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Electrophysical properties of the Rochelle salt dispersed in a porous dielectric matrix of type A zeolite

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Abstract. Electrical conductivity, real part of dielectric permittivity and dielectric losses of a novel nanocomposite material obtained by the infiltration of a NaA zeolite matrix with Rochelle salt were studied in the frequency range from 100 Hz to 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. It was shown that the kind of temperature dependence of the Rochelle salt's electrical conductivity as well as the character of the dielectric losses' frequency dependence change significantly when this ferroelectric is dispersed in the NaA zeolite.

Keywords: ferroelectrics, Rochelle salt, permittivity, dielectric losses, electrical conductivity, zeolite, nanocomposite

Introduction

The idea of using zeolites for fabricating three-dimensional superlattices from nanoparticles within the regular systems of calibrated voids and channels of these nanoporous dielectric matrices was proposed at the end of the twentieth century (Bogomolov 1978; Stucky, Mac Dougall 1990). The most promising application of zeolites is their use in the creation of quantum confined nanocomposite materials in order to study size effects.

A theoretical explanation of the T_C value shift towards lower temperatures (Zhong et al. 1994) is based on Landau phenomenological theory. A confined geometry effect has been frequently observed in experiments with small ferroelectric particles in porous matrices (Cizman et al. 2013; Matveeva, Solovyev 2022; Pan'kova et al. 1996; Tien et al. 2008). However, in some cases (Baryshnikov et al. 2011; Rogazinskaya et al. 2009) a T_C value shift towards higher temperatures is also possible in systems of ferroelectric nanoparticles in porous matrices, compared with the temperature of the phase transition in a bulk substance.

The aim of this study was to determine experimentally the electrophysical properties of the well-researched ferroelectric (Gurevich 1969; Malyshkina, Gavrilova 2002; Mitani et al. 1974; Singaravadivelu et al. 2019; Zhou et al. 2008), i. e. Rochelle salt ($KNaC_4H_4O_6×4H_2O$, hereinafter referred to as RS) embedded into a NaA-type zeolite matrix near the upper ferroelectric Curie point (T_C = 297 K for the bulk material). NaA zeolite is a porous dielectric matrix which contains an ordered system of interconnected cavities and three-dimensional channels with diameters of ~ 1 nm (Breck 1974). The Rochelle salt's cell parameters $a ≈ 1.2$ nm, $b ≈ 1.4$ nm, $c ≈ 0.6$ nm (Solans et al. 1997) are rather large; thus, we suppose that RS molecules can be located only in α-cavities along <100> directions of the NaA crystal.

Experimental methods

We used granules (spheres with a diameter of 2 mm) of the NaA zeolite as a porous dielectric matrix. The Rochelle salt was embedded into zeolite cavities from a saturated aqueous solution at room temperature; the ferroelectric/zeolite nanocomposite sample was then washed with distilled water. Then it was dried at T = 300 K, and the procedure was repeated once more to increase the pore filling factor. To remove the 'guest' substance from the surface of the sample, it was subjected to mechanical processing (surface grinding) and given the shape of a tablet with a diameter of 2 mm and a thickness of 0.5 mm. After applying graphite contacts to the surface of the sample, it was clamped between the metal electrodes of the measuring cell. For control, similar measurements were also carried out on a bulk Rochelle salt single crystal with its *c* — axis parallel to the applied electric field, as well as on the polycrystalline zeolite host matrix.

