

Original article

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EFFECT OF INTERFACE MODIFICATION BY TITANIUM DIOXIDE ON DIELECTRIC PROPERTIES OF SODIUM NITRITE NANOCOMPOSITE BASED ON POROUS GLASS

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Abstract. Dielectric properties and structure of initial nanocomposite based on porous glass with embedded ferroelectric NaNO_2 and nanocomposite identical to that but having a TiO_2 -modified pore surface, have been studied over a temperature range 300 – 450 K (on cooling) and frequency one 0.1 – $3 \cdot 10^6$ Hz. X-ray spectroscopy of the samples exhibited that NaNO_2 was in the ferroelectric phase in both composites and the percentage of crystalline NaNO_2 increased in the pores of the modified one. An increase in permittivity and conductivity was observed in the TiO_2 -modified nanocomposite. Two relaxation processes were identified and their nature was established. The charge polarization at the interfaces was found to make the main contribution to the dielectric response of the both nanocomposites. The DC-conductivity of both composites was estimated and its activation energies were determined. An activation energy change observed in a vicinity of 400 K was attributed to the phase transition to the low-temperature phase of NaNO_2 . The possibility to control the properties of nanocomposites through modifying the interfaces was shown.

Keywords: nanocomposite, ferroelectric, sodium nitrate, titanium oxide, porous glass, dielectric spectroscopy

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ВЛИЯНИЕ МОДИФИКАЦИИ ИНТЕРФЕЙСА ДИОКСИДОМ ТИТАНА НА ДИЭЛЕКТРИЧЕСКИЕ СВОЙСТВА НАНОКОМПОЗИТА НА ОСНОВЕ ПОРИСТОГО СТЕКЛА С НИТРИТОМ НАТРИЯ

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Аннотация. Исследованы диэлектрические свойства и структура исходного нанокompозита на основе пористого стекла с внедренным NaNO_2 и такого же нанокompозита, но с поверхностью пор, модифицированной диоксидом титана (температурный диапазон – 300 – 450 К, частотный – 0,1 – 3·10⁶ Гц), при охлаждении. Структурные исследования показали, что в обоих композитах NaNO_2 находится в сегнетоэлектрической фазе. При модификации поверхности процент кристаллического NaNO_2 в порах возрастает. В модифицированном композите наблюдается увеличение диэлектрической проницаемости и проводимости. Идентифицированы два релаксационных процесса и установлена их природа. Установлено, что основной вклад в диэлектрический отклик НКМ вносит зарядовая поляризация на границах раздела. Оценена проводимость на постоянном токе обоих композитов и определены соответствующие энергии активации. Изменение энергии активации, наблюдаемое в районе 400 К, связано с фазовым переходом в низкотемпературную фазу NaNO_2 . Показана возможность управления свойствами нанокompозитов через модификацию интерфейса.

Ключевые слова: нанокompозит, сегнетоэлектрик, нитрит натрия, пористое стекло, оксид титана, диэлектрическая спектроскопия

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Introduction

Nanocomposite materials (NCM) based on nanoporous matrices with embedded ferroelectrics are of undoubted interest due to broad prospects for practical applications in novel approaches in electronics, information storage devices, applied medicine and biology, etc. It is known that the dimensional effect can fundamentally change the physical properties of materials, especially when the characteristic sizes of the nanoparticles become comparable to the correlation length of critical fluctuations in the order parameter. There are various methods for preparing NCM; one of them is embedding substances into nanoporous glasses (referred to as porous glasses, or PG).

The advantages of PG is that modifying the parameters of pure (non-porous) alkali borosilicate glass allows to obtain matrices with different mean pore parameters, controllable from 3 nm to approximately 300–400 nm [1, 2].

At the same time, aside from the dimensional effect, the properties of NCM are significantly affected by the presence of the interface between the matrix and the embedded material. Modifications to the interface can also be used to tailor the overall macroscopic properties of the NCM; this approach has been adopted in several studies [3–5].

