

Temperature Evolution of Sodium Nitrite Structure in a Restricted Geometry

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The NaNO_2 nanocomposite ferroelectric material in porous glass was studied by neutron diffraction. For the first time, the details of the crystal structure including positions and anisotropic thermal parameters were determined for the solid material, embedded in a porous matrix, in ferro- and paraelectric phases. It is demonstrated that in the ferroelectric phase the structure is consistent with bulk data, but above transition temperature the giant growth of amplitudes of thermal vibrations is observed, resulting in the formation of a “premelted state.” Such a conclusion is in good agreement with the results of dielectric measurements published earlier.

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Introduction.—The problem of the physical properties of materials in a restricted geometry is one of the “hot” points of modern solid state physics and is not only of fundamental interest but also of practical importance. Along with films, filaments, etc., there is a large and important group of restricted geometry objects, namely, materials confined within porous media [hereafter we will call them confined materials (CM)]. In recent years, properties of CM and, in particular, various types of phase transitions (PT) (superconducting [1,2], superfluid [3,4], melting-freezing [5–11], and other PTs [12–22] in different CM) have been extensively studied by calorimetry [5,7,20], NMR [9,21], ultrasonic [8,9] and dielectric [12,14,15] measurements, Raman [10,13], x-ray [12,16–18], and neutron scattering [10,14,22–26], differential thermal analysis [19], etc. It has been shown that CM can form either a system of isolated particles [10] or a net of interconnected dendrite clusters [14], and their physical properties differ drastically from those in corresponding bulk samples and strongly depend on different characteristics of porous matrices and embedded substances such as pore size and geometry, wetting ability, surface tension, interaction between CM and the surface of the host matrix, and so on.

Finite-size effects in ferroelectrics were observed for the first time at the beginning of the 1950s [16]. It was shown that the physical properties of dispersed ferroelectrics are significantly different from those of the bulk materials, in particular, when the characteristic size becomes comparable with correlation length of the order parameter critical fluctuations. In detail, the modern theoretical and experimental situation is well described in the review [27] and references therein. During the past few years, the development of new nanotechnologies gave the strong impetus to the study of ferroelectric microcomposites as a new basis of ferroelectric memories or an active component in fine-composite materials; however,

the principal attention was devoted to the thin films or granular ferroelectrics. On the other hand, the very interesting and surprising results were recently obtained for ferroelectric CM. In particular, the dielectric measurements of NaNO_2 , KH_2PO_4 (KDP), and Rochelle salt confined in different porous matrices have shown [14,15,28] the growth of dielectric permittivity ϵ above the temperature of the ferroelectric phase transition T_c for all materials and all matrices and an unexpected increase of T_c at decreasing of characteristic size D for KDP. The most remarkable result was the giant growth of ϵ [up to 10^8 at 100 Hz (the record value)] at approaching the bulk melting temperature ($T_{\text{melt}} = 554$ K) that was observed for NaNO_2 embedded into an artificial opal matrix [15]. The temperature dependence of ϵ in the CM case essentially differs from analogous dependence for the bulk NaNO_2 [29] typical for classical ferroelectrics, and this giant growth of ϵ was attributed to the extremely broadened melting process [15], but no experimental evidence was presented.

We have attempted to study the temperature evolution of the structure of confined NaNO_2 in porous glass with a pore size 7 nm at temperatures below and above T_c by neutron diffraction to clarify the microscopic origin of observed anomalies of ϵ . This method was successfully used for the study of structure evolution of water, cyclohexane [23–26], and liquid mercury [10] confined within porous media at melting-freezing PT, but no diffraction study of microcomposite ferroelectric materials (except our preliminary results [14]) were performed earlier. Moreover, we do not know of any paper dealing with the detailed structure refinement (including determination of thermal parameters) of any confined solid materials.

Results.—The samples were prepared by the immersion of the preliminary warmed up platelets of the porous glass in the melted NaNO_2 in the sealed quartz container. The glass samples were tested by the mercury intrusion

porosimetry and the pore sizes were found to be 7 ± 1 nm. The volume amount of the salt was about 25%. Measurements were performed on the powder diffractometer G4-2 (LLB, Saclay, France) at 2.3434 \AA at room temperature (RT), 400, 420, 440, 450, and 460 K, i.e., below and above ferroelectric PT temperature $T_c \approx 438$ K. The diffraction patterns for 420 K (ferroelectric phase) and 460 K (paraelectric phase) are presented in Fig. 1. The diffuse background observed in addition to the normal diffraction peaks due to porous silica glass was used to determine the nearest Si-O and O-O distances. These parameters were found to be almost equal to those for glass silicate tetrahedron SiO_4 [30] and were practically temperature independent; therefore the cavity sizes in the host glass matrix do not depend on temperature. The observed diffraction peaks corresponding to the orthorhombic structure were slightly asymmetric with the width larger than the instrumental resolution, but much smaller than the value expected for the scattering on the isolated 7 nm particles. It leads to a conclusion that due to high wetting ability the sodium nitrite forms a kind of interconnected cluster probably of the dendrite type. Their average size was found from structure refinement to be about 45 nm and was practically temperature independent. This situation is quite different from the case of nonwetting compounds such as the liquid mercury, which forms on cooling a system of independent particles with characteristic size equal to the average pore diameter [10].

