

**Thermal expansion coefficients of NaNO<sub>2</sub> embedded into the nanoporous glasses**O. A. Alekseeva<sup>1</sup>, A. A. Naberezhnov<sup>2</sup>, D. Yu. Chernyshov<sup>3</sup>, A. V. Fokin<sup>2</sup>, A. A. Sysoeva<sup>2</sup>,  
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The temperature evolution of the crystal structure of sodium nitrite nanoparticles has been studied with heating and cooling using synchrotron radiation diffraction. Nanocomposites have been prepared by embedding melted NaNO<sub>2</sub> into the pores of the glasses, average diameters of the pores were 20 nm and 46 nm. Analysis of obtained diffraction patterns has revealed significant difference of the coefficients of thermal expansion (contraction) on heating and on cooling between nanostructured and massive sodium nitrite in the temperature range corresponding to the paraelectric phase. It is confirmed that in these nanocomposites the phase transition from the ferroelectric to paraelectric phase remains the first-order phase transition. Temperature hysteresis of this phase transition is about 10 K.

**Keywords:** ferroelectrics, phase transitions, nanocomposite materials, synchrotron radiation diffraction.

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**1. Introduction**

The physical properties of systems consisting of ultra-small particles, phase transitions and critical phenomena occurring in them have been intensively studied in recent years, since nanocomposite materials, which exhibit unusual electronic, thermal, structural, optical and other properties determined by size and surface effects, are in demand. The main causes for differences in physical properties between nanocomposite and bulk materials are the proximity of lengths of the characteristic interactions and the nanoparticle sizes and the growth of effects of surface atoms on the physical properties of nanoobjects with reduction of their characteristic sizes. Local symmetry and interactions of surface atoms with an environment and matrix walls differ significantly from inherent internal atoms. In recent years, ferroelectric and dielectric nanomaterials attract the steadfast attention of researchers because of the potential of their use as materials for memory elements and/or storage media with high stability and reliability of operation (FeRAM), active optoelectronic devices (tunable photonic crystals), fiber optic communication lines.

One method for nanocomposite materials (NCM) production is intrusion or synthesis of substance into the nanoscale pores of pore matrixes. Porous glass, chrysotile asbestos, artificial opals, zeolites, mesoporous matrix MCM-41 and SBA-15 can be used [1–3] as host matrices for NCM creation. In this contribution, the nanocomposites based on porous glasses are considered. To produce our nanocomposite materials, we have used porous alkali borosilicate glasses. In alkali borosilicate glasses, after special heat treatment, a phase separation takes places on two components: the acid-resistant SiO<sub>2</sub>-enriched phase (SiO<sub>2</sub> skeleton) and chemically reactive phase [4]. Selecting synthetic conditions, such as temperature and initial mixture composition, it is possible to form a system of two interpenetrating phases [4]. After chemical etching of these glasses, the 3D-structure forms. It can be defined as a continuous disordered structure of two interpenetrating percolating phases, namely a network of pores and solids. The pores in the glasses are connected to each other and their average diameter has a small spread (~ 5 – 10 %). Depending on preparation conditions the average pore diameter can vary from 30 to 500 Å. The typical example of porous silicate glass is Vycor industrial glass. The standard chemical composition is 96 % SiO<sub>2</sub>, 3 % B<sub>2</sub>O<sub>3</sub>, 0.40 % Na<sub>2</sub>O, R<sub>2</sub>O<sub>3</sub> ± RO<sub>2</sub> < 1 % (mainly Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>) [5].

NaNO<sub>2</sub> can be considered as a model object for study of crystal structure evolution and modification of macroscopic properties of nanocomposite materials. Ferroelectric properties of sodium nitrite have been studied very well, it can be easily embedded into the different natural and artificial porous matrices due to a good wetting ability. NaNO<sub>2</sub> undergoes the first order phase transition at  $T_C \approx 437$  K. Between the ferroelectric and paraelectric phases there is an incommensurate phase observed over a very narrow (~ 1.5 K) temperature interval.