Sodium nitrite (NaNO_2) is a model ferroelectric, whose macroscopic properties and phase transitions have been thoroughly analyzed [6, 7]. This compound has an orthorhombic structure at room temperature (space group $Im2m$) with the parameters of the crystal cell $a = 3.55$ E, $b = 5.56$ E and $c = 5.37$ E [8]. Sodium nitrite passes into the high-temperature orthorhombic phase $Immm$ above 438 K [9]. The dielectric properties of sodium nitrite in porous glass with a mean pore diameter of 7(1) nm (PG7 + NaNO_2 system) were considered in [10 – 12]. The authors observed an exponential increase in the dielectric response at low measuring frequencies with increasing temperature, and the presence of frequency dispersion. In this case, not only the phase transition temperature decreased to 427 K, but the type of phase transition (PS) changed [12, 13]. One of the possible reasons for this major change in the physical properties of sodium nitrite embedded in PG7 may be the influence of the interface between the matrix and the embedded material, so modifying the surface of the pores (channels) in porous glass should be expected to produce a change in the overall properties of the NCM. We used titanium dioxide TiO_2 wetting the surface of the porous glass to modify the interface in our study.

Our goal was to establish the effect that modifying the interface between the matrix and the embedded material with titanium dioxide has on the dielectric properties of the PG6 + NaNO_2 nanocomposite.

Samples and experimental procedure

The following group of samples was considered:

porous glass with an average pore diameter of 6(1) nm (PG6);

porous glass with titanium dioxide (PG6 + TiO_2);

sodium nitrite in porous glass (PG6 + NaNO_2);

sodium nitrite in porous glass with titanium dioxide (PG6 + TiO_2 + NaNO_2).

Porous PG6 glasses were prepared by etching borosilicate glasses. The diameter of the pores obtained was determined via mercury porosimetry. The pure porous glass was held in a 20% solution of tetraisopropylortitanate $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ (TTIP) in isopropanol for a day at 60 °C. This PG6 glass was then hydrolyzed in air at room temperature. Annealing was carried out at 450 °C for 4 hours. The measurements indicate that the degree of filling with titanium oxide was 11% of the pore volume. To embed sodium nitrite, porous glass samples were placed in a saturated aqueous solution of NaNO_2 at 130 °C until the water evaporated completely. The degree of filling with sodium nitrite in both samples was 59% of the pore volume.

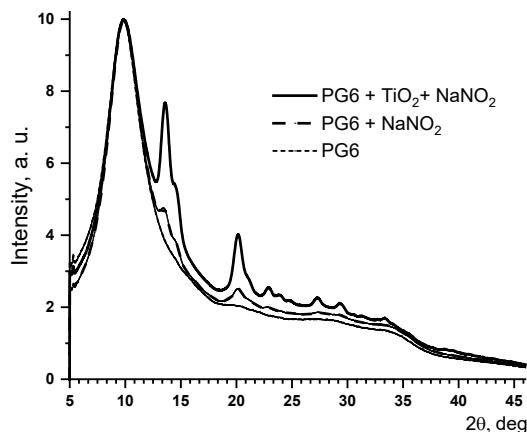


Fig. 1. Experimental X-ray patterns for PG6 + NaNO_2 , PG6 + TiO_2 + NaNO_2 and unfilled PG6 samples at room temperature

The finished samples were rectangular plates measuring $8.0 \times 5.0 \times 0.6$ mm. Dielectric studies were carried out depositing gold electrodes about 80 nm thick with a 4 nm thick chromium sub-layer (for better adhesion) onto the surface of the samples.

The dielectric response was measured with a Novocontrol BDS 80 wideband dielectric spectrometer (Germany) in the frequency range of $0.1\text{--}3.0 \cdot 10^6$ Hz and in the temperature range of 300–440 K under cooling at a rate of 1 K/min after preheating to 440 K. The phase state of NaNO_2 the NCM prepared was determined after the first heating-cooling cycle via analysis of $\text{PG6} + \text{NaNO}_2$ and $\text{PG6} + \text{TiO}_2 + \text{NaNO}_2$ NCM structures with a Oxford Diffraction SuperNova X-ray diffractometer (USA) at a wavelength $\lambda = 0.70926$ Å (Mo $K_{\alpha 1}$ radiation) in the range of angles $2\theta = 5^\circ\text{--}43^\circ$ at room temperature. Measurements were carried out in transmission geometry, the illuminated area of the samples and their thickness was the same in all cases. The contribution of the background from amorphous silica SiO_2 comprising the framework joints was determined from the XRD pattern from the empty framework.

