

Effect of interface carbonization on dielectric properties of potassium nitrate nanocomposite based on porous glasses

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Dielectric properties and structure of pure and carbon-modified nanocomposites on the base of porous glasses with an average pore diameter of 6 nm (PG6) with embedded KNO_3 have been studied at the temperature diapason of 300–430 K and at frequencies of $0.1\text{--}3 \times 10^6$ Hz on cooling. X-ray diffraction studies of these samples have shown, that in modified and unmodified composites there is a mixture of the low-temperature paraelectric phase (α -phase) and the ferroelectric γ -phase. In modified composites, a decrease in permittivity and conductivity is observed. Dielectric response has been analyzed in the framework of modern theoretical models. Two relaxation processes have been identified and their origin has been determined. It has been found that the main contribution to the dielectric response of nanocomposite material PG6+ KNO_3 is provided by charge polarization on interfaces, which can be governed by modifying the inner pore surfaces. DC-conductivity of both composites has been estimated and the activation energies have been determined. Activation energy change observed in a vicinity of 360 K is attributed to the phase transformation and the appearance of KNO_3 α -phase.

Keywords: Nanocomposites; ferroelectrics; potassium nitrate; porous glasses; dielectric properties.

1. Introduction

Nanocomposite materials (NCMs) based on nanoporous matrices with embedded ferroelectrics are of undoubted interest due to the wide perspectives of the practical application of these materials for development of new approaches in electronics, information storage devices, applied medicine and biology and so on. It is known that finite-size effects drastically change all physical properties of ultra-dispersed materials. The observed phenomena are especially significant if the characteristic sizes of nanostructured particles become comparable with the correlation length of order parameter critical fluctuations. At present, the development of new nanotechnologies strongly stimulates the studies of different types of these materials. There are various methods of NCM preparation, and one of them is the embedding of substances into nanoporous glasses (PG). These glasses can be produced with different (but controllable) average pore diameters using the special heat treatment procedure.^{1,2}

At the same time, it should be noted that, in addition to the size effect, the properties of NCMs are significantly affected by presence of the “matrix-embedded material” interface and its properties. Modification of this interface may be a

possible way to change the macroscopic physical properties of NCMs, and this approach has been implemented in a number of papers.^{3–5} In our NCM, for interface modification, we have used carbon as the material that should cover the surface of the pores. KNO_3 has been used as a guest material for filling of pore space. At room temperature, bulk potassium nitrate is a dielectric with an orthorhombic structure Pmcn (α -phase). On heating at 403 K, the structural phase transition takes place from this paraelectric α -phase to the paraelectric trigonal phase with the structure $R\bar{3}m$ (β -phase). On cooling, potassium nitrate does not return from β -phase to α -phase again, but at $T \sim 397$ K it transforms into another trigonal phase $R3m$, which is the ferroelectric γ -phase. This phase exists on cooling down to ~ 378 K, but below this temperature, potassium nitrate returns back to the paraelectric α -phase.^{6,7}

Dielectric properties of KNO_3 embedded into porous glasses with average pore diameters of 320 ± 20 nm (PG320), 46 ± 6 nm (PG46) and 7 ± 2 nm (PG7) were studied in Refs. 8 and 9. The growth of dielectric permittivity ϵ' on heating was observed for all types of NCMs— in particular, for NCM $\text{KNO}_3 + \text{PG7}$ it was almost exponential. This phenomenon

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was especially pronounced at low frequencies. On decreasing the average pore diameter, the value of ϵ' increased sharply, in addition, a large frequency dispersion was observed over the entire temperature range studied. For NCM KNO_3 +PG46 and KNO_3 +PG7, the relaxation process responsible for the ferroelectric phase transition was detected. The dielectric strength $\Delta\epsilon$ of this process had a maximum at the phase transition point, the position of this peak shifted towards lower temperatures with decreasing particle size, and the maximum itself broadened.

The temperature evolution of crystal structure of potassium nitrate embedded into porous glasses PG320, PG46 and PG7 on heating and cooling has been studied by X-rays and neutron diffraction in Refs. 10–12. It has been found that the type of phase diagram depended on the prehistory of sample preparation and on the method of pore space filling (from an aqueous solution or from a melt). It is shown that at room temperature there is a coexistence of α - and γ -phases and γ -phase in NCM KNO_3 +PG7 is predominant and remains stable upon cooling down to 5 K.