The diffraction patterns in the ferroelectric phase were fitted in the frames of the $Im2m$ space group and, following the paper [31], a pseudomirror plane perpendicular to the b axis was included at $y = 0$ to take into account incomplete ordering of the NO_2 groups. In this case, the long-range order parameter can be determined as $\eta = f_1 - f_2$ [31], where the fraction f_1 of the NO_2 groups was placed on one side of the plane and $f_2 = 1 - f_1$ on the other side.

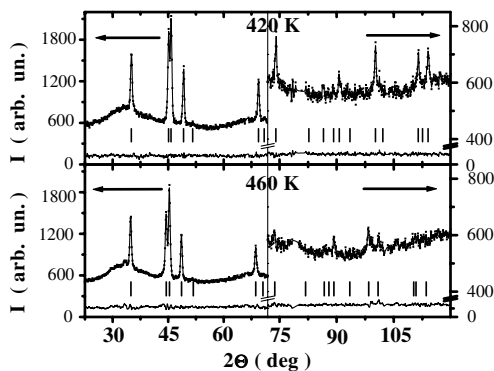


FIG. 1. Neutron diffraction patterns for NaNO_2 in porous glass at 420 K (ferroelectric phase) and 460 K (paraelectric phase). The right sides present diffraction patterns at large 2θ in enlarged scale.

Below T_c , our results are in good agreement with published data for the bulk NaNO_2 ; however, the anisotropic thermal parameters β_{ij} are slightly higher than for the bulk [31]. The diffraction patterns above T_c correspond to the paraelectric phase with space group $Immm$. The heating through T_c results in the decrease of intensity of most of the peaks. The observed effect is much stronger than that in the case of bulk NaNO_2 [31] and is in agreement with our earlier data [14].

Discussion.—The results of the refinement procedure have revealed two main distinguishing features of the temperature evolution of the structure of embedded sodium nitrite.

The first one is the essential increase of unit cell volume upon passing through T_c (inset of Fig. 2). Here, one can note that a similar phenomenon was observed for the overwhelming majority of different materials at melting [33]. The detailed analysis of temperature dependences of lattice parameters a , b , and c shows that in the ferroelectric phase the confined NaNO_2 expands in the a and b directions and contracts in the c direction similar to the bulk material, but above T_c the lattice parameters a and b increase rapidly and c decreases slowly than in the bulk. As far back as 1961, Nomura [29] had shown that the misalignment of the NO_2 anion is responsible for the anomalous thermal expansion in the b direction (along macroscopic polarization). He had also supposed that the expansion in the a direction and the contraction in the c direction could be explained by rotation or rotational vibration about the arbitrary axis of the nonspherical NO_2 group, which holds its long axis parallel to the c direction in the equilibrium. Later Takahashi and Kinase [34] proposed the microscopic mechanism of the ferroelectric PT and showed that the mixed type of NO_2 group rotation around the a and c axes was achieved. They also showed that in the ferroelectric phase there are potential barriers which have strong angular dependences and limit the rotation of the NO_2 around the a and c axes. In terms

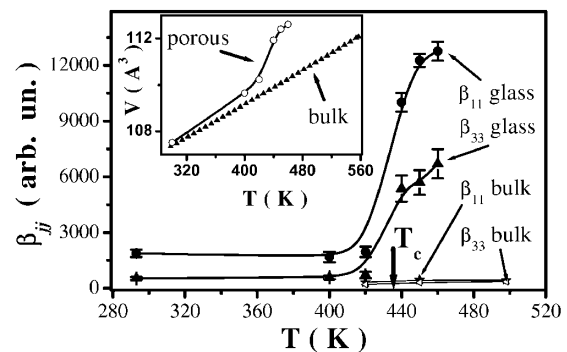


FIG. 2. Temperature dependences of thermal parameters β_{ij} for oxygen for bulk [31] and porous samples. Inset: temperature dependences of unit cell volume for bulk [32] and CM are presented. Vertical arrow indicates temperature of ferroelectric PT for the bulk.

