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The influence of preparation technology on phase transitions in $NaNO_2$ embedded into porous glass

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The dielectric properties of sodium nitrite embedded into porous glasses with the average pore diameter of 45 nm and 320 nm have been studied. The samples were obtained by immersion of empty porous glass into the melted $NaNO_2$ and then they stayed there for 24 and 8 hours. The sequence of phase transitions (PT) from the paraelectric phase to the sinusoidal antiferroelectric phase and to the ferroelectric phase has been observed in these nanocomposite materials on cooling. It is shown that due to the size effect, the temperatures of these PTs are lower than in bulk $NaNO_2$.

Keywords: porous glass, ferroelectric, phase transition, size effect.

1. Introduction

Nano-sized ferroelectrics attract great attention because of their practical application; in particular, they can be used for production of non-volatile memories, piezoelectric and pyroelectric sensors, microcomposites, *etc*. [1, 2].

There are various methods of producing ferroelectric nanoparticles. Two of them are noble gas condensation [3] and evaporation alkoxide process [4]. The other method based on embedding of ferroelectric materials into nanopores of porous glasses is presented in [5–8]. In [7, 8] the method of introducing ferroelectric materials (KNO_3 and $NaNO_2$) into porous glasses, both from water solution and from melt, is presented. However, the temperature dependence of dielectric permittivity $\varepsilon(T)$ obtained for samples with materials introduced from water solution were different from $\varepsilon(T)$ for samples filled with melted ferroelectric.

The scope of this work is to investigate how the preparation technology affects the temperature dependence of dielectric permittivity and, in particular, the phase transitions and their temperatures. In this work, sodium nitrite ($NaNO_2$) was chosen as a ferroelectric material.

T a b l e. Parameters of the porous glass texture.

Glass parameter	PG1	PG2
Specific surface [m^2/g]	28.9	5.9
Pore volume [cm^3/g]	0.440	0.470
Average diameter [nm]	45	320
Porosity [%]	50	48

Bulk sodium nitrite undergoes the first order ferroelectric phase transition of the order-disorder type. The phase transition from the paraelectric phase to the sinusoidal anti-ferroelectric phase is observed at the Neel temperature T_N = 437.7 K and the phase transition to the ferroelectric phase at the critical temperature T_C = 436.3 K [9].

2. Experimental

Porous glass was fabricated by leaching sodium borosilicate glass (62.6 wt% of SiO_2, 30.4 wt% of B_2O_3 and 7.0 wt% of Na_2O) with phase separation. The original glass was subjected to heat treatment at 763 K for 165 h (in case of glass PG1) and 933 K for 100 h (in case of glass PG2). After leaching in the hydrochloric acid, the glass samples were etched in a KOH solution. The obtained porous glasses contained about 90% of SiO_2; their basic parameters relevant to the present article are given in the Table. Rectangular porous glass plates 10×10×0.5 mm^3 were immersed in the melted $NaNO_2$ for 24 hours (PG1-24 and PG2-24) and 8 hours (PG1-8 and PG2-8), respectively. The samples were taken out of the melt and cooled from the temperature of 544 K to room temperature at constant rate 3 K per minute. In [7, 8] the dielectric results were obtained for samples that were cooled very fast from melt temperature to room temperature. The chemical composition of the samples was examined by the scanning electron microscope (SEM). Temperature dependences of dielectric permittivity were measured at frequencies 1 kHz and 10 kHz. Dielectric permittivity was measured by Escort ELC-3133A LCR-meter. At every frequency the samples were heated up to 460 K and measurements were performed on cooling to room temperature.

3. Results and discussion

Scanning electron microscope pictures of the PG1 samples with and without $NaNO_2$ embedded into pores are shown in Fig. 1. It is evident that after the filling procedure, the pores of samples contain sodium nitrite. SEM pictures of PG2 samples after 8 hours (PG2-8) and 24 hours (PG2-24) introduction of $NaNO_2$ are presented in Figs. 2**a** and 2**b**. It can be clearly seen that the pores of samples PG2-8 are less filled with ferroelectric material than in samples PG2-24. The volume amount of $NaNO_2$ was about 80% in PG1-24 and PG2-24. For PG2-8 the volume amount was nearly 40%.

