

## Order-Parameter Temperature Dependences in Nanocomposites of Porous Glass–Sodium Nitrite

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**Abstract**—Temperature dependences of the order parameter in nanocomposites based on porous borosilicate glasses with mean pore diameters of 20 and 46 nm and filled with sodium nitrite are studied via the diffraction of synchrotron radiation. The mean diffraction sizes of NaNO<sub>2</sub> nanoparticles in the pores of these matrices and the temperatures of the transition of sodium nitrite to the ferroelectric state are determined. It is shown that the phase transition for these nanoparticles remains a first-order phase transition.

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### INTRODUCTION

Nanocomposite materials (NCMs) have been of particular interest lately because they have a number of unusual macroscopic properties that bulk substances and compounds do not have. The emergence of these properties is largely due to a number of fundamental differences between nanoparticles and massive materials:

—The correlation lengths of interactions become comparable to (or even longer than) the characteristic dimension of a particle.

—For ultradispersed particles, the number of atoms in surface layers is comparable to the total number of atoms in a particle.

—The local symmetry of surface atoms differs considerably from the symmetry of a bulk material.

—There is an interface of matrix–embedded material; i.e., there is interaction with the environment or walls of the matrix channel that differs fundamentally from the interaction between the internal atoms of the embedded substance.

A number of ways of creating NCMs have been developed. One is to inject substances (materials) into porous matrices with mean diameters of the channels (pores) ranging from several to hundreds of nanometers. Porous glasses are one such matrix [1]. Different materials can be injected into their pore space (or synthesized inside them). At the same time, the technologies for obtaining these glasses allow the creation of matrices with a pre-controlled mean pore diameter. The pores form a random dendritic three-dimensional

(3D) system of connected end-to-end channels in these glasses; the total porosity of the system can be as high as 40%. Another advantage of these matrices which is important in performing diffraction experiments is that the frame is formed from amorphous silicon dioxide and does not produce sharp diffraction peaks that complicate the analysis of diffractograms.

Sodium nitrite (NaNO<sub>2</sub>) is a ferroelectric of the order–disorder type at room temperature and transitions to the paraelectric phase upon heating to  $T \sim 437$  K. It can be considered a model object when investigating the effect of confined geometry (or the dimensional effect) on the modification of its macroscopic properties and structure. NaNO<sub>2</sub> easily fills the pores of a silicate matrix, both from a solution and from a melt, due to its good wettability. The degree of pore-space filling can therefore be as high as 90–95%. A number of interesting results were obtained earlier for NCMs containing NaNO<sub>2</sub> in pores. It was shown that a sharp increase in dielectric permittivity in the paraelectric phase [2, 3] is observed for such nanocomposite materials. This increase is accompanied by one in the amplitudes of thermal oscillations of atoms [4] and their mobility [5]. It was also found that a crossover of a first-order phase transition to the second one [6, 7] is observed for NCMs based on porous glasses with a mean pore diameter of 7 nm and containing ultra-small (<50 nm) sodium nitrite particles.

The aim of this work was to investigate the temperature evolution of a structure via the diffraction of synchrotron radiation and obtain the temperature

dependence of the order parameter for  $\text{NaNO}_2$  embedded in porous glasses with a mean pore diameter of 20 (porous glasses PG20) and 46 (PG46) nm, since the expected size of sodium nitrite nanoparticles in these glasses should exceed the critical size of 50 nm for which a change in the transition type was observed earlier.