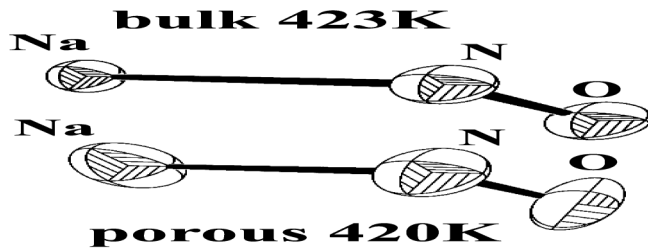


FIG. 3. 50% ellipsoids of thermal vibrations for bulk and porous samples at 420 K (below T_c).

of such a model, the observed behavior of unit cell parameters could be explained by the increase of these rotations above T_c , experimentally displaying as a growth of thermal vibrations of ions. Indeed, the second distinguishing feature is the steep growth of the thermal parameters β_{ij} (Fig. 2) above T_c pointing out the “looseness” (or softening) of the structure.

Using obtained β_{ij} , the thermal vibration ellipsoids for constituent ions were constructed at all measured temperatures and have been compared with those for the bulk material [31]. The results of refinement at 420 K (below T_c) and 460 K (above T_c) are presented as ellipsoids of 50% probability in Fig. 3 and as ellipsoids of 5% probability in Fig. 4 (inasmuch as oxygen thermal displacements are very large for porous sample). For the bulk material, these ellipsoids are close to a sphere at all temperatures, and their characteristic sizes increase insignificantly on heating. For sodium nitrite in porous glass below T_c , these ellipsoids are clearly anisotropic and slightly larger than for the bulk, but on heating through T_c the shape and size of the thermal vibration ellipsoids change drastically. In the paraelectric phase (above T_c), the vibrations of Na and N form practically flat disks perpendicular to the b direction for Na and the a direction for N as a result of mixed rotation around the a and c axes, while oxygen ions form very stretched ellipsoids predominantly along the a and c directions, as should be expected at increasing rotation around the b axis. The obtained values of oxygen thermal displacements along the c and a directions at 460 K (above T_c) are equal to 1.21 and 0.93 Å, respectively [i.e., more than 25% of O-O (3.34 Å) distance for neighboring NO_2 groups], and essentially exceed the Lindemann criterion, which states that bulk material will melt when the average value of thermal displacements of nuclei exceeds 10%–15% of internuclear distances [33,35,36].

Having the picture of ion thermal vibrations and keeping in mind the results of structure refinement, we can suppose that the “looseness” (or softening) of the structure is a distinctive (and true intrinsic) feature of this CM corresponding to the formation above T_c (more than 100° below the bulk T_{melt}) “premelted state” initially manifesting itself in the oxygen sublattice. In this case, the mentioned above growth of dielectric permittivity of NaNO_2 above T_c [15] could be explained by appearance

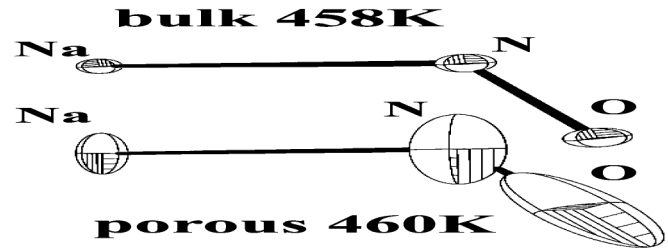


FIG. 4. 5% ellipsoids of thermal vibrations for bulk and porous samples at 460 K (above T_c). Note that the ellipsoids of 5% probability are presented, inasmuch as oxygen thermal vibrations are very large for the porous sample.

of ionic current due to jumping diffusion of constituent ions, first the oxygen ones.

Early analogous premelted effects were studied in minerals [37–39], where it was demonstrated that premelting takes place at 100–200 K below T_{melt} and represents unquenchable configurational changes within phases remaining crystalline up to congruent melting points [39]. It is different from premelting of confined ice [40,41], where the premelted state is formed at the surface layer between the ice and the host matrix and strongly depends on surface curvature. In our case, the “premelted state” has a volume character and probably originates from some size effect of yet unclear nature.

In conclusion, for the first time, the details of the structure of a solid material embedded in a porous matrix were determined by neutron diffraction. The temperature evolution of a structure in a restricted geometry was studied for the ferroelectric NaNO_2 embedded in a porous glass and it was shown that this CM forms a kind of interconnected cluster probably of the dendrite type with practically temperature independent average size about 45 nm. Above T_c , the volume “premelted” state is formed, manifesting itself in a sharp growth of the thermal motion parameters, a softening of the lattice, and an increase of lattice volume. In such a case, the possible appearance of ionic current due to oxygen jumping diffusion is proposed as a reason for observed giant growth of dielectric permittivity. On cooling below T_c , macroscopic polarization and potential barriers suppress the lattice softening and the normal ferroelectric phase exists, but even at room temperature the thermal vibrations are different from those for the bulk material.

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