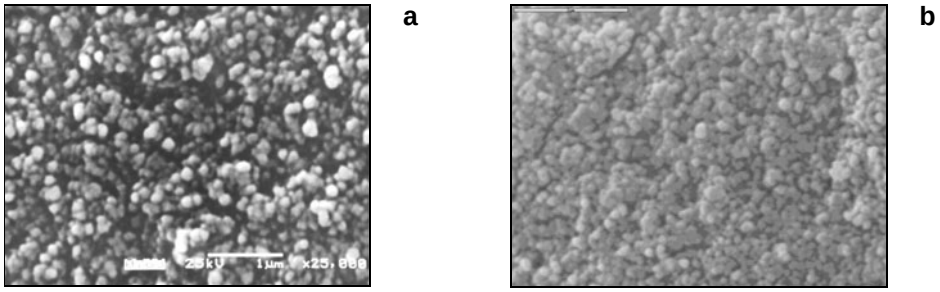

Fig. 1. SEM pictures of PG1: empty (**a**), with $NaNO_2$ introduced from the melt (24 h) (**b**).

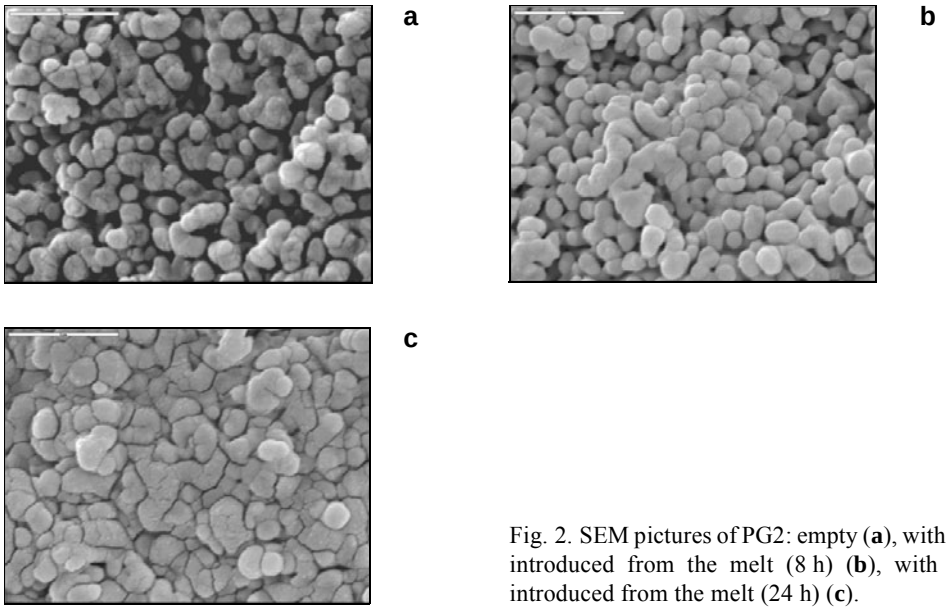

Fig. 2. SEM pictures of PG2: empty (**a**), with $NaNO_2$ introduced from the melt (8 h) (**b**), with $NaNO_2$ introduced from the melt (24 h) (**c**).

Chemical analysis confirmed the existence of sodium atoms in both kinds of samples. The result of electron dispersion spectroscopy (EDS) measurements is presented in Figure 3.

Temperature dependence of dielectric permittivity $\varepsilon(T)$ measured for PG1 with $NaNO_2$ introduced from the melt for filling time equal to 24 hours (PG1-24) is shown in Fig. 4. The shapes of curves presented in Figs. 4**a** and 4**b** are similar. Analogous dependences at 1 kHz and 10 kHz were observed for all measured samples, and the results at 1 kHz or 10 kHz are presented further in this contribution. Two phase transitions are observed as peaks on the temperature dependences of dielectric permittivity. The results obtained for samples with $NaNO_2$ introduced from the melt

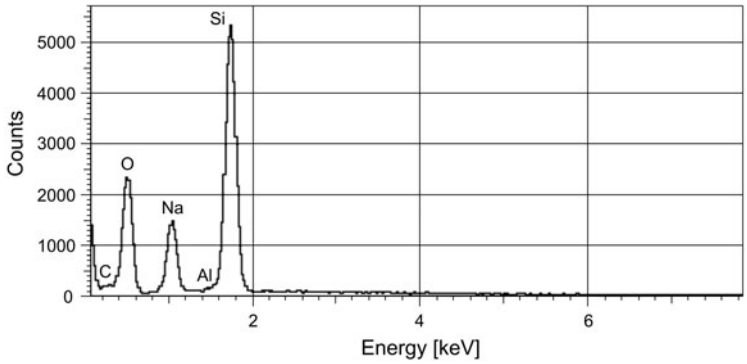

Fig. 3. EDS spectrum of PG2 with $NaNO_2$ introduced from the melt (filling time 24 h).