The temperature dependences of the nanocomposite electrophysical characteristics (electric conductivity σ, dielectric permittivity ε` and dielectric losses *tg*δ) were studied using a high-precision bridge (RLC-meter MS5308) at frequencies of 100 Hz, 120 Hz, 1 kHz, 10 kHz and 100 kHz by the method of two parallel conductors (copper plates between which our nanocomposite was placed). 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 ε` for the bulk RS (curve 1) and for the ferroelectric / zeolite nanocomposite (curve 2)) are presented in Fig. 1.
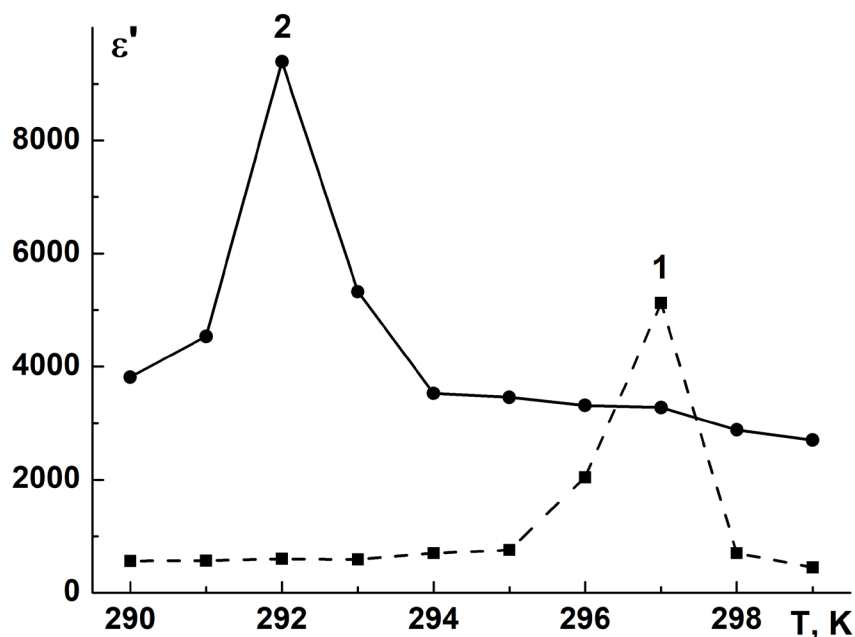

Fig. 1. Temperature dependences of the dielectric permittivity for the bulk RS (curve 1)
and for the ferroelectric / zeolite nanocomposite (curve 2) at 120 Hz

It is easy to see that due to the confined geometry there is a significant shift of T_C ($\Delta T \approx 5K$) towards lower temperatures.

It should be noted that the initial zeolite matrix has a much smaller ε` value ($\varepsilon$` ≈ 200 at 120 Hz) without any observable temperature dependence in the studied temperature range.

The temperature dependence of the reference sample's (a bulk RS crystal) electrical conductivity at 1 kHz (Fig. 2) is qualitatively consistent with the previously published results (Gurevich 1969).
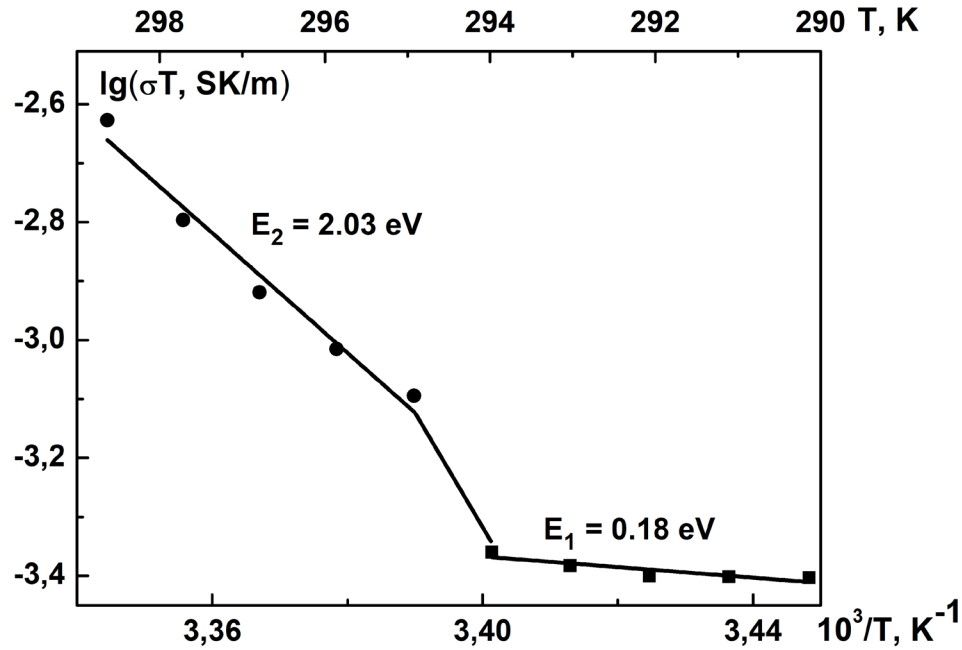

Fig. 2. Temperature dependence of the electrical conductivity for the bulk RS at 1 kHz

As one can see from the graph, there are two sections on the Arrhenius temperature dependence of conductivity with different activation energies: $E_1 = (0.18 \pm 0.05)$ eV at temperatures below T_C and $E_2 = (2.03 \pm 0.19)$ eV at temperatures above T_C.

