Optica Applicata, Vol. XXXVIII, No. 1, 2008

Dynamical heterogeneity of $NaNO_2$ confined within porous glasses

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Frequency dependences of imaginary part of the dielectric response $\varepsilon''(f)$ of SiO_2–$NaNO_2$ nanocomposite, prepared by embedding of sodium nitrite into porous glasses with 7 nm average pore diameter, have been studied within a temperature range of 360–520 K. It has been found that the spectrum $S(\omega) = \varepsilon''(f)/f$ contains the component $\sim 1/f^{\alpha}$, where α is a coefficient indicating the dynamical heterogeneity of dipoles. Peculiarities of the temperature dependence of α are discussed.

Keywords: nanostructured ferroelectrics. porous glasses, dielectric responce.

1. Introduction

It is known that physical properties of ultradispersed solids differ essentially from those of bulk materials. In particular, size effects result in drastic changes of phase transition features, and one can expect these effects to be especially significant if the characteristic sizes (film thickness, filament or granular diameters) become comparable with the correlation length of order parameter critical fluctuations [1–4].

Recently it has been found [5–8] that the low-frequency dielectric permittivity of nanocomposites obtained by embedding of $NaNO_2$ into various porous matrices (glasses, opals, chrysotile asbestos) reaches giant values (up to $\approx 10^8$) at temperatures above T_C, *i.e.*, in the paraelectric phase. In the paper [9] it has been suggested that this growth of dielectric response is observed due to a significant increase in sodium mobility in a restricted geometry. In particular, the neutron diffraction studies of $NaNO_2$ embedded into porous glasses with 7 nm average pore diameter have shown [4] that amplitudes of Na^+ thermal vibrations become comparable with interatomic distances at ≈ 100 K, below the bulk sodium nitrite melting temperature

($T_m \approx 554$ K), indicating the "softening" of lattice. This "softening" has been confirmed by the study of spin-lattice relaxation time of ^{23}Na within this nanocomposite material [10].

These results permit to conclude that the confined sodium nitrite is characterized by a strong increase in dynamical lattice disordering on heating. Obviously, this kind of disordering is accompanied by disordering in the dipole subsystem. The principle aim of present contribution is to study the effect of structural disordering in the confined sodium nitrite on peculiarities of the electrical noise spectrum $S(\omega)$.

2. Results and discussion

It is known that heterogeneous electrical (or magnetic) dipole systems show the $1/f^{\alpha}$ noise [11], where the coefficient α, characterizing spontaneous fluctuations of dipole moments, can be determined using the fluctuation-dissipation theorem [12]. The value of the coefficient α indicates the degree of dynamical dipole heterogeneity. In particular, $\alpha = 2$ corresponds to the monodispersive Debye relaxation, while $\alpha = 1$ corresponds to the wide relaxation spectrum.

It is known that the noise spectrum $S(\omega, T)$ can be expressed by the following formula [11]:

$$S(\omega) = \frac{\varepsilon''}{\omega} \sim \frac{1}{f^{\alpha}}$$

where $\omega = 2\pi f$, *i.e.*, the parameter α can be determined from the results of dielectric measurements within a wide frequency range.

The measurements were performed on the samples prepared by the method described in detail in the paper [13]. The host porous glass matrices had a random interconnected 3D network of pores with an average pore diameter of 7 ± 1 nm. The former value was obtained from the mercury intrusion porosimetry. The confined material was prepared by immersion of the preliminary warmed up platelets of porous glass into melted $NaNO_2$ in a sealed quartz container. The filling of pores by sodium nitrite achieved 90% and the volume occupied by the salt embedded into the porous glass was about 22% of the total sample volume.

The samples for dielectric studies were flat plates of about $7 \times 3 \times 1.5$ mm^3. The frequency measurements were carried out on a computer controlled dielectric spectrometer Solatron 1260 operating in the frequency domain mode. The temperature and frequency dependences of complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ were measured on the plates of about $7 \times 3 \times 1.5$ mm^3 with Ni electrodes. Every time before measurements the sample was kept up at ~373 K for several hours to remove possible remnant water. (Removing of water from the sample is checked using the measurements of AC conductivity variation.) After that, it was installed into a thermostat and slowly cooled down to the room temperature. All measurements were carried out in the thermostatic regime and in two wires mode. Temperature

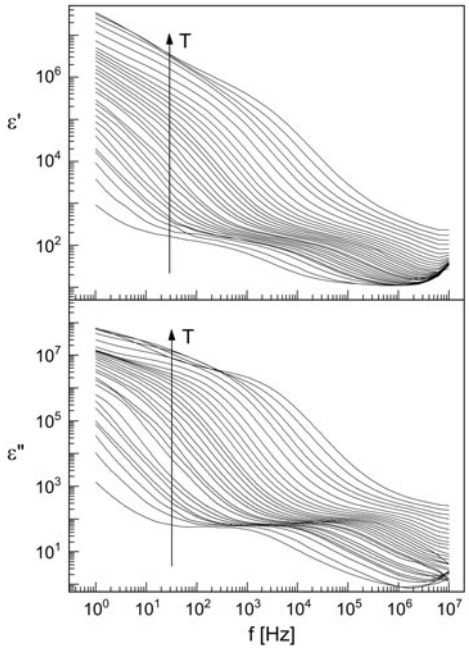

Fig. 1. Frequency dependences of ε' (**a**) and ε'' (**b**) at temperatures 363–518 K.

stability was better than 0.5 K; the errors of measured real and imaginary parts of dielectric permittivity were smaller than 0.1% and 1%, respectively.

