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Porous glasses with sodium nitrite impregnations

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The properties of sodium nitrite introduced in porous glasses have been investigated. SEM graphs indicate existence of sodium nitrite inside glass pores. It has been shown that FTIR and Raman spectra are similar for bulk sodium nitrite and sodium nitrite embedded into porous glass. The nature of FTIR and Raman bands has been determined. The size-effect of sodium nitride introduced into porous glass was observed on the basis of dielectric measurements.

Keywords: porous glass, ferroelectric, Raman spectra, FTIR.

1. Introduction

The physical properties of a ferroelectric depend on the size of particles. The size-effect results in a change of the material physical properties, particularly the phase transition features. There are many ways of fabricating small size ferroelectric particles: noble gas condensation [1] or evaporation alkoxide process [2]. In this paper, a method of introducing ferroelectric into porous glasses is presented. The porous matrices allow to obtain confined ferroelectric materials. Using matrices with different pore sizes, one can obtain ferroelectric particles with different sizes. Introducing a ferroelectric in porous glass offers not only a study of the ferroelectric in a nanoscale but also its practical application in microelectronics and optoelectronics. Previously, this method was applied to embed potassium dihydrogen phosphate (KDP) [3], deutered KDP (DKDP) [4], Rochelle salt [5] and triglycine sulphate (TGS) [6] in porous glasses.

The aim of this work is to introduce sodium nitrite ($NaNO_2$) into porous glass of various pore sizes. The scanning electron microscope graphs, FTIR, Raman and dielectric measurements confirm the presence of $NaNO_2$ within glass pores.

The properties of confined $NaNO_2$ were examined by NABEREZHNOV *et al.* [7] and COLLA *et al.* [5] but using other methods.

The bulk sodium nitrite exhibits the first order ferroelectric phase transition of order-disorder type. It shows transition from the paraelectric phase to the sinusoidal anti-ferroelectric phase near the Neel temperature (T_N = 437.7 K) and to the ferroelectric phase near the critical temperature (T_C = 436.3 K) in this crystalline system [8].

2. Experimental

Porous glasses were fabricated by leaching sodium borate phase from phase separated glasses [9–11]. The phase separation temperature was 763 K for glass 1 and 933 K for glass 2. After leaching microporous glasses were formed. For removing the secondary silica from the pores of glass the samples were additionally treated in KOH. The total porosity determined from the mass decrement after etching was 50 and 48% for glasses 1 and 2, respectively. The texture parameters of the glasses were determined by adsorption and porosimetry method. The average pore radii were 23 and 160 nm for glasses 1 and 2, respectively. The average pore volume was 364 mm^3/g for glass 1 and 470 mm^3/g for glass 2, whereas the average surface areas were 28.9 and 5.9 m^2/g for glasses 1 and 2, respectively. The dimensions of the samples for all measurements were $10\times10\times0.5$ mm^3. The porous glass samples were immersed in $NaNO_2$ melt for several hours.

The morphology and elemental chemical composition of porous glasses before and after embedding the ferroelectric into pores were examined with the help of SEM (JOEL JSM 5800LV) equipped with energy dispersive X-ray spectroscopy.

The temperature dependence of dielectric permittivity was measured at frequencies from 8 Hz to 24 kHz using Novocontrol Alpha L impendance analyzer. Dielectric measurements were carried when cooling the sample after heating to 460 K. The dielectric permittivity was registered step by step at constant temperature.

The infrared spectra were registered using Biorad 575C FTIR spectrometer. The Raman spectra were measured with Bruker FT-Raman RFS 100/S spectrometer (180°-scattering geometry). Excitation was performed with a 1064 nm line of the YAG:Nd^{3+} laser. The FTIR and Raman spectra were recorded with spectral resolution of 2 cm^{-1}.

3. Results

Scanning electron microscope graphs of the samples investigated before and after $NaNO_2$ introduction into porous glasses 1 and 2 are presented in Fig. 1. It is evident that the pores of both glasses are filled to a substantial degree by sodium nitrite. The chemical analysis confirms the existence of sodium and nitrogen (contained in sodium nitrate) in the pores of glasses 1 and 2.