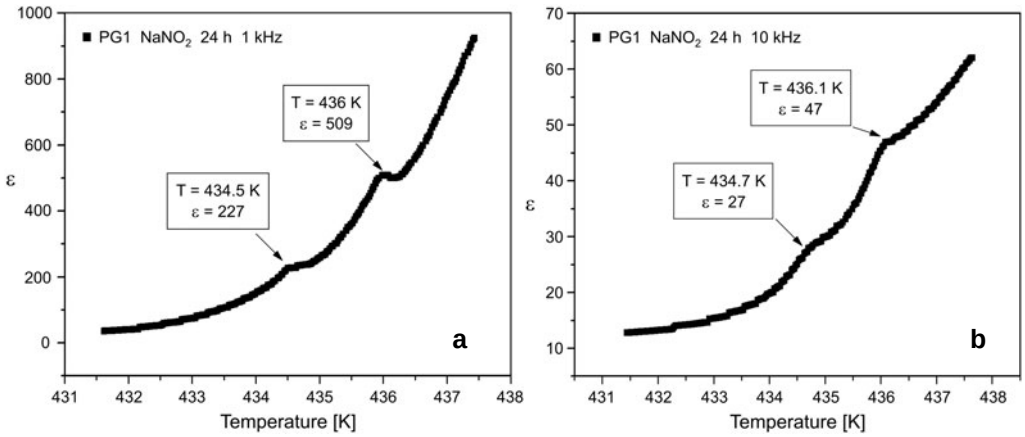

Fig. 4. Temperature dependences of dielectric permittivity of PG1 with $NaNO_2$ introduced from the melt (filling time 24 h) at frequencies 1 kHz (**a**) and 10 kHz (**b**).

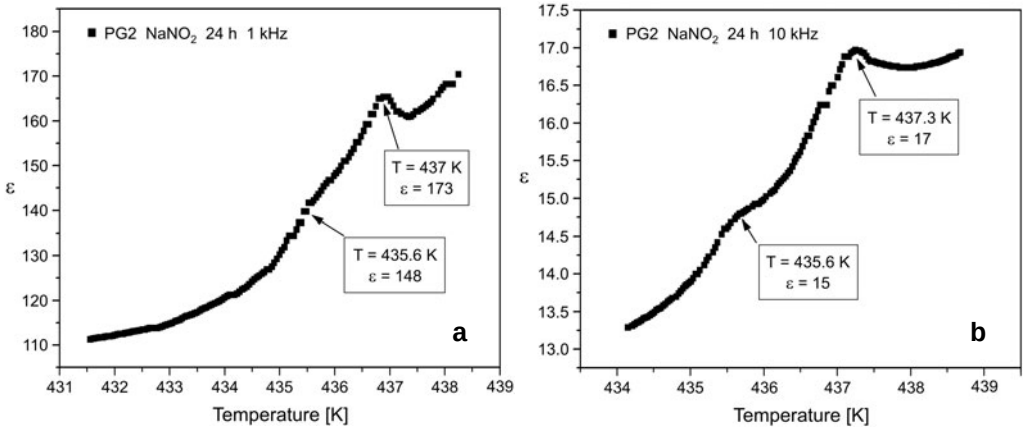

Fig. 5. Temperature dependences of dielectric permittivity of PG2 with $NaNO_2$ introduced from the melt (filling time 24 h) at frequencies 1 kHz (**a**) and 10 kHz (**b**).

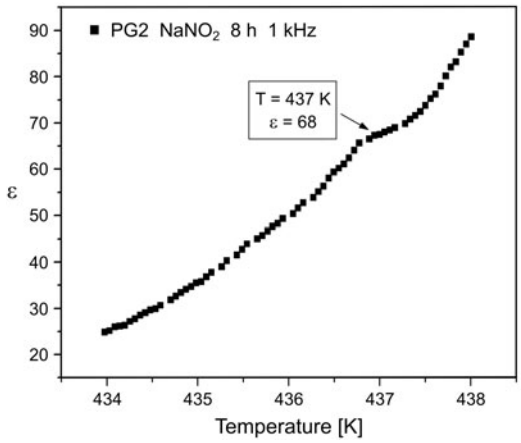

Fig. 6. Temperature dependence of dielectric permittivity of PG2 with $NaNO_2$ introduced from the melt (filling time 8 h) at frequency 1 kHz.

differ from the results presented in [6, 7] where only one peak was observed for samples obtained from the melt. In [7] two peaks were observed only for samples fabricated from water solution of $NaNO_2$. The reason for observing two peaks is probably the effect of the technology of samples preparation from the melt. Slow cooling (3 K per minute) from melting temperature to room temperature affects the structure of the material confined within the pores. It can be stated that the physical properties of sodium nitrite microcrystals are similar to those observed in bulk material but phase transition temperatures are lower comparing to those of bulk crystal (the size effect). The growth of dielectric permittivity above 437 K is probably connected with the volume "pre-melted" state which is formed above T_N [6].