Experimental results and discussion

Fig. 1 shows the XRD patterns for three models (unfilled PG6, $\text{PG6} + \text{TiO}_2 + \text{NaNO}_2$ and $\text{PG6} + \text{NaNO}_2$). The XRD pattern for $\text{PG6} + \text{TiO}_2$ (not shown in Fig. 1) does not contain any elastic peaks corresponding to the titanium oxide structure; moreover, the XRD patterns for the PG6 and $\text{PG6} + \text{TiO}_2$ samples are almost identical. A broad peak is observed in the vicinity of the angle $2\theta \approx 10^\circ$, associated with scattering by the amorphous material of the SiO_2 framework. Fig. 1 shows that the diffraction spectra are similar for NCM with sodium nitrite but the integral intensities of the peaks differ significantly.

The phase state of sodium nitrite in NCM was determined by subtracting the background from scattering by the amorphous framework from the spectra of $\text{PG6} + \text{NaNO}_2$ and $\text{PG6} + \text{TiO}_2 + \text{NaNO}_2$ samples; the data were then compared with the model spectrum for bulk sodium nitrite at this wavelength (Fig. 2).

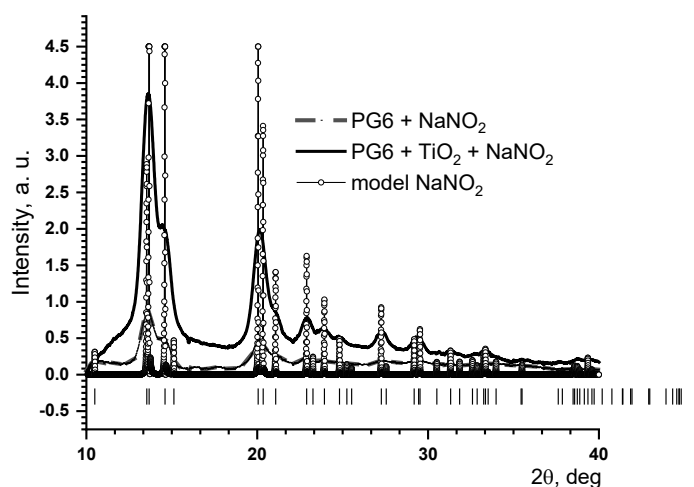


Fig. 2. Comparison of XRD patterns from Fig. 1, subtracting the background from the framework (amorphous SiO_2), with the model spectrum of bulk NaNO_2 at room temperature (vertical bars indicate the positions of elastic Bragg peaks)

Due to a number of considerations, we did not conduct a detailed quantitative analysis for the crystalline structure of these NCM, but comparing the data presented with the model spectrum for bulk material allows to draw some conclusions about the phase state of sodium nitrite in the framework pores.

As seen from Fig. 2, the spectrum of the $\text{PG6} + \text{NaNO}_2$ sample contains all the main peaks characteristic for the low-temperature orthorhombic phase of sodium nitrite, which is even more pronounced in the corresponding spectrum for the sample with titanium dioxide. In addition, the integral intensity of the peaks significantly increased when sodium nitrite was embedded into the titanium dioxide glass, even though both PG6-based NCM had the same degree of filling with



sodium nitrite. This result can be associated with an increase in the fraction of the crystalline phase in the pores upon crystallization of sodium nitrite in porous glass with titanium dioxide. The remaining sodium nitrite is most likely in an amorphous state. The presence of a significant fraction of the amorphous phase, along with the crystalline phase in the NCM based on porous glasses, is unsurprising, since it was observed earlier for nanocomposites with embedded selenium [14] and low-melting+point metals [15].

Fig. 3 shows the temperature dependences of dielectric permittivity ϵ' (left) and conductivity σ' (right) at frequencies of 1 kHz and 0.1 Hz during cooling. Comparing these dependences, we can conclude that adding titanium dioxide increases the magnitudes of ϵ' and σ' in these glasses throughout the temperature range considered. The σ' values in glass with TiO_2 increase by almost an order of magnitude, compared to PG6 at low frequencies. Unfortunately, it was not possible to measure σ' in the entire temperature range in empty porous glass at high frequencies. It is clear from the given temperature dependences of σ' for PG6 and PG6+ TiO_2 that titanium dioxide increases the conductivity of the porous matrix.