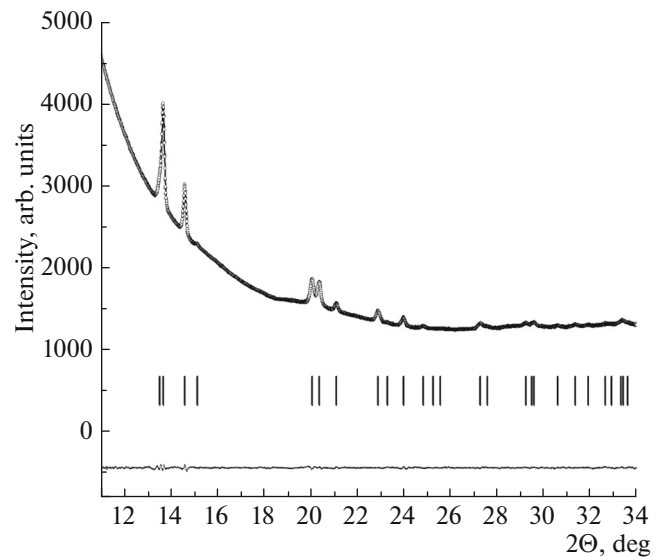
### EXPERIMENTAL

Bulk sodium nitrite is in the ferroelectric phase ( $a = 3.57 \text{ \AA}$ ,  $b = 5.578 \text{ \AA}$ , and  $c = 5.39 \text{ \AA}$ ) with orthorhombic symmetry ( $Im2m$  spatial group) at room temperature and up to  $\sim 436 \text{ K}$ ; the incommensurate phase lies in the region of  $436\text{--}437 \text{ K}$ ; the  $\text{NaNO}_2$  transitions to the paraelectric phase with the  $Immm$  spatial group at a temperature above  $437 \text{ K}$ . Spontaneous polarization in the ferroelectric phase is directed along the  $b$  axis and arises due to the ordering (accompanied by the displacement of sodium ions) of  $\text{NO}_2$  groups at crystallographically equivalent positions that are equally populated in the high-temperature phase. The physical manifestation of the order parameter in this compound is the difference  $\eta = f_1 - f_2$  [8], where  $f_1$  and  $f_2$  are the populations of the crystallographically equivalent positions of the  $\text{NO}_2$  groups. The following relation is generally valid for the intensity of sodium nitrite's elastic peaks [9]:

$$I \sim |F|^2 = F_{\text{re}}^2 + \eta^2(T)F_{\text{im}}^2. \quad (1)$$

Here,  $F_{\text{re}}$  is the real component and  $F_{\text{im}}$  is the imaginary component of the structural factor;  $\eta$  is the order parameter. There are thus two sets of reflections for sodium nitrite with fundamentally different dependences of intensity on the order parameter. For example,  $F_{\text{im}}^2 = 0$  for the (101), (002), and (200) reflections in the scattering of X-rays, and their intensities do not depend on the order parameter.  $F_{\text{re}}^2 \ll F_{\text{im}}^2$  for (022), (222), and (123) reflections; the intensity of these peaks depends mainly on the square of order parameter  $\eta^2$ . This provides a unique opportunity to obtain information on the order parameter's behavior not only from the results of profile analysis, but also directly from the temperature dependences of these peaks' intensities.

Porous glasses PG20 were manufactured at the Ioffe Institute, and porous glasses PG46 were kindly provided by colleagues from the Institute of Physics, Wrocław University of Technology. The glasses (plates with sizes of  $10 \times 10 \times 0.5 \text{ mm}^3$ ) were filled from a melt in vacuum at the Ioffe Institute. After filling, the surfaces of the glasses were thoroughly cleaned of the bulk material's remains, and thin ( $\sim 200$  micron) samples  $\sim 10 \text{ mm}$  in length were made from them. These samples were placed directly in the synchrotron radiation beam. Measurements were made at the BM01 line (ESRF, France, wavelength



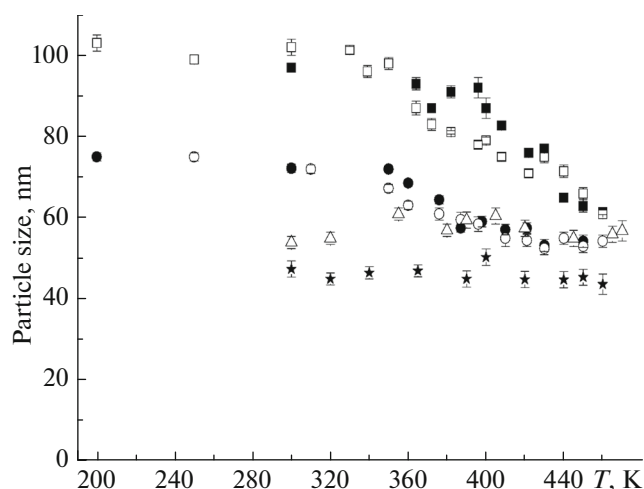
**Fig. 1.** Diffraction spectrum for the PG46 +  $\text{NaNO}_2$  nanocomposite at a temperature of  $330 \text{ K}$ . The line below is the discrepancy between the experimental spectrum and the processing. Vertical strokes are the positions of elastic peaks for the  $\text{NaNO}_2$ . The points and the line passing through them are the experimental data and the processing results, respectively.