The dielectric properties of NCM “porous glasses+ $\text{NaNO}_2$ ” have been previously studied [6–10] and the significant rapid growth of NCM dielectric permittivity (up to  $10^8$  at 100 Hz) above  $T_C$  has been observed [6–8] for ultra-dispersed sodium nitrite nanoparticles. It has also been shown that the volume pre-melted state characterized by significant values of thermal vibrations and ion mobilities is formed above  $T_C$  [11, 12]. The temperature dependencies of order parameters for  $\text{NaNO}_2$  embedded into porous glasses with different average pore diameters (3, 7, 20, 46 and 320 nm) have been obtained [12]. It is shown that for nanoparticles with average size less than 50 nm there is a crossover of the phase transition from the first order to the second one.

The goal of this work was to study the peculiarities of thermal expansion and contraction of  $\text{NaNO}_2$  nanoparticles with the average size larger than the critical size ( $> 50$  nm) in a wide temperature interval including ferro- and paraelectric phases.

## 2. Experiment

The studies of structural evolution of NCMs with  $\text{NaNO}_2$  were performed in the temperature interval 100 – 460 K (*i.e.* below and above Curie temperature  $T_C$  of bulk  $\text{NaNO}_2$ ) using synchrotron radiation diffraction (BM01A station, ESRF, France) at  $\lambda = 0.703434$  Å. The temperature step was 2 K in a vicinity of  $T_C$  and 5 K in other regions, temperature stability during the measurements was better than 1 K. The measurements were performed on heating and on cooling. The experimental results were treated by FullProf program. We have used two types of samples: NCM-20 corresponds to  $\text{NaNO}_2$  embedded into porous glass with average pore size of 20 nm (PG20) and NCM-46 corresponds to sodium nitrite into porous glass with an average pore size of 46 nm (PG46). The diffraction patterns of bulk  $\text{NaNO}_2$ , empty PG20 and empty PG46 were measured in the same experimental conditions as the reference samples. In this case, the powder sodium nitrite was placed in a special thin quartz capillary.

Porous glasses PG20 were manufactured at Ioffe Institute, porous glasses PG46 – at Wrocław University of Science and Technology. The glasses (plates with sizes of  $10 \times 10 \times 0.5$  mm<sup>3</sup>) were filled from a melt in vacuum at Ioffe Institute. After filling, the surfaces of the glasses were thoroughly cleaned from the remnants of bulk material and thin ( $\sim 200 \times 200$  micron) parallelepipeds with  $\sim 10$  mm in length were made from them. These samples were placed directly on the synchrotron radiation beam.

## 3. Results and discussion

The typical diffraction pattern for NCM PG46+ $\text{NaNO}_2$  at  $T = 330$  K and results of fitting procedure are shown in Fig. 1. All Bragg peaks correspond to  $\text{NaNO}_2$  structure, and no admixtures were observed. The diffuse background is due to scattering on amorphous  $\text{SiO}_2$ , which forms the skeleton of porous glasses.

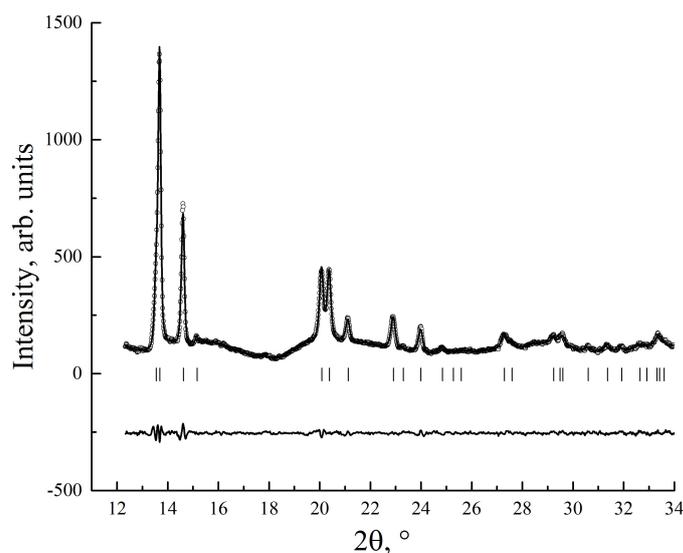


FIG. 1. Diffraction pattern for NCM-46 sample at 330 K. Solid line corresponds to calculated pattern, open circles – experimental data. Vertical bars – Bragg positions, the line in the bottom part is the difference between the experimental data and fitting

Bragg peaks are broadened due to size effect, the sizes of NaNO<sub>2</sub> nanoparticles were estimated from reflection widths at different temperatures. The values for NCM-20 are 72 (2) nm at room temperature and 54 (2) nm at 460 K in the paraelectric phase. The size for NCM-46 is 102 (2) nm in the ferroelectric phase and gradually decreases on heating (60 (2) nm at 460 K) [13].