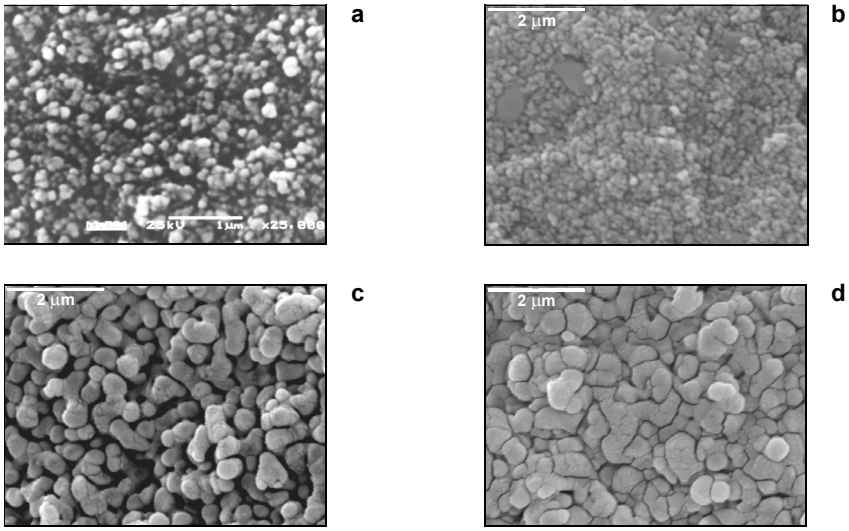

Fig. 1. SEM graph of: porous glass 1 (**a**), porous glass 1 embedded with $NaNO_2$ (**b**), porous glass 2 (**c**), porous glass 2 embedded with $NaNO_2$ (**d**).

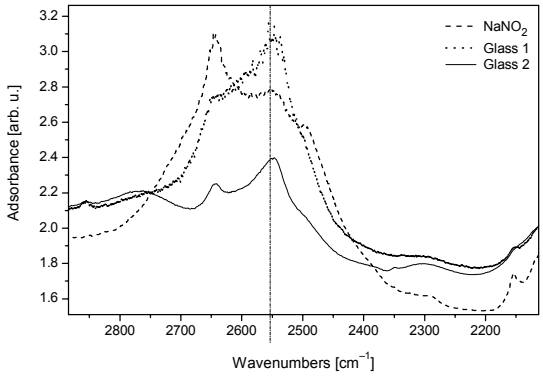

Fig. 2. FTIR spectra of polycrystalline $NaNO_2$ and $NaNO_2$ introduced in porous glasses 1 and 2.

Figure 2 shows FTIR spectrum for porous glasses 1 and 2 after introducing sodium nitrite into pores and polycrystalline $NaNO_2$. Our earlier experiments show the absence of this FTIR peak for both empty porous glasses 1 and 2 [11].

The Raman spectra of the glass samples 1 and 2 with $NaNO_2$ embedded as presented in Fig. 3 show the appearance of four strong and medium intensity bands at 1326, 828, 158 and 121 cm^{-1}, as well as two weak bands at 225 and 189 cm^{-1}.

The temperature dependence of dielectric permittivity for different frequencies, after embedding $NaNO_2$ in glass 2, is shown in Fig. 4. Two maxima are observed on

$\varepsilon(T)$ curves: one at about 435 K and a lesser one at about 433 K. The dielectric permittivity measurements for empty porous glass 2 show that there are no ε maxima in this temperature and frequency region. It can be stated that the appearance of

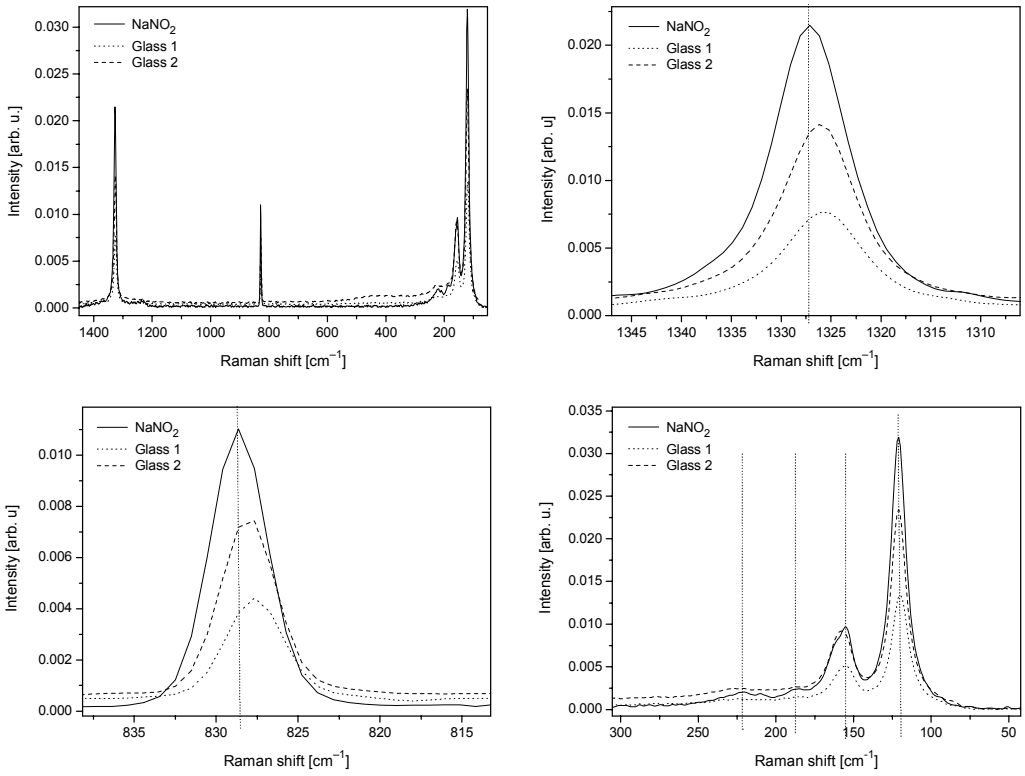

Fig. 3. Raman spectra for polycrystalline $NaNO_2$ and porous glasses 1 and 2 embedded with $NaNO_2$.

