a second order one is observed.

We have studied the dielectric properties of CFM. Dielectric losses for the $(NaNO_2)_{1-x}$–$(KNO_2)_x$ solid solutions with x=0; 0.05 and 0.1 were determined. It is demonstrated, that doping sodium nitrite with potassium nitrite results in a considerable decrease of tgδ. We expect to be able to reduce the still large losses by a change of the pore size. The possibility of a significant decrease of the losses opens up new perspectives for the practical use of such confined materials.

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