As a result of fitting procedure we have obtained the temperature dependences of the lattice parameters (Fig. 2) for NCMs and for bulk sodium nitrite. It can be seen that temperature dependencies of  $a$  and  $b$  parameters practically coincide on heating for NCMs and for bulk NaNO<sub>2</sub> (for  $a$  throughout the measurement temperature interval, for  $b$  only in the ferroelectric phase below  $T_C = 437$  K), but above  $T_C$  parameter  $b$  grows faster in NCMs than in bulk NaNO<sub>2</sub>. On cooling  $a(T)$  and  $b(T)$  curves for NCMs lay significantly higher than in bulk material. Moreover one can note that the temperatures, where the dependences  $a(T)$  and  $b(T)$  change the slope due to ferroelectric phase transition, are much lower ( $\sim 10$  K) than in the bulk. It is necessary to note that the pronounced hysteresis loop in the temperature dependences of order parameter reported in our previous works [13] has the same value. A small hysteresis between heating and cooling curves have been observed for the bulk sodium nitrite but its value is noticeable smaller ( $\sim 4$  K) and can be explained by inertia of heating (cooling) of powder sample in a glass capillary.

Parameter  $c$  demonstrates the inverse behavior: for NCM  $c(T)$  curves are close to the bulk one on cooling, but on heating these curves for NCM pass significantly higher than for the bulk NaNO<sub>2</sub>.

Respectively we have observed the fast growth of the unit cell volume on heating above phase transition temperature in NCMs in comparison with bulk material (Fig. 2(b)).

Based on these results, the temperature dependences of the linear and volume thermal expansion coefficients (TEC) in NaNO<sub>2</sub> nanoparticles and bulk NaNO<sub>2</sub> have been calculated (Fig. 3).

Below Curie temperature and far from  $T_C$ , TECs exhibit a weak, close to linear growth on heating. Near the Curie temperature, the anomalies in the temperature dependences of TECs in the form of a characteristic peak are observed. One can note that the positions of TEC anomalies on heating and on cooling for NaNO<sub>2</sub> nanoparticles are significantly shifted against each other. This is in agreement with our data obtained for temperature dependences of order parameter [13], which also shows pronounced temperature hysteresis in these NCMs. It can be also seen that below the Curie temperature, TEC temperature dependences for NCMs and bulk NaNO<sub>2</sub> are quite similar, both on heating and on cooling. In the paraelectric phase, a noticeable difference of TEC values can be seen in the bulk material and in NCMs: upon heating in both NCMs TECs are larger than in the bulk, upon cooling we can see an opposite situation.

The temperature dependences of all parameters in the paraelectric phase of NaNO<sub>2</sub> were approximated by a linear dependence and the average TEC values in this temperature range were calculated. The obtained values are presented in Table 1.

It can be seen a significant difference in TEC values for NaNO<sub>2</sub> nanoparticles in both NCMs on heating and on cooling, which is not observed in the bulk material. This difference can be associated with a formation of specific pre-melted state above  $T_C$ , described in the papers for similar NCM on base of porous glasses with average pore diameter 7 nm [14] and for NCM on base of mesoporous sieves MCM-41 and SBA-15 [15]. This state takes place at temperatures significantly (about 100 degrees) below the melting point of NaNO<sub>2</sub> embedded into the porous glass and is characterized by anomalously large amplitudes of atomic thermal vibrations reaching the values exceeding Lindemann's criteria for melting. This causes a sharper growth of unit cell parameters and volume in NaNO<sub>2</sub> nanoparticles compared with the bulk material on heating and a significant difference between the corresponding TEC values on cooling.