In Figure 5, the temperature dependence of dielectric permittivity is shown for PG2 filled with $NaNO_2$ (filling time 24 h). The phase transition temperatures are shifted towards lower values in comparison to bulk $NaNO_2$. The shift depends on the average pore diameter. The phase transition temperature for the glass with smaller pores is lower than that for the glass with larger pores (Figs. 4 and 5).

The temperature dependence of dielectric permittivity for PG2-8 is presented in Fig. 6. It is evident that the filling time influences the number of observed phase transitions. Comparing to PG2-24, only one maximum is observed. SEM pictures and chemical analysis indicate that both glasses are filled with $NaNO_2$. Some pores are filled completely, others – partially. The degree of filling depends on the time the samples were kept in the melt. These observations and results of dielectric measurements allow to conclude that the appearance of only one maximum on $\varepsilon(T)$ relation can be connected with different microcrystals size distribution and the film thickness of $NaNO_2$. Structural investigations would be very useful. Further research is planned.

The time of keeping porous glass samples in the melt of ferroelectric material is a very important factor having an influence on temperature dependence of dielectric permittivity. However, this is not the unique factor. In Figure 7, the temperature dependence of dielectric permittivity is shown for PG2 sample cooled fast from melt

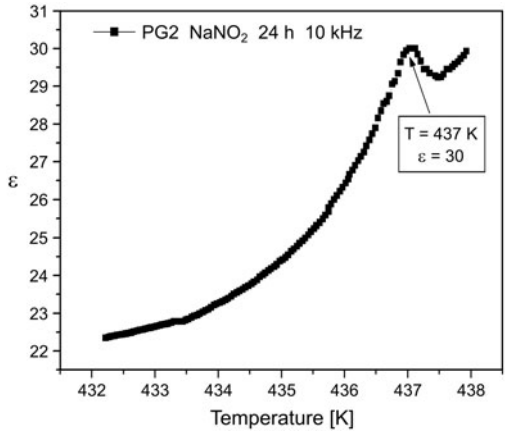

Fig. 7. Temperature dependence of dielectric permittivity of PG2 with $NaNO_2$ introduced from the melt (filling time 24 h, fast cooling) at frequency 10 kHz.

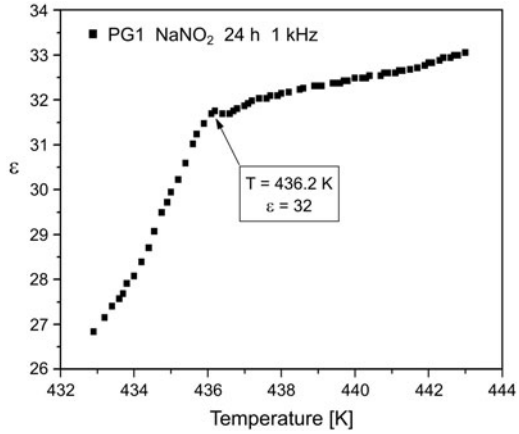

Fig. 8. Temperature dependence of dielectric permittivity of PG1 with $NaNO_2$ introduced from the melt (filling time 24 h). The measurements have been carried out in 20 days after the sample preparation.

to room temperature. It can be seen that fast cooling affects the shape of temperature dependence of dielectric permittivity and the number of observed phase transitions. The reason of this phenomenon is possibly the influence of fast cooling on the structure of $NaNO_2$ inside the pores. Our previous investigations [7] indicated that only one maximum of dielectric permittivity temperature dependence was also observed for a polycrystalline sample grown by fast cooling from $NaNO_2$ melt. The comparison of $\varepsilon(T)$ relation for polycrystalline $NaNO_2$ [7] with this of PG2-24 (Fig. 7) indicates that physical properties of $NaNO_2$ microcrystals obtained during slow cooling are more similar to those observed in bulk crystals than those of $NaNO_2$ obtained by fast cooling.

The other technological parameter that has to be taken into account is the period between the sample was removed from the melt and the moment it was measured. Dielectric permittivity temperature dependence for a sample that was measured after 20 days since it was prepared is presented in Fig. 8. Only one maximum of dielectric permittivity is observed. The explanation of this phenomenon is not known yet [5] and

may be the subject of a future work. Probably one of the reasons is the fact that porous glasses and sodium nitrite are hygroscopic.

4. Conclusions

The number of phase transitions observed in the temperature dependences of dielectric permittivity, the shapes and smearing of peaks of dielectric permittivity are dependent on the technology of embedding the ferroelectric materials into glass pores.

The time of filling of porous glasses by melted ferroelectric material is the principal technological parameter having an effect upon the above-listed characteristics.

The rate of sample cooling from melting temperature to room temperature and the time between production of the composite material and its measurement also play a great role.

The reductions of T_C and T_N for confined $NaNO_2$ are caused by a size effect.

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