It is well known, that the modification of the interface with carbon leads to a change in the wettability of the inner surface of the pores (channels) by the material introduced from the aqueous solution. In this case, it should be expected that such a modification could lead to significant changes in the properties of NCM with potassium nitrate. Verification of this assumption has been the principle goal of this work.

2. Samples and Experimental Procedure

Porous glasses have been obtained by an etching of sodium borosilicate glass after phase separation procedure.^{1,2} The average pore diameters were determined by the mercury porosimetry. Carbon was introduced into the pores by impregnating the glass with the sugar solution followed by annealing at 300°C. The percentage of filling with carbon was about 15% of total porous space. According to our structure and small-angle neutron scattering studies of PG6+C matrices, carbon covers the inner pore (channel) surface with the thin amorphous layer.¹³ Potassium nitrate was introduced into porous glasses from an aqueous solution (our attempts to embed KNO_3 from the melt led to the destruction of the carbon interface). The percentage of filling with KNO_3 in carbon-free nanocomposite was 75% and for carbonized sample — 39% of empty porous space. It is necessary to note that the aqueous solution of KNO_3 doesn't wet the carbonized surface. So, the decreasing of filling is associated not only with a decrease in the diameter of channels, but also with the principle change of nanoclusters organization due to non-wetting conditions.

We have studied the electrical properties of empty porous glasses with the average pore diameter of 6(1) nm (PG6), empty PG6 modified by carbon (PG6+C), PG6 filled by KNO_3 (KNO_3 +PG6) and PG6+C filled by KNO_3 (KNO_3 +PG6+C).

Samples were rectangular plates in size of 8 mm × 5 mm with the thickness of 0.6 mm.

To carry out dielectric studies, gold electrodes about 80 nm thick with 4 nm chromium sublayer for better adhesion were deposited on the sample surfaces. The study of dielectric response has been carried out on the broadband dielectric spectrometer Novocontrol BDS80 in the frequency range of 0.1 – 3 × 10⁶ Hz and in the temperature diapason 300–440 K on cooling at 1 K/min rate.

To determine the phase state of KNO_3 in these nanocomposites after the first “heating–cooling” circle, we have studied the structure of KNO_3 +PG6 and KNO_3 +PG6+C NCMs on SuperNova Oxford Diffraction X-ray diffractometer at $\lambda = 0.70926 \text{ \AA}$ (Mo $\text{K}_{\alpha 1}$ line) in the angle range of 2θ 5°–43° at room temperature. The background from amorphous SiO_2 formed a skeleton of PG6 that has been determined from the diffraction pattern of empty matrix. The experiments were carried out in the transmission geometry, the thickness of all samples was the same.

3. Results and Discussion

3.1. X-ray diffraction

In Fig. 1, the experimental diffraction patterns for empty PG6 (dotted green line), KNO_3 +PG6+C (solid black line) and KNO_3 +PG6 (dashed red line) samples are presented. The observed broad and pronounced peak with the maximum near $2\theta \approx 10^\circ$ is associated with scattering on amorphous silica (SiO_2). It is clearly seen, that the diffraction spectra for NCM with embedded potassium nitrate differ significantly both from each other and from the diffraction pattern for empty porous glass PG6. It indicates not only the presence of embedded material in the pores, but also the difference in the phase state of KNO_3 itself in the matrices. In the next step, in order to obtain information about this state in NCMs, we have subtracted the background from scattering on the amorphous

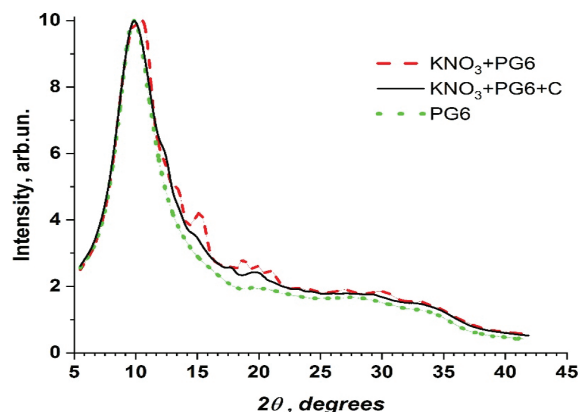


Fig. 1. (Color online) Experimental diffraction patterns for KNO_3 +PG6 (dashed red line), KNO_3 +PG6+C (solid black line) and empty PG6 (dotted green line) at room temperature.

