Structure and properties of confined sodium nitrite


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Abstract. The temperature evolution of the structure of NaNO$_2$ nanocomposite ferroelectric material in a porous glass with 7 nm pores was studied by neutron diffraction in temperature region from room temperature up to the melting, i.e. in the ferro- and paraelectric phases. It is demonstrated that in the ferroelectric phase the structure is consistent with the structure of the bulk, but above the ferroelectric phase transition (and up to $\approx$ 513 K) a volume premelted state is formed, manifesting itself in a growth of amplitudes of ion thermal vibrations, a steep increase of elementary cell volume and “softening” of lattice. For the first time the temperature dependence of order parameter $\eta$ for confined sodium nitrite is determined, $\eta (T)$ follows a power law with $T_C = 425.6 \pm 2.1$ K and $\beta = 0.31 \pm 0.04$, which is essentially different from that for bulk NaNO$_2$. Our obtained data are in a good agreement with the results of earlier dielectric and neutron diffraction measurements.

PACS. 77.84.Lf Dielectric, piezoelectric, ferroelectric, and antiferroelectric materials – 61.43.Gt Powder, porous materials – 61.12.Ld Neutron diffraction

1 Introduction

It is known that finite-size effects result in drastic changes of physical properties of dispersed materials. The study of such materials is not only of fundamental interest but also of practical importance. During recent years these studies are strongly stimulated by development of new nanotechnologies because these materials demonstrate unique physical properties. One can expect the observed phenomena to become especially significant if the characteristic size of the dispersed particles becomes comparable with the correlation length of the order parameter critical fluctuations. There are different methods of preparation of such dispersed substances and one of them is an intrusion of materials into artificial or natural porous matrices. Such nanocomposites (so-called confined materials (CM) or materials in a restricted geometry) and phase transitions (PT) in these CM have been extensively studied by different experimental methods including calorimetry [1,2], NMR [3], ultrasonic [3,4] and dielectric [5,6] measurements, Raman [7], X-ray [8,9,10] and neutron diffraction [11,12,13,14] etc. Very interesting and sometimes surprising results were obtained. In particular, the dielectric measurements of NaNO$_2$ in a porous glass have shown the unexpected growth of the real and imaginary parts of the dielectric susceptibility $\epsilon$ above the temperature $T_C$ of the ferroelectric PT [15]. In such a situation the increase of the imaginary part of $\epsilon$ could be attributed to an appearance of conductivity, but in this case the microscopic origin of such conductivity was absolutely unclear. The most remarkable result was the giant growth of $\epsilon$ (up to $10^9$ at 100 Hz) upon approaching the bulk melting temperature that was observed for NaNO$_2$ embedded in artificial opals. The authors have suggested that this phenomenon is related to the extremely broadened melting process [5], but this suggestion remained without any experimental confirmation. These experimental results were the starting point for a detailed study of the temperature evolution of structure of confined NaNO$_2$. Our measurements [16,17] have shown that below $T_C$ the structure of embedded sodium nitrite corresponds to the bulk one, but above the bulk $T_C$ a volume premelted state is formed, manifesting itself in a steep growth of the thermal motion parameters and an increase of lattice volume. The present paper is devoted to the clarification of two essential questions, the temperature dependence of the order parameter and the region of existence of the premelted state, that were unanswered in our previous papers.

2 Sample

Sodium nitrite belongs to the order-disorder ferroelectrics and undergoes the first order phase transition at $T_C \approx 437$ K. At room temperature (RT) NaNO$_2$ has a body centered orthorhombic lattice ($a = 3.57$ Å, $b = 5.578$ Å, $c = 5.39$ Å) with two molecules per unit cell, and its space group is $Im2m$. In the low-temperature
ferroelectric phase the spontaneous polarization points along the b-axis and appears due to a partial alignment of NO₂ groups along this axis, accompanied by the displacement of sodium ions. At high temperature (above \( T_C \)) a mirror plane perpendicular to the b-axis appears and the space group changes to \( \text{Immm} \) [19]. Bulk sodium nitrite melts at 554.1 K. The porous samples with embedded NaNO₂ were obtained by immersion of pure porous glass into the melted NaNO₂ and then stood there during several hours. Due to high wetting ability sodium nitrite penetrated into the pores and filled their volume. The total volume amount of embedded NaNO₂ reached 25%. The pore sizes were tested by the mercury intrusion porosimetry and the average pore diameter was found to be 7 ± 1 nm.

3 Experiment

The study of structural evolution of nanocomposite NaNO₂ was performed in the temperature region RT - 523 K, i.e. below and above temperature of the ferroelectric phase transition, on neutron powder diffractometers G4-2 (LLB, Saclay, France) at \( \lambda = 2.3434 \) Å and D20 (ILL, Grenoble, France) at \( \lambda = 2.41 \) Å. The temperature stability was better than ± 1 K for G4-2 and D20. The experimental results were treated by the FullProf program [20], and coordinates of atoms, lattice parameters \( a, b, c \), parameters of thermal motions \( \beta_{ij} \) of constituent ions, root mean square (RMS) ion displacements etc. were determined.

The typical diffraction patterns at 300 K, 420 K and 460 K (above \( T_C \)) are presented in Figure 1. At all temperatures the structure of embedded sodium nitrite corresponds to the orthorhombic structure of the bulk NaNO₂, but in addition to normal diffraction peaks a diffuse background due to scattering on porous silica glass is observed also. The observed diffraction peaks are slightly asymmetric, with width larger than the instrumental resolution, but clearly smaller than the value expected for scattering on isolated 7 nm particles. The average size (≈45 nm) of clusters was determined from the structure refinement and was found to be practically temperature independent up to 460 K. Heating through \( T_C \) results in the decrease of intensity of most of the peaks at large scattering angles \( 2\theta \), i.e. at large \( h k l \), and this effect is much stronger than in the bulk material. Above 523 K we did not observe any diffraction peaks corresponding to the sodium nitrite structure, i.e. nanocomposite NaNO₂ melted entirely below the melting temperature for the bulk materials. Upon subsequent cooling to RT the diffraction peaks were restored completely.

4 Discussion

4.1 Ferroelectric phase

As mentioned above, one of the important questions is the temperature dependence of the order parameter. In the case of NaNO₂ there are two principal distinguishing groups of Bragg peaks. As it has been shown [21,22], the intensity of diffraction peaks is proportional to

\[
|F|^2 = F_{\text{re}}^2 + \eta^2(T) \times F_{\text{im}}^2,
\]

where \( F_{\text{re}} \) and \( F_{\text{im}} \) are the real and imaginary parts of the structure factor \( F \), and \( \eta \) is the order parameter for the ferroelectric phase. The values of \( F_{\text{re}} \) and \( F_{\text{im}} \) presented in Table 1 are calculated with positions of Na, N and O obtained from our structure refinement at RT.

The intensities of underlined reflections are practically order parameter independent below \( T_C \) (Fig. 2a), but the intensities of the second group (bold indices) strongly depend on \( \eta \) (Fig. 2b). It provides a unique possibility to determine the temperature dependence of the order parameter \( \eta \) in the ferroelectric phase directly from intensities of these Bragg peaks. The value of \( \eta \) was determined from the intensities of (022), (132) and (132) reflections, for which \( F_{\text{im}}^2 \gg F_{\text{re}}^2 \). The obtained temperature dependence is given in Figure 3 (dashed line), where the solid line presents the analogous dependence for the bulk material [22]. It is easy to see that in the case of confined sodium nitrite this dependence differs significantly from that for...