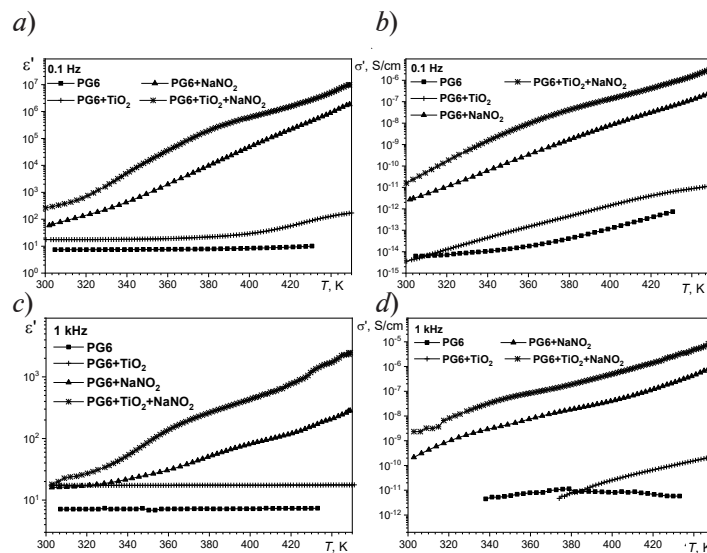


Fig. 3. Temperature dependences of dielectric permittivity ϵ' (a, c) and conductivity σ' (b, d) for PG6, PG6 + TiO_2 , PG6 + NaNO_2 and PG6 + TiO_2 + NaNO_2 NCM at 0.1 Hz (a, b) and 1 kHz (c, d)

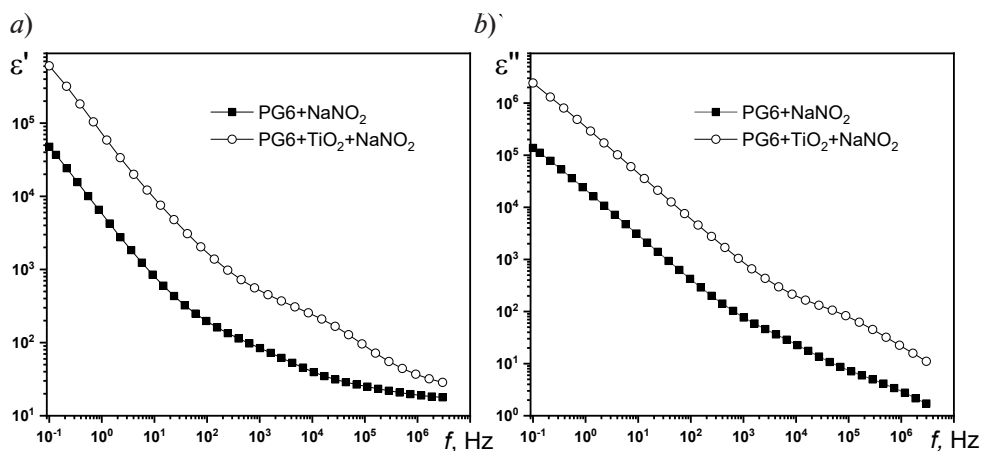


Fig. 4. Frequency dependences of dielectric permittivity ϵ' (a) and dielectric losses ϵ'' (b) for PG6 + NaNO_2 and PG6 + TiO_2 + NaNO_2 samples at 400 K

In the next step, we analyzed the behavior of dielectric response in composites with embedded sodium nitrite. Comparing the behavior of the curves related to the temperature dependences of ε' and σ' for these nanocomposites, we can see that the level of ε' and σ' values in the NCM with TiO_2 is higher than for the samples without it both at low (0.1 Hz) and high (1 kHz) frequencies in the entire measured temperature range. The ε' and σ' values of the $\text{PG6} + \text{TiO}_2 + \text{NaNO}_2$ composite at high temperatures (above 400 K) are an order of magnitude greater than those of $\text{PG6} + \text{NaNO}_2$. The difference in ε' values is small at low temperatures (near room temperature). This behavior of the dielectric response in NCM with titanium dioxide confirms our assumption based on the results of structural studies that the percentage of crystalline sodium nitrite is higher in $\text{PG6} + \text{TiO}_2 + \text{NaNO}_2$ than in $\text{PG6} + \text{NaNO}_2$ samples.

The respective frequency dependences were obtained and investigated to analyze the physical nature of the dielectric response. These dependences at 400 K are shown in Fig. 4.