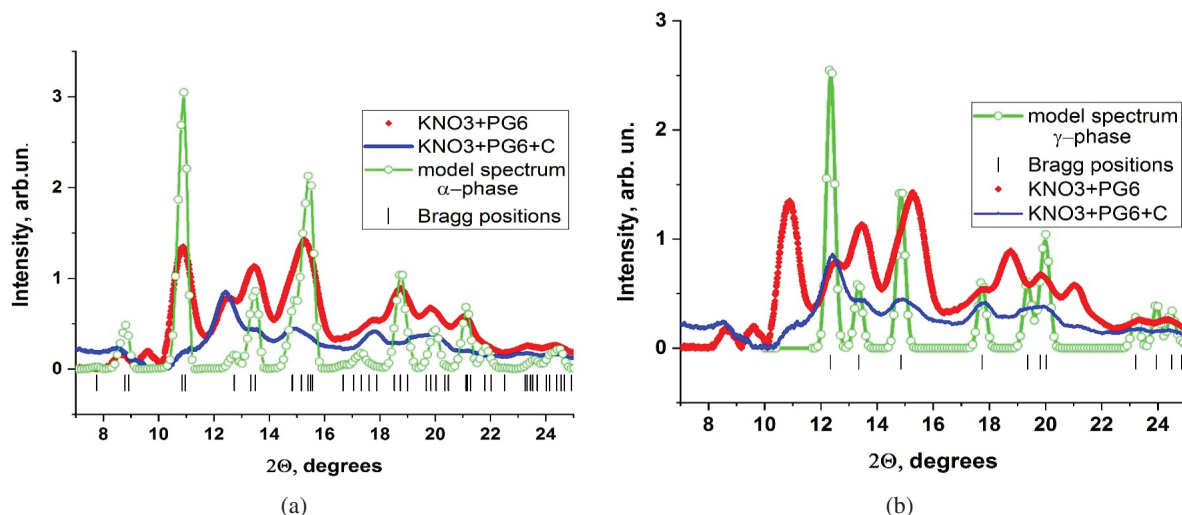


Fig. 2. (Color online) Green lines with open circles – simulated diffraction spectra for bulk KNO₃ in α -phase (Fig. 2(a)) and γ -phase (Fig. 2(b)). Open red rhombs are the experimental spectra after background subtraction for NCM KNO₃+PG6 NCM, blue lines correspond to the similar spectrum for NCM KNO₃+PG6+C. The vertical dashes at the bottom of every panels indicate the positions of the elastic Bragg peaks for bulk material: α -phase in Fig. 2(a) and γ -phase in Fig. 2(b).

matrix from the spectra for KNO₃ + PG6 and KNO₃ + PG6 + C and have compared them to simulated patterns for different phases of KNO₃ (Fig. 2).

In Fig. 2, the simulated patterns for bulk material indicate by solid green lines with open circles and correspond to the paraelectric low-temperature α -phase (Fig. 2(a)) and the ferroelectric γ -phase (Fig. 2(b)). Solid blue lines in Figs. 2(a) and 2(b) indicate the experimental pattern for NCM KNO₃+PG6+C, and red rhombs correspond to the diffraction data for NCM KNO₃+PG6.

Unfortunately, insufficient statistics due to the small amount of nanostructured material and size effects leading to a significant broadening of the elastic peaks did not allow to perform a detailed quantitative analysis of the crystal structure of these NCMs, but a comparison of these data with the model spectra permits to make a number of conclusions about the phase states and characteristic sizes of potassium nitrate nanoparticles. From the broadening of elastic peaks after convolution with the instrumental function, we have estimated the average size of nanoparticles as 17(6) nm for both the composites. Also, it is easy to see (Fig. 2(a)) that NCM KNO₃+PG6 contains all principle peaks of the paraelectric α -phase, but, at the same time, there is also the clearly observed admixture of γ -phase: For example, there is a sufficiently intensive peak at $2\theta \approx 12.3^\circ$, which is typical only for the ferroelectric phase (see Fig. 2(b)). It is necessary to note that this peak is the most intensive for X-ray scattering (open circles in Fig. 2(b)). Thus, we can conclude that in NCM KNO₃+PG6 the coexistence of α - and γ -phases exists, and the α -phase is dominant. In the case of KNO₃+PG6+C sample, we have a completely different situation— comparing Figs. 2(a) and 2(b) one can see that for this NCM, the most intense peak for α -phase at $2\theta \approx 11^\circ$ is strongly