#### 4. Conclusion

The temperature evolution of crystal structure of NaNO<sub>2</sub> embedded in the porous glasses with average pore sizes 20 and 46 nm have been studied upon heating and cooling. It is shown that the linear and volume thermal expansion coefficients of NaNO<sub>2</sub> nanoparticles in the paraelectric phase differ essentially from these parameters that characterize bulk sodium nitrite. The pronounced thermal hysteresis of lattice parameters and TECs have been observed on heating and on cooling. The value of thermal hysteresis ( $\sim 10$  K) does not depend on nanoparticle sizes for these NCM and corresponds to the hysteresis observed in temperature dependences of order parameter for these NCM in the paper [13]. It confirms the statement that the phase transition from a ferroelectric to a paraelectric phase remains a first-order phase transition. The observed differences in TEC between NCM and bulk NaNO<sub>2</sub> in the paraelectric phase can be associated with formation of pre-melted state in nanostructured sodium nitrite above its Curie temperature.

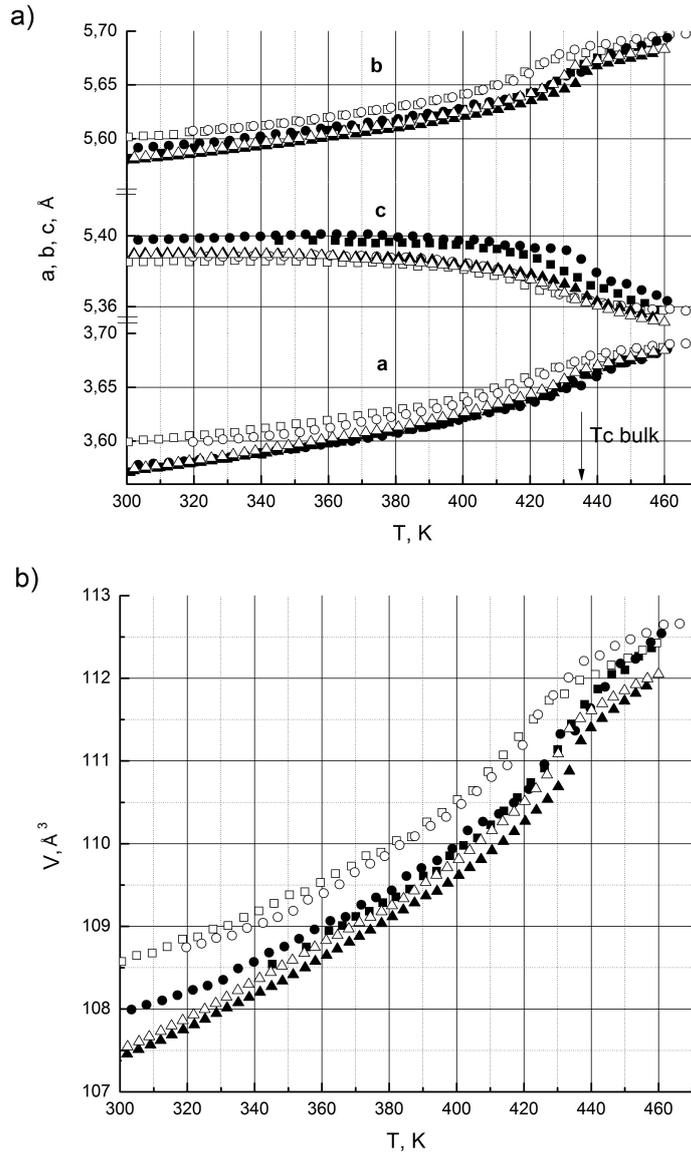


FIG. 2. Temperature dependencies of lattice parameters (a) and unit cell volume (b) for NCM-20 (circles), NCM-46 (squares) and the bulk  $\text{NaNO}_2$  (triangles) on heating (filled symbols) and on cooling (open symbols)