$\lambda = 0.703434 \text{ \AA}$ ) in the temperature range of  $100\text{--}460 \text{ K}$  upon heating and cooling. The stability of temperature maintenance was better than  $1 \text{ K}$ . The temperature step near the phase transition was  $2 \text{ K}$ ; all other measurements were made in steps of  $5 \text{ K}$ . The results were processed using the FullProf program for full profile analysis.

### RESULTS AND DISCUSSION

A typical diffraction pattern for the PG46 +  $\text{NaNO}_2$  nanocomposite material obtained at  $330 \text{ K}$  is shown in Fig. 1. The positions of the elastic peaks correspond well to the crystalline structure of sodium nitrite, and the high background level is associated with scattering on the matrix skeleton. We observed no extraneous peaks on the diffractograms; all peaks corresponded to  $\text{NaNO}_2$ . We may therefore state that sodium nitrite with no foreign impurities crystallized in the pores. Note there were no weak peaks corresponding to the incommensurate phase in the vicinity of the phase transition in this experiment. We therefore cannot speak of possible enlargement of this phase's region of existence due to the dimensional effect (or confined geometry).

The Bragg peaks are clearly broadened in all diffractograms, compared to the instrumental line width due to the dimensional effect. The sizes of the  $\text{NaNO}_2$  nanoparticles injected into the PG20 and PG46 matrices at all temperatures upon heating and cooling were determined from the profile analysis. The tem-

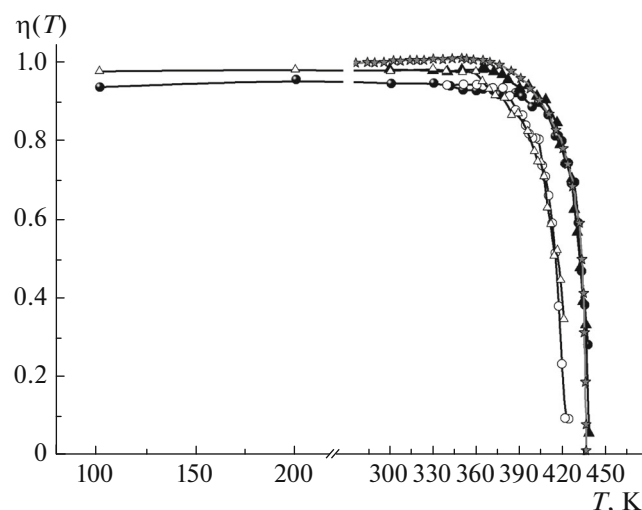


**Fig. 2.** Temperature dependences for the sizes of sodium nitrite nanoparticles in porous glasses of PG7 [10] (black stars), PG20 (white triangles represent neutron data from [10]; black dots (heating) and white dots (cooling) are from data on the diffraction of synchrotron radiation), and PG46 (black squares (heating) and white squares (cooling) are from data on the diffraction of synchrotron radiation). Errors are shown in the figure.

perature dependences of these sizes are shown in Fig. 2. The figure also gives the sizes of sodium nitrite nanoparticles in porous glass with a mean pore diameter of 7 nm, obtained from neutron diffraction data in [10]. The sizes for PG20 + NaNO<sub>2</sub> are 72 (2) nm at room temperature and 54 (2) nm at 460 K in paraelectric phase. The size for PG46 + NaNO<sub>2</sub> is 102 (2) nm in the ferroelectric phase and declines smoothly upon heating to 60 (2) nm at 460 K. We therefore can see that in both cases, the characteristic mean size of sodium nitrite nanoparticles is larger than the mean pore diameter of the corresponding matrix.