suppressed, as are the rest of the intense peaks of this phase. At the same time, for NCM KNO₃+PG6+C (black line and points in Fig. 2(b)) all principle elastic peaks of the ferroelectric phase are clearly present. This allows us to conclude that γ -phase is predominant in this NCM, and the admixture of the paraelectric phase is small. So, we can state that the carbonization of inner channel surfaces leads to a change of ratio of potassium nitrate crystal phases. It can be associated with channels diameter and nanoclusters space organization (due to non-wetting conditions) changes.

3.2. Dielectric response

In Fig. 3, the temperature dependences of permittivity (ϵ') at 179 kHz (left) and 0.1 Hz (right) on cooling for PG6, PG6+C, KNO₃+PG6 and KNO₃+PG6+C are presented, and in Fig. 4 the corresponding dependences of conductivity (σ') are shown.

Black squares correspond to empty PG6, red points – carbonized glass (PG6+C). Comparing these curves one can see that carbonization of porous glasses increases ϵ' of these glasses at all measured temperatures and frequencies.

At low frequencies, the conductivity of carbonized glass decreases by an order of magnitude compared to the empty glass. Unfortunately, at high frequencies it was not possible to measure σ' due to the capacitance-resistance ratio in empty porous glass. This behavior can point out that carbon suppresses the conductivity over the pore surfaces.

Let us now consider the behavior of composites with embedded ferroelectric. In Figs. 3 and 4, blue triangles correspond to KNO₃ in PG6 (KNO₃+PG6), green triangles – KNO₃ in carbonized glass (KNO₃+PG6+C). To compare

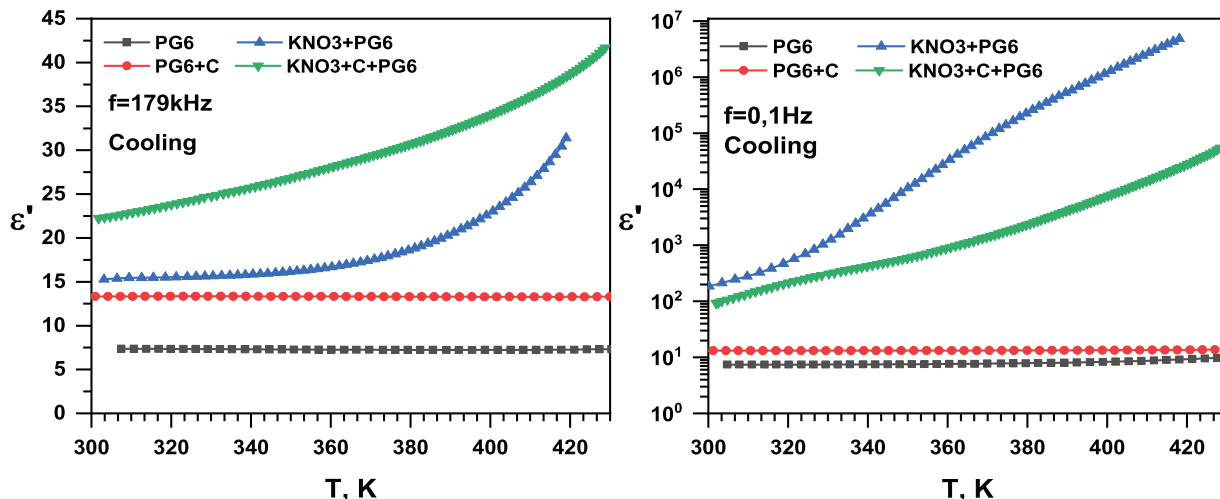


Fig. 3. Temperature dependences of permittivity on cooling at 179 kHz (left figure) and 0.1 Hz (right figure) for PG6, PG6+C, KNO₃+PG6, KNO₃+PG6+C.

