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Electrophysical properties of the Rochelle salt / asbestos nanocomposite material

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Abstract. Electrical conductivity, dielectric permittivity and dielectric losses of a novel nanocomposite material obtained by the infiltration of an asbestos matrix with Rochelle salt were studied in the frequency range 100 Hz – 100 kHz. A low-temperature shift of the Curie point T_C of the “guest” substance’s upper ferroelectric transition due to the influence of confined geometry was observed.

Keywords: Rochelle salt, Curie point, asbestos, matrix nanocomposites

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Электрофизические свойства нанокомпозиционного материала сегнетова соль / асбест

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Аннотация. В диапазоне частот 100 Гц – 100 кГц исследованы электропроводность, диэлектрическая проницаемость и диэлектрические потери нового нанокомпозиционного материала, полученного введением сегнетовой соли в матрицу асбеста. Обнаружен низкотемпературный сдвиг верхней точки Кюри T_C сегнетоэлектрического перехода вещества-«гостя», обусловленный ограниченной геометрией.

Ключевые слова: сегнетова соль, точка Кюри, асбест, матричные нанокомпозиты

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Introduction

The idea of using nanoporous “host” matrices (examples include opal, zeolite, and asbestos, etc.) for fabricating three-dimensional superlattices from nanoparticles of “guest” substances within the regular systems of calibrated voids and channels of these dielectric “host” matrices was proposed at the end of the twentieth century [1, 2].

One of the interesting applications of regular porous dielectric matrices is their use in the creation of quantum confined nanocomposite ferroelectric materials in order to study confined geometry effects. A theoretical explanation of the Curie point T_C shift towards lower temperatures [3] is based on Landau phenomenological theory. This low-temperature shift of the T_C value has been frequently observed in experiments with ferroelectric nanoparticles in porous matrices [4–8]. However, in some cases [9, 10] a T_C value shift towards higher temperatures is also possible in systems of ferroelectric nanoparticles in “host” porous matrices, compared with the temperature of the phase transition in a bulk “guest” substance.

The aim of this study was to determine experimentally the dielectric properties of the well-researched ferroelectric substance [11–18], i. e. Rochelle salt ($KNaC_4H_4O_6\times4H_2O$, hereinafter referred to as RS) embedded into a chrysotile-asbestos matrix near the upper ferroelectric Curie point (T_C = 297 K for the bulk RS material). Chrysotile-asbestos ($Mg_3Si_2O_5(OH)_4$, magnesium hydrosilicate) consists of fibers formed from twisted MgO and SiO_2 layers and contains parallel channels (tubes) with an internal diameter of ~ 5 nm (Fig. 1). This nanoporous “host” matrix was successfully used earlier for fabrication different nanocomposites [19, 20].

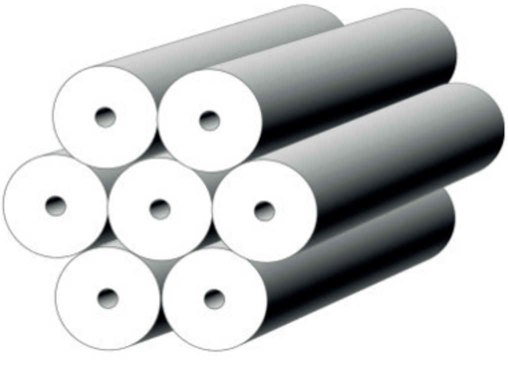

Fig. 1. Structure of asbestos porous dielectric matrix [20]

Materials and Methods

The Rochelle salt was embedded into asbestos matrix from a saturated aqueous solution at room temperature (mass concentration of the initial supersaturated solution was 1500 g/L at T = 303 K); the RS / asbestos nanocomposite sample was then washed with distilled water. Then the sample was dried at T = 300 K, and the procedure was repeated to increase the pore filling factor. After applying graphite contacts to the sample surfaces, it was clamped between two copper electrodes (their sizes were 2mm×2mm) of the measuring cell. The thickness of the asbestos fiber bundle was about 1 mm. For control, similar measurements were also carried out on a bulk Rochelle salt, as well as on the asbestos "host" matrix. Temperature dependences of the nanocomposite electrophysical characteristics (dielectric permittivity, dielectric losses and electric conductivity) were studied using a high-precision RLC-meter MS5308 at frequencies of 100 Hz, 120 Hz, 1 kHz, 10 kHz and 100 kHz. The error bars did not exceed 5%. The temperature was measured on one of the electrodes using a two-channel thermometer GM1312 (instrument accuracy 0.1 K).

Results and Discussion

The temperature dependences of dielectric permittivity ε\` for the initial asbestos matrix (curve *1*), for the bulk ferroelectric (curve *2*) and for the RS / asbestos nanocomposite (curve *3*) are presented in Fig. 2.