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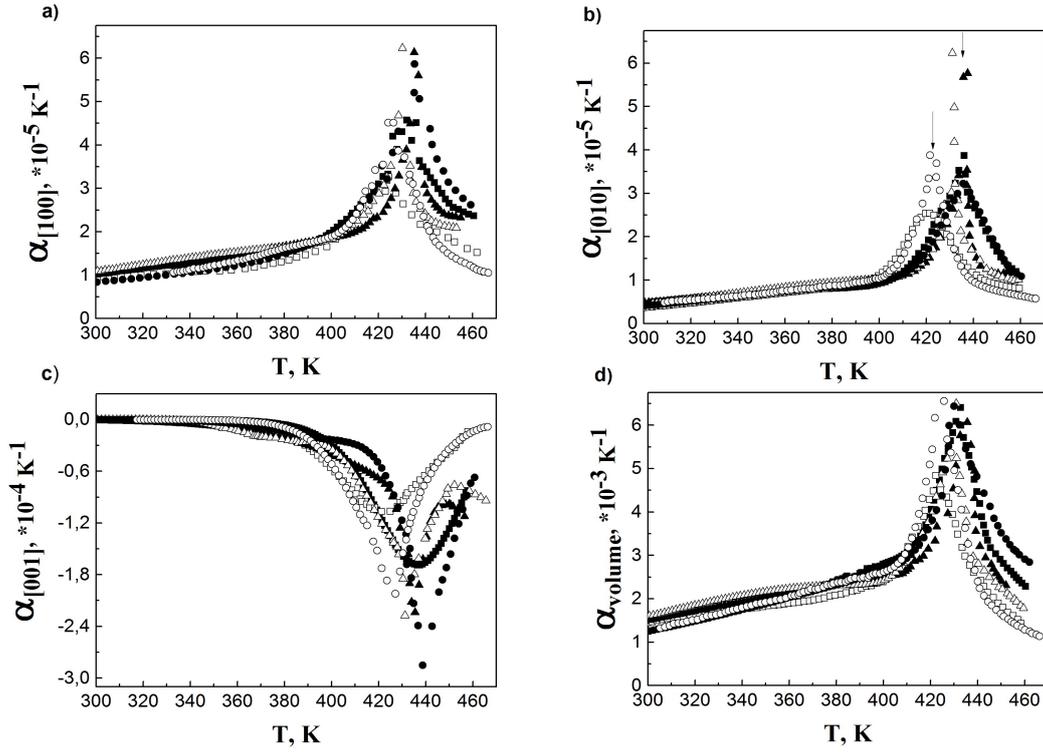


FIG. 3. Temperature dependences of the linear and volume thermal expansion coefficients (TEC) of  $\text{NaNO}_2$  nanoparticles obtained by incorporation into the pore space of nanoporous glasses with an average pore diameter of 20 (circles) and 46 nm (squares), and of bulk  $\text{NaNO}_2$  (triangles) on heating (filled symbols) and on cooling (open symbols). The arrows in Fig. 3(b) indicate  $T_C$  on heating and cooling obtained from temperature dependences of order parameter [13]. Errors do not exceed the symbol size

TABLE 1. The linear and volume thermal expansion (contraction) coefficients of  $\text{NaNO}_2$  nanoparticles and of bulk  $\text{NaNO}_2$  in the paraelectric phase

	TEC	$10^{-5} \text{ K}^{-1}$	
		heating	cooling
bulk $\text{NaNO}_2$	$\alpha_a$	$26 \pm 1$	$22 \pm 1$
	$\alpha_b$	$12 \pm 1$	$10 \pm 1$
	$\alpha_c$	$-10 \pm 1$	$-9 \pm 1$
	$\alpha_{vol}$	$28 \pm 1$	$25 \pm 1$
NCM $\text{NaNO}_2$ +PG46 nm	$\alpha_a$	$28 \pm 1$	$16 \pm 1$
	$\alpha_b$	$15 \pm 1$	$9 \pm 1$
	$\alpha_c$	$-13 \pm 1$	$-6 \pm 1$
	$\alpha_{vol}$	$31 \pm 1$	$19 \pm 1$
NCM $\text{NaNO}_2$ +PG20 nm	$\alpha_a$	$32 \pm 1$	$14 \pm 1$
	$\alpha_b$	$20 \pm 1$	$8 \pm 1$
	$\alpha_c$	$-15 \pm 1$	$-5 \pm 1$
	$\alpha_{vol}$	$38 \pm 1$	$18 \pm 1$

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