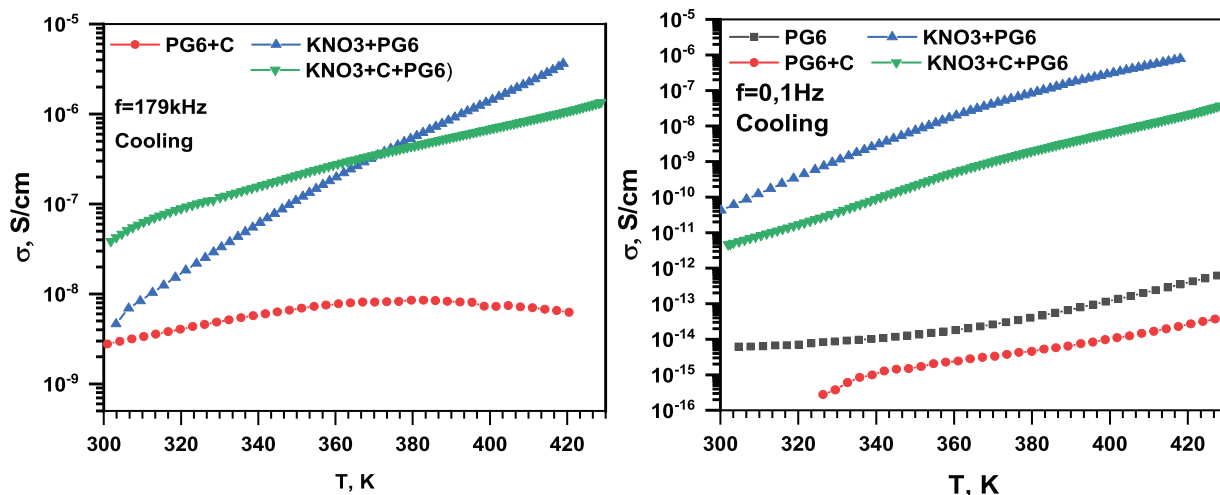


Fig. 4. Temperature dependences of AC-conductivity at 179 kHz (left figure) and 0.1 Hz (right figure) for PG6, PG6+C, KNO₃+PG6, KNO₃+PG6+C on cooling.

the permittivity and conductivity of these nanocomposites, one can see that at low frequencies at room temperature, ϵ' and σ' of the composite with carbon are smaller than those of the samples without carbon (Figs. 3 and 4 right panels). At high temperatures (above 400 K), the values of ϵ' and σ' of KNO₃+PG6 composite are by several orders of magnitude more than those of KNO₃+PG6+C. At high measuring frequencies (hundreds kHz), the situation changes. At high temperatures, the conductivity of the unmodified composite is higher than that of the carbonized NCM. On cooling, the decreasing of ϵ' and σ' of KNO₃+PG6 occurs faster than those of NCM with carbon, and at room temperature, the permittivity and conductivity of KNO₃+PG6 become lower than those of KNO₃+PG6+C. This behavior of carbonized NCM dielectric response indicates that the conductivity over the pore surfaces makes the

significant contribution to the dielectric response of NCM KNO₃+PG6, i.e., it looks like the carbon decreases the surface conductivity.

In order to analyze the nature of the observed dielectric response, its frequency dependences have been obtained and analyzed, and these dependences at 400 K are presented in Fig. 5.

Up-to-now there is no rigorous theory for describing dielectric spectra other than the Debye one.^{14,15} To analyze the results, usually the empirical distributions are used, which describe well the dispersion curves of various substances from liquids to polymers. As a model function, we have used Eq. (1), consisting of the following terms: The sum of the empirical Cole–Cole functions describing relaxation processes, the contribution of phonon modes in ϵ and DC conductivity term:

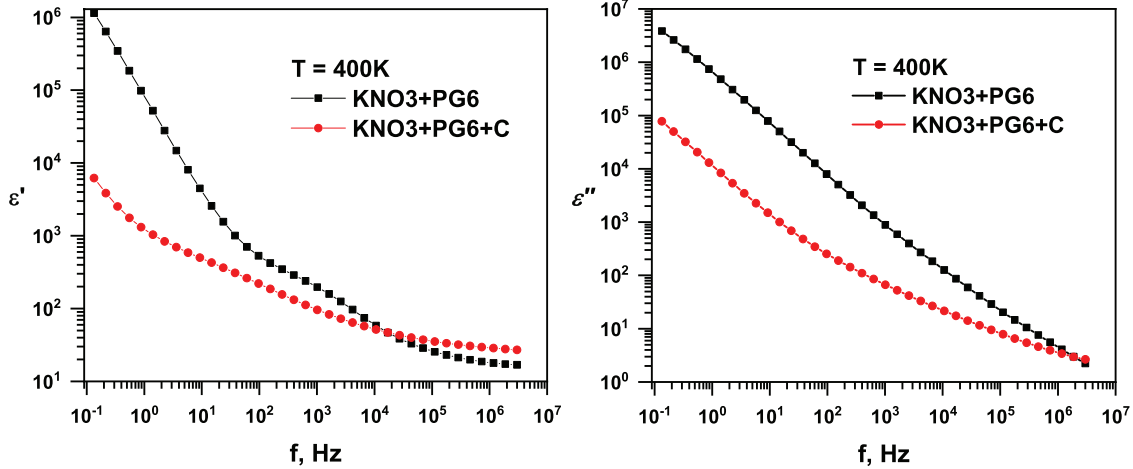


Fig. 5. Frequency dependences of dielectric permittivity (ϵ') and losses (ϵ'') for $\text{KNO}_3 + \text{PG6}$ and $\text{KNO}_3 + \text{PG6} + \text{C}$ at 400 K.

$$\epsilon^*(\omega) = \epsilon_\infty + \sum_j \frac{\Delta\epsilon_j}{1 + (i\omega\tau_j)^\alpha} + \frac{i\sigma_{DC}}{\epsilon_0\omega}, \quad (1)$$

where $\Delta\epsilon$ is the dielectric strength of the relaxation process, τ is the characteristic relaxation time, $0 < \alpha \leq 1$ is the exponent responsible for the broadening of the spectrum in comparison with the Debye spectrum ($\alpha = 1$), ϵ_∞ is the contribution of phonon modes and electron polarization, ω is the cyclic frequency, ϵ_0 is the dielectric permittivity of vacuum and σ_{DC} – DC conductivity.

To fit the dispersion curves by model function (1), we have carried out a nonlinear approximation of frequency dependences of dielectric permittivity and losses using the Levenberg–Marquardt algorithm.¹⁶ It should be noted that ϵ' and ϵ'' have been fitted simultaneously, that significantly reduces the errors of parameters calculation. The result of the fitting procedure for NCM $\text{KNO}_3 + \text{PG6}$ at 400 K and the decomposition into the separate contributions are drawn in Fig. 6.

From this fitting, two relaxation processes have been identified, the contribution of DC conductivity has been determined, and the temperature dependences of the relaxation processes parameters have been obtained. The temperature dependences of $\Delta\epsilon$ and τ of two observed relaxation processes for $\text{KNO}_3 + \text{PG6}$ and $\text{KNO}_3 + \text{PG6} + \text{C}$ are presented in Fig. 7.

The first process (red closed circles) provides the main contribution to dielectric response of the carbon-free composite, and $\Delta\epsilon$ of this process increases on heating. The characteristic relaxation time of this process is of the order of seconds. A similar relaxation process (red open circles) also exists in NCM with carbon, but it is much weaker and essentially slower, i.e., interface modification affects this process essentially. We attribute this process to the charge polarization on the pores' boundaries. Surface pore modification by carbon changes the interface significantly (suppressing the potassium ion jumps on interfaces due to crystallization from

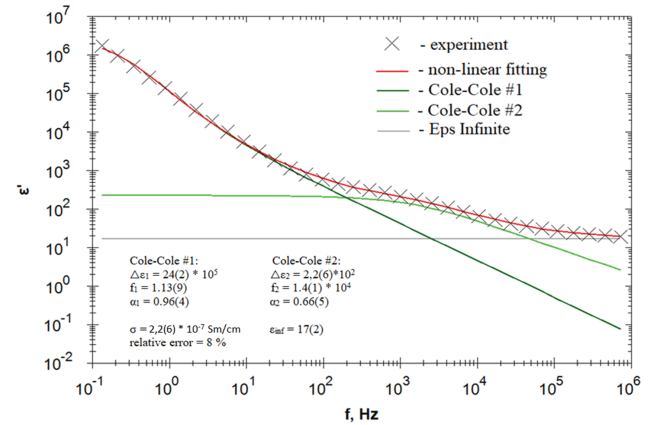


Fig. 6. (Color online) Nonlinear approximation of the frequency dependence of the dielectric response of $\text{KNO}_3 + \text{PG6}$ by Eq. (1) at 400 K. Crosses show the experimental data; the red curve is the result of nonlinear approximation; light green and dark green lines are contributions of two Cole–Cole processes; gray line is ϵ_∞ .

non-wetting solution) and the parameters of this relaxation process.