Note that the data on the size of nanoparticles in PG20, obtained from neutron diffraction analysis (the white triangles in Fig. 2), coincide quite well with the results from this work, at least in the region of temperatures near the phase transition. A drop in particle size was observed in our experiment for the NCM data at temperatures near the phase transition upon heating. This could be due either to the melting of material on the surface and/or in areas that form weak bonds between adjacent crystallites in the matrix, or to the possible amorphization of sodium nitrite as the phase transition temperature approaches the paraelectric phase. A similar phenomenon (the emergence and increase in the amorphization of nanostructured material) was observed in [11] for, e.g., selenium nanoparticles in the PG7 matrix as the melting temperature approached [11].

The next step in data processing was to obtain the temperature dependences of the order parameter for sodium nitrite nanoparticles in both of the above matrices upon heating and cooling. They are given



**Fig. 3.** Temperature dependences of the order parameter of sodium nitrite nanoparticles in porous glasses PG20 (black dots denote heating; white dots, cooling), PG46 (black triangles denote heating; white triangles, cooling) and for bulk material (grey stars from [9]). Errors do not exceed the sizes of the symbols.

together with the data from [9] for bulk NaNO<sub>2</sub> in Fig. 3 (grey stars). Dependences of  $\eta(T)$  for the PG46 + NaNO<sub>2</sub> and PG20 + NaNO<sub>2</sub> upon heating correspond well to the analogous dependence for bulk sodium nitrite, and the phase transition to the paraelectric phase occurs at  $T \sim 436$  K, as in the bulk material. The intensity of the peaks, depending on the order parameter upon cooling, becomes different from the background at a temperature below 425 K. The  $\eta(T)$  dependences for both types of NCM from 425 to  $\sim 370$  K are virtually identical.

The order parameter for both NCMs at temperatures below 360 K is temperature-independent and coincides with the values observed upon heating. The  $\eta$  value at a temperature of 100 K is 0.98 (1) for the PG46 + NaNO<sub>2</sub> and is 0.94 (1) for the PG20 + NaNO<sub>2</sub>. The  $\eta(T)$  dependences for both types of NCMs and the bulk material in the region of the phase transition upon heating coincide, and there is also a temperature hysteresis with  $\Delta T \sim 10$  K in the behavior of  $\eta(T)$  between the heating and cooling regimes for the order parameter in these NCMs. We may therefore state that the phase transition for these nanocomposite materials remains a first-order phase transition. The small drop in the order parameter of the PG20 + NaNO<sub>2</sub> nanocomposite at low temperatures could be due to nanoparticles with disrupted long-range ferroelectric order lying on the surface. We estimated the possible thickness of the layer in which the long-range order is disrupted using the order parameter's value. We also assumed in the first approximation that the sodium nitrite nanoparticles were cylindrical; i.e., they were stretched along the pore axis (their mean

size was greater than the mean pore diameter). The thickness of the layer was 6 (1) Å (i.e., on the order of one or two parameters of the sodium nitrite cell).

### CONCLUSIONS

Nanocomposite materials containing sodium nitrite, injected into porous glasses with mean pore diameters of 20 and 46 nm, were investigated. The temperature evolution of their structure was studied via the diffraction of synchrotron radiation. The temperature dependences of the order parameter in nanostructured  $\text{NaNO}_2$  were obtained. It was shown that the phase transition to the ferroelectric state remains a first-order transition for these NCMs, while a hysteresis of  $\sim 10$  degrees was observed for both NCMs in the temperature dependences of the order parameter upon heating and cooling. The characteristic sizes of sodium nitrite nanoparticles in the PG20 and PG46 matrices were determined. It was confirmed that there was no crossover of the ferroelectric phase transition's type for sodium nitrite in confined geometry at particle sizes greater than 50 nm.

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