The frequency dependences of ε' and ε'' obtained at different temperatures are shown in Fig. 1. It is easy to see that both (imaginary and real) parts of dielectric response as well as the dispersion increase out-of-the-way upon heating. Predominantly the dispersion is caused by electrical conductivity, owing to high mobility of Na^+ ions in embedded sodium nitrite [10].

The measured values of $\varepsilon''(f)/f$ versus frequency at several temperatures (below T_C, in the vicinity of T_C and essentially above T_C) are presented in Fig. 2. These curves consist of three (at low, middle and high frequencies) linear regions which correspond to different values of α. This experimental fact indicates the complex $S(\omega)$ spectrum.

The value of α corresponding to the low frequency region approaches 2 at heating, owing to a growth of DC conductivity contribution into the imaginary part ε'' ($\varepsilon'' \sim \sigma_{dc}/2\pi f$). At high frequencies this part of dielectric permittivity has the smallest value, therefore we have used the results (obtained from treatment of $\log(\varepsilon''/2\pi f)$ *vs.* $\log(f)$ dependence in the "high frequency region") to study the temperature evolution of the $S(\omega)$ spectrum.

The calculated temperature dependence of the "high frequency" α is presented in Fig. 3. It is easy to see that the coefficient α varies within a range of 1.4–1.7. It indicates that the electrical subsystem of this nanocomposite material is dynamically heterogeneous and characterized by a broad spectrum of relaxation times. Evidently, this fact is first of all a result of structural disordering of embedded material.

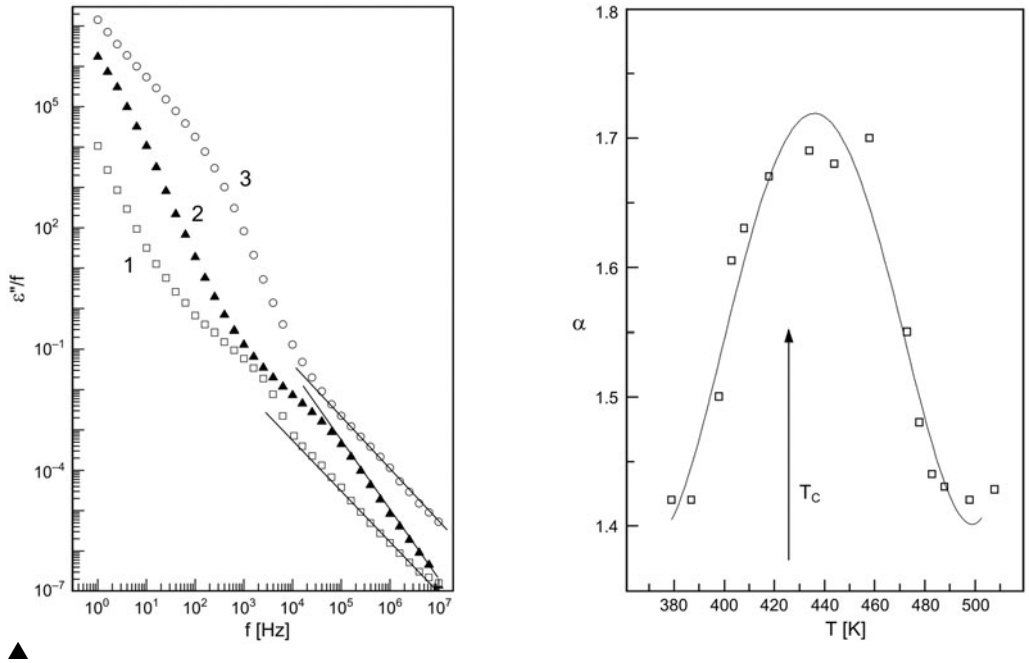

Fig. 2. Frequency dependences of ε''/f at 370 K (curve 1), 423 K (curve 2) and 488 K (curve 3).

Fig. 3. Temperature dependence of the coefficient α.

However, it should be noted that the dependence $\alpha(T)$ demonstrates the broad diffuse maximum in the vicinity of 450 K. It means that the electrical subsystem achieves the maximal degree of homogeneity within a temperature range of 430–460 K. At first sight the obtained $\alpha(T)$ dependence is inconsistent with the results of neutron [3, 9] and ^{23}Na NMR [10] studies of confined $NaNO_2$. To explain the experimental $\alpha(T)$ dependence, we must take into account the fact that the experimental dielectric response is a result of several temperature dependent mechanisms of polarization. One can suppose that the observed peak of α corresponds to the temperature at which one of these polarization mechanisms dominates. As a result the dynamical dielectric homogeneity increases.

In fact, the comparison of temperature dependences of α and DC electrical conductivity σ shows that the maximum of α corresponds to the maximal contribution of low temperature mechanism of σ, which decreases at about 450–470 K [14].

Thus, the experimental results reveal the complex spectrum $S(\omega)$ characterizing the dynamical heterogeneity of polarization in confined $NaNO_2$. It has been found that the "parameter of dynamical heterogeneity" α goes through the diffuse maximum near 450 K.

Acknowledgements – This work was supported by the Russian Foundation for Basic Researches (Grants No. 08-02-01089 and No. 06-02-17313) and CRDF (project No. PG 05-010-1).

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Received September 18, 2007
in revised form March 17, 2008