The second relaxation process in $\text{PG6} + \text{KNO}_3$ (black closed squares) is weaker by three orders of magnitude than the first one. This process has relaxation times increasing from 10^{-5} at 415 K to 10^{-2} s at 350 K and an almost constant $\Delta\epsilon$ in the temperature diapason 350–420 K. Such behavior of the process parameters can be attributed to hopping conductivity in KNO_3 clusters and between neighboring ones. In potassium nitrate, it can only be potassium ions jumping over defects, since the NO_3 group is very tightly bound.⁸ In NCM with modified surface, this process (black open squares) is by one order of magnitude stronger and by six orders slower. Modification of pore surface by carbon leads not only to the decrease of average pore diameter, but also to the decrease of characteristic KNO_3 nanoparticle size.¹³ Moreover, potassium nitrate wets the carbonized surfaces essentially worse

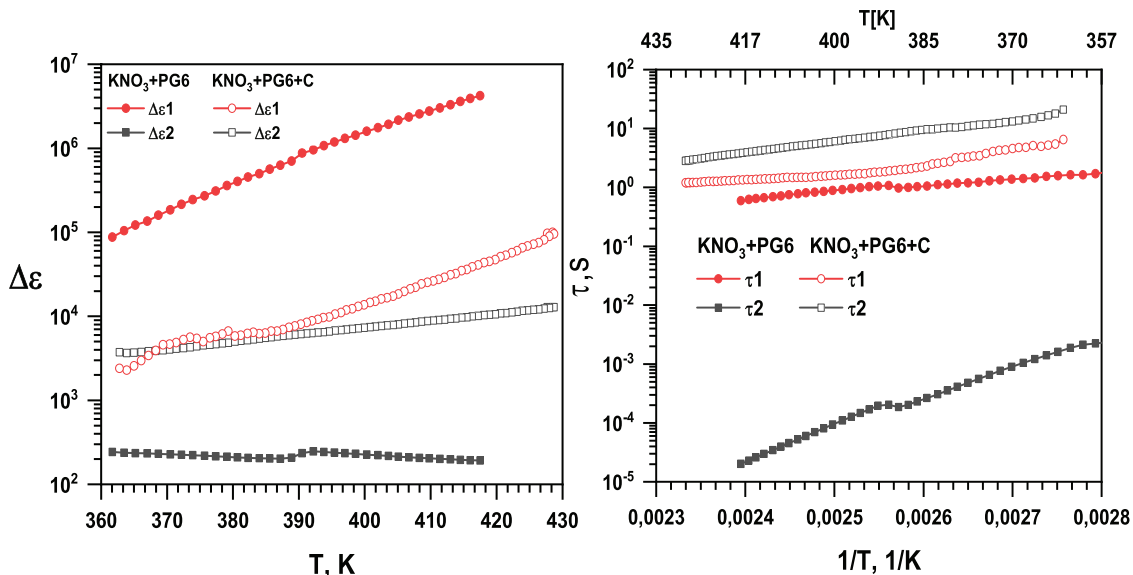


Fig. 7. (Color online) Temperature dependences of $\Delta\varepsilon$ (left) and relaxation times τ (right) of $\text{KNO}_3+\text{PG6}$ and $\text{KNO}_3+\text{PG6+C}$, closed squares and circles – $\text{KNO}_3+\text{PG6}$, open squares and circles – $\text{KNO}_3+\text{PG6+C}$.