It is easy to see that due to the confined geometry there is a noticeable shift of T_C ($\Delta T \approx 3$ K) towards lower temperatures. This shift value is smaller than the low-temperature shift of T_C ($\Delta T \approx 5$ K) observed earlier [7] in the RS / zeolite nanocomposite since the diameters of the channels in asbestos (~ 5 nm) are larger than the diameters of the pores in NaA zeolite crystal (~ 1 nm). It should be also noted that the initial asbestos matrix has a much smaller ε\` value (ε\` ≈ 6 at 100 Hz) without any observable temperature dependence in the studied temperature range.

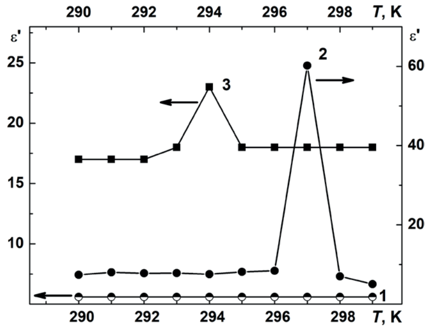

Fig. 2. Temperature dependences of the dielectric permittivity for the asbestos "host" matrix (curve *1*), for the bulk Rochelle salt "guest" substance (curve *2*), and for the RS / asbestos composite (curve *3*) at a frequency of $f = 100$ Hz

Arrhenius temperature dependence of the electrical conductivity for the RS / asbestos nanocomposite is presented in Fig. 3. One can see that the curve has a kink near the temperature $T_C \approx 294$ K of the ferroelectric-paraelectric phase transition in composite. The composite's electrical conductivity as well as the conductivity activation energy value $E = (0.56 \pm 0.02)$ eV in the paraelectric phase are higher than those for the initial asbestos matrix, where Arrhenius plot with very small activation energy (~ 0.04 eV) is monotonic without any features in the temperature region under study [21].

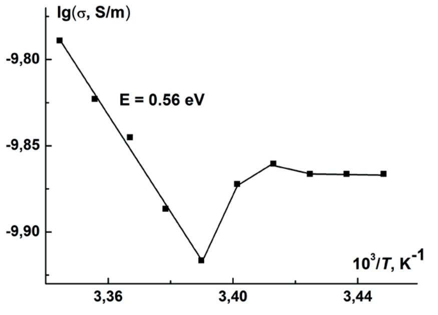

Fig. 3. Arrhenius temperature dependence of the electrical conductivity for the RS / asbestos nanocomposite at a frequency of $f = 100$ Hz

Figure 4 shows the frequency dependences of dielectric losses tgδ for the initial asbestos "host" matrix (curve *1*) as well as for the RS / asbestos nanocomposite (curve *2*). In both cases, it is possible to observe a power-law dependence of dielectric losses tgδ on frequency f (tgδ ~ f^{-n}), where the exponent is $n \approx 0.07$ for the initial asbestos "host" matrix and $n \approx 0.20$ for the RS / asbestos nanocomposite. Thus, both graphs display a smooth decrease of dielectric losses with frequency without any extremes in the studied frequency range from 100 Hz to 100 kHz which is typical for many dielectrics.

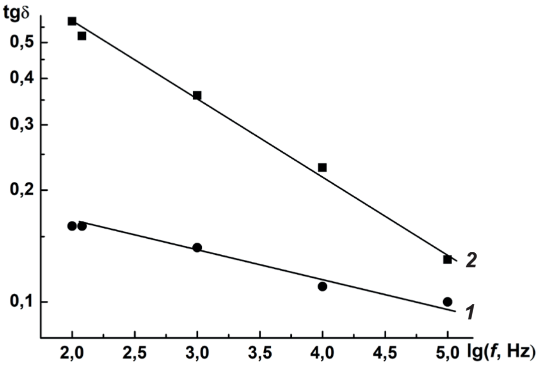

Fig. 4. Frequency dependences of dielectric losses for the asbestos "host" matrix (curve *1*) and for the RS / asbestos nanocomposite (curve *2*) at a temperature of $T = 295$ K

Conclusion

The novel nanocomposite ferroelectric / asbestos material obtained by the infiltration of a chrysotile-asbestos "host" matrix with a Rochelle salt "guest" substance demonstrates a shift of the Rochelle salt's upper ferroelectric transition Curie point T_C by ~ 3 K towards lower temperatures, compared with the temperature of the phase transition in a bulk ferroelectric. This shift value is smaller than the low-temperature shift of T_C observed earlier in the ferroelectric / zeolite nanocomposite since the diameters of the asbestos channels are larger than the diameters of the zeolite pores.

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