Notably, no rigorous theory has been formulated this far for describing the relaxation contributions other than from Debye relaxation [16, 17], so empirical distributions are used to analyze the results, characterizing the dispersion dependences for a large number of substances sufficiently well. Expression (1) is used as a model function; consisting of the following terms: the sum of the empirical Cole–Cole functions, describing relaxation processes, the term from the contribution of phonon modes, and the term responsible for DC conductivity:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_j \frac{\Delta\varepsilon_j}{1 + (i\omega\tau_j)^\alpha} + \frac{i\sigma_{DC}}{\varepsilon_0\omega}, \quad (1)$$

where $\Delta\varepsilon$ is the dielectric strength of the relaxation process, τ is the mean relaxation time, α is the exponent characterizing the broadening of the spectrum relative to Debye behavior, ε_∞ is the contribution of phonon modes and electron polarization, ω is the angular frequency, ε_0 is the dielectric constant of vacuum, σ_{DC} is the DC conductivity.

The dispersion curves can be described by expression (1), if we first carry out nonlinear approximation of the frequency dependences of the dielectric permittivity and dielectric losses. Approximation was performed by the Levenberg–Marquardt algorithm [18]. The curves of the ε' and ε'' dependences were simultaneously fitted, allowing to significantly reduce the error. Two relaxation processes were detected in the frequency and temperature ranges considered. The contribution of DC conductivity was found, consequently yielding the temperature dependences for the parameters of relaxation processes, $\Delta\varepsilon$ and τ (Fig. 5).

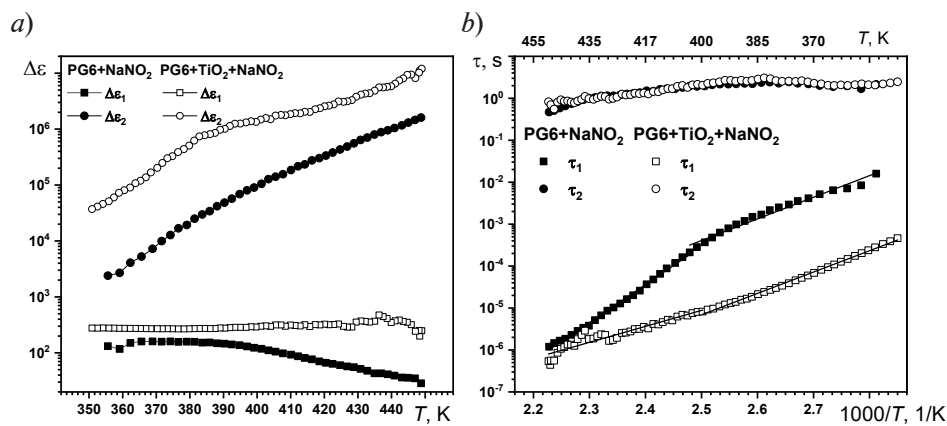


Fig. 5. Temperature dependences for dielectric strength of the relaxation process $\Delta\varepsilon$ (a) and the characteristic values of mean relaxation time τ (b) for two relaxation processes (denoted by subscripts 1 and 2) for $\text{PG6} + \text{NaNO}_2$ and $\text{PG6} + \text{TiO}_2 + \text{NaNO}_2$ samples

The main contribution to the dielectric response of both composites is made by the quantity $\Delta\varepsilon_2$, and this contribution increases with increasing temperature. The characteristic relaxation times of this process for both composites are equal to about a second, and their temperature dependences are almost identical throughout the temperature region considered. This confirms that these processes are equivalent, even though the strength of the process is higher in modified NCM than in the one not modified with TiO_2 (this may be due to a higher percentage of the crystalline phase of sodium nitrite in the given NCM). We associate this process with charge polarization at the grain (nanoparticle) boundaries of sodium nitrite.