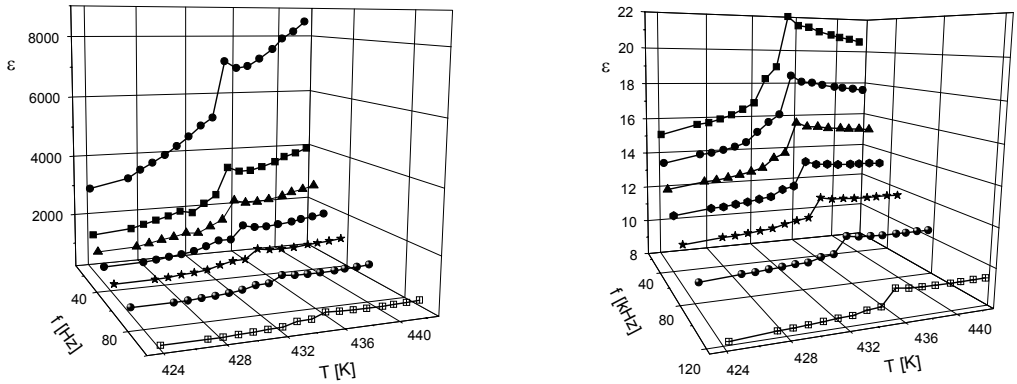

Fig. 4. Temperature dependence of dielectric permittivity ε for porous glass 2 after embedding $NaNO_2$.

dielectric maxima is related to the phase transition in $NaNO_2$ embedded in porous glass. A similar result for glass 1 was also observed.

4. Discussion

The SEM graphs and the chemical analysis confirm that sodium nitrite penetrates into glasses under investigation. The results of FTIR, Raman and dielectric measurements also indicate the existence of $NaNO_2$ within glass pores.

Three fundamental internal modes of vibration (ν_2, ν_3 and ν_1) and a combination mode ($\nu_1 + \nu_3$) were found in the infrared spectra of bulk sodium nitrite, investigated in the temperature range 300–523 K. These modes of vibrations are the symmetric bending mode ν_2 (approx. 830 cm^{-1}), the asymmetric stretching mode ν_3 (approx. 1270 cm^{-1}) and the symmetric stretching mode ν_1 (approx. 1383 cm^{-1}). The combination mode ($\nu_1 + \nu_3$) at about 2552 cm^{-1} was observed in [12].

The obtained FTIR spectrum for polycrystalline $NaNO_2$ is similar to the standard FTIR curve for the bulk $NaNO_2$. A representative peak at 2552 cm^{-1} appears on FTIR curves for polycrystalline $NaNO_2$ and $NaNO_2$ embedded in the porous glasses investigated (Fig. 2).

$NaNO_2$ crystallizes in the $C_{2\nu}^{20}$ structure at room temperature. Since the primitive cell contains only one formula unit, there are nine optical modes distributed among $3A_1 + A_2 + 3B_1 + 2B_2$ irreducible representations [13]. All of these modes are Raman-active. They can be subdivided into 3 internal vibrations (the symmetric stretching, the asymmetric stretching and the bending vibrations) and 6 lattice vibrations (the librational motions of the NO_2^- ions, and translations of the NO_2^- and Na^+ ions). A comparison of the Raman spectra for $NaNO_2$ introduced into porous glasses (Fig. 3) with those of $NaNO_2$ crystal presented in [13] shows very clearly that the observed bands can be assigned to $NaNO_2$ embedded in the glass pores. Comparing our spectra with those from literature allows us to conclude that the observed Raman bands at 1326, 828, 225, 189, 158 and 121 cm^{-1} can be assigned to the symmetric bending (A_1), the symmetric stretching (A_1), the librational (B_2), the translational (B_1), the librational (B_1) and the librational (A_2) modes, respectively.

The dielectric investigations indicate that properties of sodium nitrite introduced into porous glass are different from those for the bulk sodium nitrite. The results (Fig. 4) show the shift of the phase transition temperatures for $NaNO_2$ embedded in porous glass towards lower temperatures in comparison with the transition temperatures for bulk $NaNO_2$. This can be explained as the size-effect of a ferroelectric material. The shift of the phase transition temperature was discussed by us in [6] and by other authors [2, 14].

5. Conclusions

It was shown that sodium nitrite can be introduced into porous glasses. The scanning electron micrographs, FTIR and Raman investigations confirmed the existence of

sodium nitrite inside the pores. Chemical analysis shows the presence of sodium and nitrogen within the glass pores.

Lower phase transition temperatures in porous glasses with $NaNO_2$ embedded compared with bulk sodium nitrate were registered and attributed to the size effect.

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