Such an abrupt change in the activation energy of carriers in the case of impurity electronic electrical conductivity of the ferroelectric may be due to a significant difference in the electronic components of the permittivity of para- and ferroelectric phases (Gurevich 1969). At the same time, it is noted in the literature (Ovchinnikova et al. 1997) that the electrical conductivity of the RS can be largely associated with proton transport.

Arrhenius temperature dependence of the ferroelectric / zeolite sample's electrical conductivity (Fig. 3) also has two sections with different activation energy values. However, in this case, the value of the activation energy in the ferroelectric phase $E_3 = (1.14 \pm 0.08)$ eV is higher than the value of the activation energy in the paraelectric phase $E_4 = (0.49 \pm 0.08)$ eV. At the same time, specific conductivity of the composite significantly exceeds the corresponding value for a bulk ferroelectric. It was pointed out (Gurevich 1969) that the processes of hydration and dehydration have a noticeable effect on the electro-physical properties of $KNaC_4H_4O_6 \times 4H_2O$ crystals. For an ultradispersed ferroelectric, when its nanoparticles with a developed surface intensively interact with zeolite water in the pores of the matrix, this effect can be even more significant.

The frequency dependences of $tg\delta$ for the bulk RS (Fig. 4) as well as for the initial zeolite matrix (Fig. 5) display a smooth decrease in the value of $tg\delta$ with increasing frequency f without any maxima in the studied frequency range which is typical for many dielectrics (Woodward 2021).