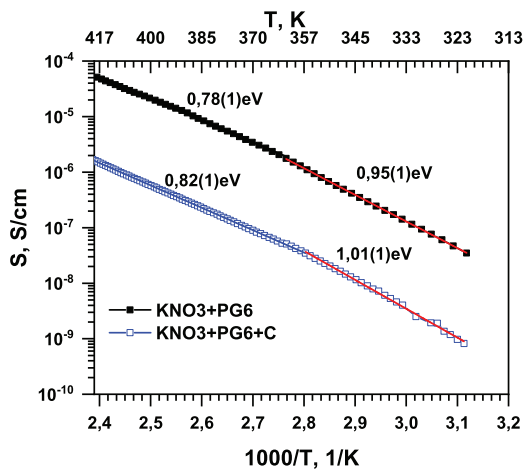


Fig. 8. Temperature dependences of $\text{KNO}_3+\text{PG6}$ and $\text{KNO}_3+\text{PG6+C}$ DC-conductivity in the Arrhenius coordinates for clarity. The corresponding activation energies are indicated.

than conventional porous glasses. Therefore, one can expect a decrease in the connectivity of nanoclusters, which leads to a growth of $\Delta\varepsilon$ and τ . Keeping in mind these facts, we can conclude that this process associates with potassium ions hopping conductivity.

On fitting the experimental data by Eq. (1), we have estimated the contribution of DC-conductivity of NCMs. The temperature dependences of DC-conductivity of $\text{KNO}_3+\text{PG6}$ and $\text{KNO}_3+\text{PG6+C}$ samples are shown in Fig. 8 in the Arrhenius coordinates for clarity. Carbon surface modification leads to decreasing DC-conductivity of NCMs by two orders of magnitude over the entire studied temperature range. Conductivity has a thermoactivated character.

We have determined the corresponding activation energies values, and it is easy to see that the activation energy of modified NCM is somewhat higher than unmodified NCM. These energies are in order to 1 eV and are in good agreement with the typical energy of potassium ions hopping.¹⁷ In a vicinity of 360 K, there is a change in the slopes of $\sigma(T)$ for both composites, i.e., the activation energies transform. This fact correlates perfectly with phase transformations observed early for NCM $\text{KNO}_3+\text{PG7}$ and $\text{KNO}_3+\text{PG46}$ ^{10–12} on cooling. Indeed, according to the phase diagram for these NCMs, the formation of the low-temperature α -phase begins in the diapason 360–380 K (depending on nanoparticle sizes), and a decrease of the average pore diameter of porous glasses (and, accordingly, the size of nanoparticles) reduces this temperature.¹²

4. Conclusion

Effect of pore surface carbonization on structure and dielectric properties of NCM on the base of PG6 with embedded potassium nitrate has been studied at the temperature diapason 300–430 K and at frequencies of 0.1– 3×10^6 Hz on cooling. Analysis of X-ray diffraction patterns have shown that at room temperature, the coexistence of the paraelectric α -phase and the ferroelectric γ -phase of KNO_3 are observed. In NCM $\text{KNO}_3+\text{PG6}$ α -phase predominates, in NCM $\text{KNO}_3+\text{PG6+C}$, contra versa, γ -phase plays the leading role.

It is experimentally found that at low frequencies above 400 K the values of ε' and σ' of $\text{KNO}_3+\text{PG6}$ composite are by several orders of magnitude more than those of $\text{KNO}_3+\text{PG6+C}$. Dielectric response of carbonized NCM indicates that the hopping conductivity over the pore surfaces makes a significant contribution to the dielectric response of

NCM KNO₃+PG6, i.e., it looks like the carbon suppresses the surface conductivity.

Analysis of temperature and frequency dependencies of dielectric response reveals two relaxation processes. The first one provides the main contribution to the dielectric response of the carbon-free composite, and $\Delta\epsilon$ of this process decreases on cooling from 10⁷ to 10⁵, τ is order of ~ seconds. We attribute this process to the charge polarization on the pores' boundaries. A similar relaxation process also exists in NCM with carbon, but it is much weaker and essentially slower, i.e., interface modification affects this process essentially. The second relaxation process in KNO₃+PG6 is weaker by three orders of magnitude and has an almost constant $\Delta\epsilon$. Relaxation times increase from 10⁻⁵ to 10⁻² s on cooling. In KNO₃+PG6+C, the process becomes by six orders slower. We believe that this process corresponds to a hopping conductivity in KNO₃ clusters and between neighboring ones.

We have estimated DC-conductivity of NCMs, and activation energies in order of 1 eV for both nanocomposites have been determined. It corresponds to the typical energy of potassium ions hopping. The activation energy changes slightly in a vicinity of 360 K in both NCMs, which is attributed to the phase transformation and the appearance of KNO₃ α -phase.

The main contribution to the dielectric response of NCM PG6+KNO₃ is provided by charge polarization on interfaces, which can be governed by modifying the inner pore surfaces.

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