Structural study of NaNO_2 embedded into porous glass

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Temperature-dependent Raman study of NaNO_2 confined within porous glass with a pore size of 46 nm has been performed. It is demonstrated that the bandwidths and frequencies of the Raman bands as a function of temperature show similar behaviour, but not identical, as those observed for bulk NaNO_2 . This result indicates that the first-order phase transition mechanism is only slightly modified by embedding NaNO_2 into the porous glass. It seems that formation of “premelted state” is not significant in the studied material, at least up to 40–50 K above T_c . At higher temperatures, however, a significant increase of bandwidth of the 1326 cm^{-1} band is observed, which could indicate appearance of “premelted” state. The dielectric measurements are consistent with this view since they show large increase of dielectric permittivity above 480 K, well below the NaNO_2 melting temperature (554 K).

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1 Introduction Upon cooling NaNO_2 exhibits a second-order phase transition at 438.2 K from paraelectric structure ($D_{2h}^{25} - \text{Immm}$) into antiferroelectric phase and a first-order phase transition at 436.9 K into ferroelectric structure ($C_{2v}^2 - \text{Im}2m$) [1]. Recently, many studies have been carried out on the thermal and physical properties of materials in confined geometry, especially for ferroelectrics, where finite-size effects are of fundamental interest in thin film ferroelectric memories, microcomposites etc. NaNO_2 embedded into a porous glass has been the subject of a few studies [2–5]. The measurements of this material in a porous glass have shown a large growth of the dielectric constant and the amplitudes of thermal vibrations above the phase transition temperature [2, 3]. In the present work temperature-dependent Raman and dielectric studies of NaNO_2 in a porous glass have been performed to obtain deeper insight into the effect of confined geometry on properties and phase transition mechanism of NaNO_2 .

2 Experimental Porous glass was obtained as a result of etching a sodium borosilicate glass, after thermal annealing at 763 K for 165 h. After leaching the glass samples were treated additionally in KOH solution for removal of high-dispersed secondary silica gel. The average size of pores determined by nitrogen adsorption method was 46 nm. Porous glass exhibits narrow pore size distribution. NaNO_2 was introduced to porous glass from the melt at 578 K.

Raman spectra were measured in back-scattering geometry with a Bruker FT-Raman RFS 100/S spectrometer and the 1064 nm excitation. The spectra were recorded with a spectral resolution of 2 cm^{-1} . Frequencies and bandwidths of the observed bands were evaluated by fitting the spectra to Lorentzian

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function. Dielectric measurements in wide frequency (20 Hz–1 MHz) and temperature (420–530 K) were performed by using a Novocontrol Alpha impedance analyzer.

3 Results and discussion The crystal structure of NaNO₂ at room temperature is C_{2v}²⁰. The factor group analysis predicts that there are 9 optical modes distributed among 3A₁+A₂+3B₁+2B₂ irreducible representations [6]. All of these modes are Raman-active. The measured Raman spectra, presented in Fig. 1, show the presence of 4 strong and medium intensity bands at 1326, 828, 158 and 121 cm⁻¹, and three weak bands at 1240, 220 and 180 cm⁻¹. The comparison of the measured spectra with the spectra of bulk NaNO₂ confirms that these bands come from NaNO₂. The bands at 1326, 828, 158 and 121 cm⁻¹ can be assigned to A₁ symmetric bending mode, A₁ symmetric stretching mode, B₁ librational mode and A₂ librational mode, respectively [6].

Fig. 1 Temperature-dependent Raman spectra of NaNO₂ in a porous glass.

The main changes observed in the spectra can be followed by analyzing the frequency ω vs temperature T plot shown in Fig. 2. The obtained results indicate clearly that the material experiences structural modification at about 438 K, in good agreement with results reported in literature for bulk NaNO₂ [1, 6]. Near this temperature the 1326 cm⁻¹ mode exhibits significant increase in frequency whereas the remaining modes show frequency decrease. We observe also that the observed modes exhibit large bandwidth increase with increasing temperature. Figure 2 shows full width at half maximum (FWHM) vs T for the four most intense bands. The obtained results show that the magnitude of the observed frequency and FWHM changes near the phase transition temperature are very similar to those observed for bulk NaNO₂ [6]. However, the observed changes are observed at a broader temperature range. This result indicates that properties of NaNO₂ embedded into the glass with a pore size of 46 nm are very similar to the properties of bulk NaNO₂, but the phase transition seems to be smeared out due to presence of different size NaNO₂ crystallites in the glass.

As mentioned above the former neutron studies of NaNO₂ embedded in a glass with pore diameter of 7 nm revealed unusual growth of the amplitudes of thermal vibrations of all ions on heating through the phase transition temperature [3]. This behaviour was attributed to formation of a soft “premelted”

Fig. 2 Raman shifts and bandwidths for the 1326 (squares), 828 (circles), 158 (triangles) and 121 cm^{-1} modes (diamonds), respectively. The accuracy of the frequencies (bandwidths) is better than 0.1 (0.2) cm^{-1} for the 828 cm^{-1} band and 0.2 (0.5) cm^{-1} for the remaining bands.

state [3]. The large growth of the thermal vibrations should lead to large increase in bandwidth of the studied modes. However, the present results show that the bandwidth increase is very similar to that observed for bulk NaNO_2 . This result clearly indicates that formation of “premelted state” is not significant in the studied material, at least up to 40–50 K above T_c . At higher temperatures, however, a significant increase of FWHM of the 1326 cm^{-1} band is observed, which could indicate appearance of “premelted” state. The observed difference in the behaviour of the studied here glass and the glass studied in Ref. [3] can be attributed to significant difference in the pore diameters, i.e. large size of the pores in the present case leads to narrower temperature range, in which “premelted state” may exist, and hence weaker temperature dependence of Raman bandwidths as well as smaller increase of the dielectric constant at high temperatures.

A typical view of the 3D plots of the dielectric permittivity versus frequency and temperature is shown in Fig. 3.

The dielectric permittivity displays maxima due to the phase transitions in the region 430–440 K. Above 480 K the growth of dielectric permittivity is observed. The giant growth of ϵ' (up to 10^7 Hz) can be related with the formation of “premelted state” [3] This result is in a good agreement with the results obtained from Raman spectra.

Fig. 3 Three-dimensional plot of the frequency and temperature dependence of the dielectric permittivity ϵ' for the porous glass filled with NaNO_2 .

4 Conclusion We have performed studies of NaNO_2 embedded in a glass with a pore diameter 46 nm. It has been shown that properties and phase transition mechanism are only slightly modified by confinement of this ferroelectric material. In particular, no evidence for formation of the “premelted” state can be found in the temperature range up to 480 K. It seems, however, that this state is formed above 480 K.

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