On the other hand, the frequency dependences $tg\delta = F(f)$ for the ferroelectric / zeolite sample (Fig. 6) have clearly expressed maxima at frequencies of ~10 kHz in the ferroelectric phase and ~1 kHz in the paraelectric phase (above the upper Curie point $T_C \approx 292$ K for the nanocomposite). These results can be interpreted within the framework of Debye theory taking into account the relaxation processes in a heterogeneous nanocomposite ferroelectric / zeolite, which has a sufficiently high ionic conductivity and a significant difference in the static (low-frequency) and high-frequency permittivity values:
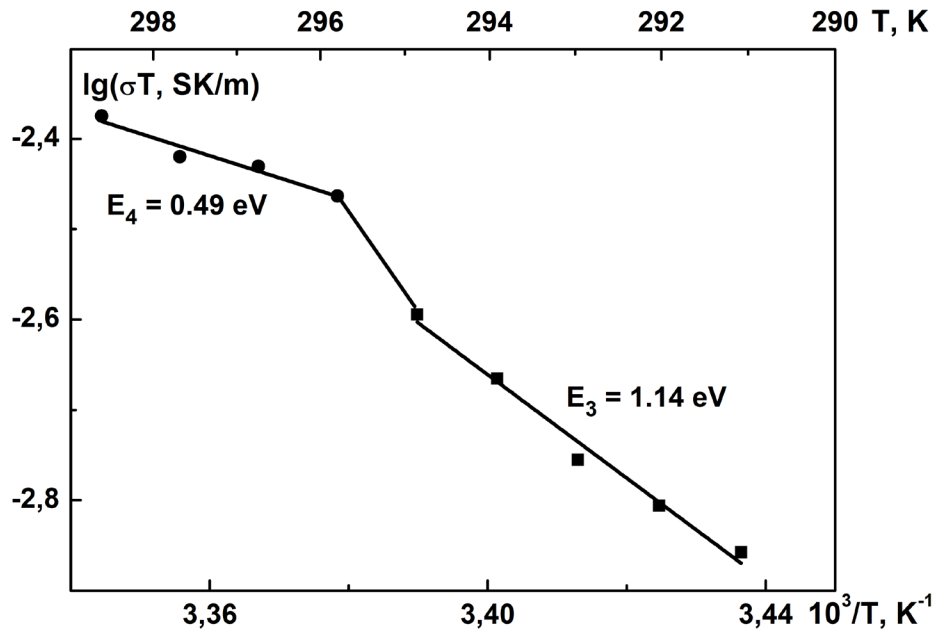
Fig. 3. Temperature dependence of the electrical conductivity
for the ferroelectric / zeolite nanocomposite at 1 kHz
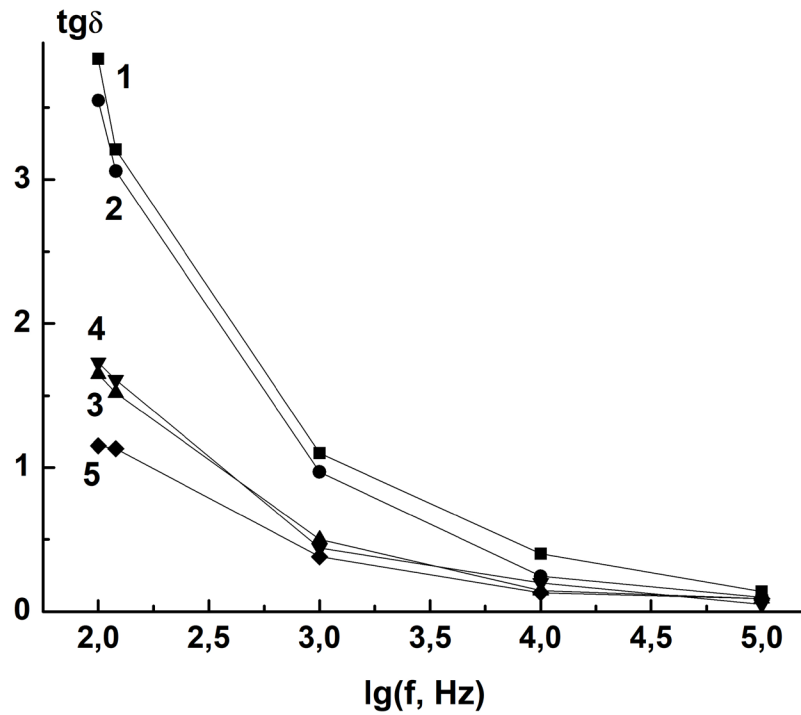
Fig. 4. Frequency dependences of *tg*δ for the bulk RS at 290 K (curve 1), 292 K (curve 2),
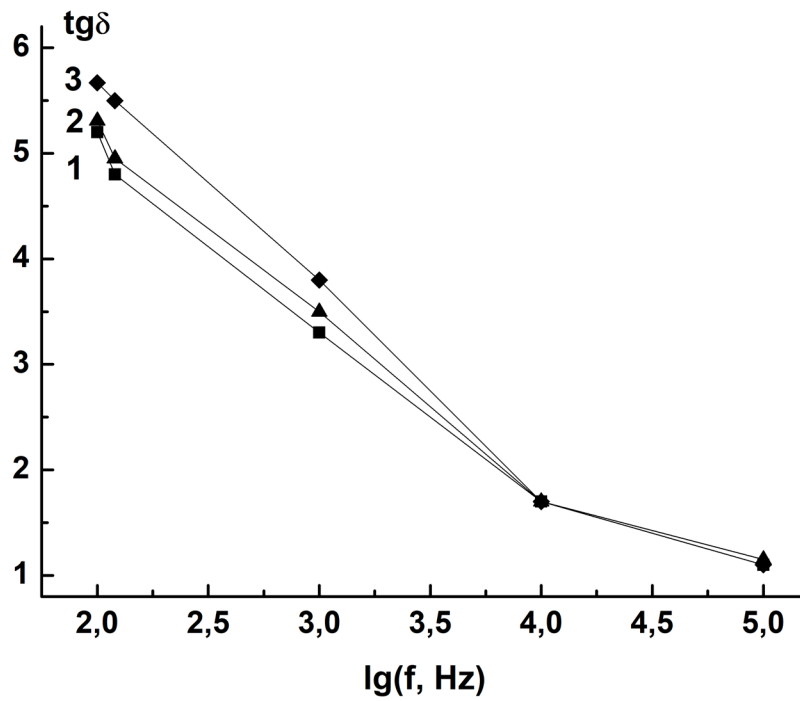294 K (curve 3), 296 K (curve 4) and 298 K (curve 5)