The magnitude of $\Delta\varepsilon_1$ is virtually independent of temperature in modified NCM. The process is somewhat weaker in unmodified NCM, and its value of $\Delta\varepsilon$ decreases within the same order of magnitude with increasing temperature. Relaxation times vary from 10^{-2} s (at 350 K) to 10^{-6} s (at 450 K) for unmodified NCM and from 10^{-3} to 10^{-7} s for the NCM modified with TiO_2 . Such values and temperature behavior observed for the parameters of the relaxation process allow to relate it to hopping conductivity of sodium ions, which has already been detected earlier in the $\text{PG7} + \text{NaNO}_2$ NCM [19, 20]. This process is faster by an order of magnitude faster in the NCM with a modified surface, i.e. it can be assumed that modification of the pore surface with titanium dioxide facilitates the hopping conductivity of sodium ions. The dependences of relaxation time for the second type of processes exhibit a thermally activated behavior in both NCM. Two regions with different activation energies (with a change in the slope of the curves) can be detected for each dependence near 400 K, which may be due to a PT to the low-temperature phase of sodium nitrite, shifting in temperature due to the size effect.

Estimates of DC conductivity in both NCMs were also obtained by fitting the experimental data using Eq. (1). The temperature dependences of conductivity for $\text{PG6} + \text{NaNO}_2$ and $\text{PG6} + \text{TiO}_2 + \text{NaNO}_2$ samples are shown in Fig. 6 in Arrhenius coordinates. Modifying the surface with titanium dioxide produces an increase in the DC conductivity of the NCM by an order of magnitude in the entire temperature range considered. The conductivity has a thermally activated nature; two regions with different activation energies can be observed on each curve, while the change in activation energy is observed at about 400 K. This correlates well with the data obtained for relaxation times. The activation energy of the composite containing TiO_2 turns out to be somewhat lower, i.e., the modification of the surface seems to facilitate the hopping conductivity of sodium ions.

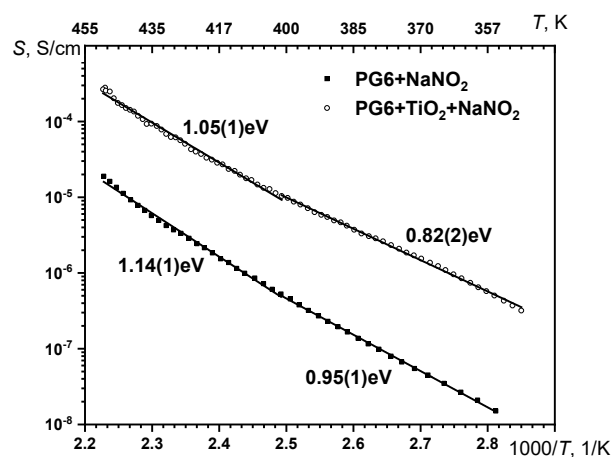


Fig. 6. Dependences of DC conductivity on inverse temperature (the corresponding values of T are given on the upper scale) for $\text{PG6} + \text{NaNO}_2$ and $\text{PG6} + \text{TiO}_2 + \text{NaNO}_2$ samples. Straight lines correspond to Arrhenius approximations (the corresponding activation energies are also given)

Conclusion

We have investigated the electrical and structural properties of nanocomposite materials based on pure porous glasses with an average pore diameter of 6(1) nm, porous glasses with the pores modified with titanium dioxide and filled with a ferroelectric (sodium nitrite). Structural studies revealed a crystalline phase of sodium nitrite in the samples (no peaks from TiO_2 were detected), so there is reason to believe that TiO_2 is in amorphous state. It was established from XRD patterns that the integral intensity of the diffraction peaks is significantly higher for the $\text{PG6} + \text{TiO}_2 + \text{NaNO}_2$ sample than for $\text{PG6} + \text{NaNO}_2$. This suggests an increase in the percentage of sodium nitrite crystalline phase in the pores of modified NCM, compared to the content of this phase in the NCM without titanium dioxide.

We have found an increase in the dielectric permittivity and conductivity of the modified NCM compared to the unmodified sample. The dielectric response of both composites was analyzed, with two relaxation processes observed in the selected temperature and frequency ranges. Evidently, the main contribution to the dielectric response of NCM is made by a relaxation process associated with charge polarization at grain (nanoparticle) boundaries, and this relaxation process is more pronounced in the NCM with titanium dioxide, due to increased volume of crystalline sodium nitrite in NCM pores. We attributed the second relaxation process to hopping conductivity of sodium ions along the channels. This process is as intense in the NCM containing TiO_2 but it proceeds much faster, pointing to a possible increase in the number of conduction channels and/or a decrease in the hopping length due to modification of the pore surface with titanium dioxide.

Thus, it is confirmed that modifying the surface allows to control the dielectric properties of nanocomposite materials based on porous matrices.

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