Fig. 5. Frequency dependences of *tg*δ for the zeolite NaA at 290 K (curve 1),
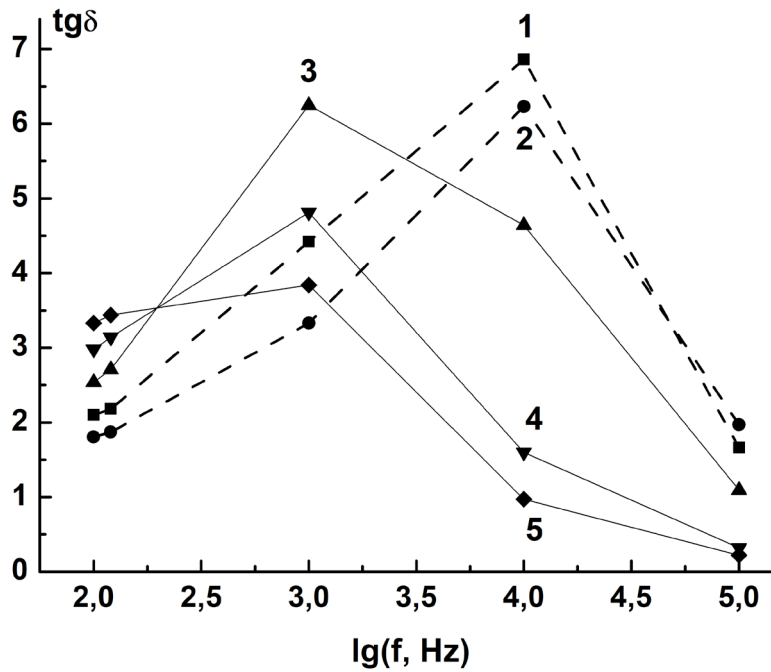294 K (curve 2) and 298 K (curve 3)

Fig. 6. Frequency dependences of *tg*δ for the ferroelectric / zeolite nanocomposite at 290 K (curve 1),
292 K (curve 2), 294 K (curve 3), 296 K (curve 4) and 298 K (curve 5)

$\Delta\varepsilon = (\varepsilon_{st} - \varepsilon_{\infty}) > 8\varepsilon_{\infty}$ (Bogatin et al. 2002; Bogatin 2012). It should be emphasized that the components of the nanocomposite differ significantly in electrical characteristics, which makes the development of interlayer polarization possible.

It is pointed out in literature (Steeman, van Turnhout 2003) that conductivity differences in the phases of an inhomogeneous medium give rise to interfacial polarization — the build-up of space charges near the interfaces between various phases. Such a polarization usually occurs at frequencies lower than the time scales typical of dipolar polarizations. Moreover, the contribution of interfacial polarization to the dielectric properties of a material is often much larger than dipolar contributions.

Conclusions

The novel nanocomposite ferroelectric / zeolite material obtained by the infiltration of a NaA zeolite host matrix with a Rochelle salt guest substance demonstrates a shift of the Rochelle salt's upper ferroelectric transition Curie point T_C by ~ 5 K towards lower temperatures, compared with the temperature of the phase transition in a bulk ferroelectric.

The character of the temperature dependence of the Rochelle salt's electrical conductivity (namely, the sequence of sections with high and low activation energies) changes significantly when it is dispersed in the NaA zeolite matrix, which is probably due to the influence of water molecules.

On heating through T_C, the position of a maximum on the $tg\delta$ frequency dependence of the ferroelectric / zeolite nanocomposite shifts towards lower frequencies. A possible interpretation of this effect has been given within the framework of Debye theory, taking into account the electrical conductivity of the heterogeneous nanocomposite consisting of components with different electrical characteristics, which makes the development of interlayer polarization possible.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

All the authors discussed the final work and took part in writing the article.

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