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Dielectric properties of composites based on nanocrystalline cellulose, potassium dihydrogen phosphate and ammonium dihydrogen phosphate

© A.S. Sidorkin[1], M.A. Pankova[2], N.A. Tolstykh[3], L.N. Korotkov[3]

[1] Voronezh State University,
Voronezh, Russia
[2] Voronezh Institute of the Ministry of Internal Affairs of the Russian Federation,
Voronezh, Russia
[3] Voronezh State Technical University,
Voronezh, Russia
E-mail: l_korotkov@mail.ru

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The dielectric properties of potassium dihydrogen phosphate and ammonium dihydrogen phosphate with nanocrystalline cellulose $(1-x)$KDP $-$ xnC and $(1-x)$ADP $-$ xnC of composites of various compositions: $x = 0.0; 0.25; 0.5$ and 0.75 the components mass fractions were studied within the temperature range of $100-300$ K. It was found that the presence of nanocrystalline cellulose in the $(1-x)$KDP $-$ xnC composite leads to an increase in the Curie temperature of KDP particles and practically has no effect on the Neel temperature in ADP in the $(1-x)$ADP $-$ xnC composite. A decrease in the dielectric response of the composites with an increase in the x concentration is approximately described within the framework of the Lichtenecker model.

Keywords: ferroelectric, antiferroelectric, nanocrystalline cellulose, composite, Curie temperature.

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1. Introduction

Composite materials based on ferroelectrics have been used in various electronic devices for a long time [1–6]. These include not only conventional ferrote piezoceramic composites [1–3], but also film structures deposited on a substrate [3–6]. In some cases, when the sizes of the components that make up the composite material approach submicron, their mutual influence becomes noticeable [7–10]. The interaction is complex, but one type of interaction can be dominant, usually mechanical, electrostatic, or chemical. In this case, the response in the ferroelectric component of the composite is usually more pronounced due to its structural instability.

Examples include ultrathin films of strontium titanate [11], or hafnium oxide [12] — paraelectrics in which tensile elastic stresses induce a ferroelectric phase already at room temperature. The experimentally observed increase in the Curie temperature in nanocrystallites of the potassium dihydrogen phosphate family embedded in porous glass matrices [8,9] is associated with tensile elastic stresses arising from different coefficients of thermal expansion of the components of the composite material.

These voltages can be varied using dielectric matrices made of different materials.

Recently, publications have appeared on composites based on nanocrystalline cellulose and ferroelectrics TGS [13] and KIO_3 [14].

This paper is devoted to the synthesis and study of the dielectric properties of composite materials based on the model ferroelectric potassium dihydrogen phosphate (KH_2PO_4 — KDP) and the model antisegroelectric ammonium dihydrogen phosphate ($NH_4H_2PO_4$ — ADP) with nanocrystalline cellulose, which have not been studied to date.

Potassium dihydrogen phosphate and ammonium dihydrogen phosphate have similar chemical composition and phase transition mechanism, as well as similar temperature coefficients of linear thermal expansion (TKL). At the same time, they have different baric coefficients characterizing the effect of pressure on the temperature of the phase transition: $dT_C/dp \approx -4.5 \cdot 10^{-8}$ and $dT_N/dp \approx -3.4 \cdot 10^{-8}$ K/Pa [15], for KDP and ADP respectively (T_C is the Curie temperature, T_N is the Néel temperature, p is the hydrostatic pressure.) This circumstance makes it possible to expect for them a different magnitude shift in the temperatures of phase transitions under the influence of elastic stresses that occur in composites during their cooling.

2. Experimental methods and samples

The composite materials $(1-x)$KDP $-$ xnC and $(1-x)$ADP $-$ xnC (nC is the nanocrystalline cellulose — $[C_6H_{10}O_5]_n$) with $x = 0.0$; 0.25; 0.5; 0.75 and 1.0 were used for the experiments, where x is the mass fraction of nC. They were produced using KH_2PO_4 (KDP), $NH_4H_2PO_4$ (ADP) UHP salts and commercial nanocrystalline cellulose $(C_6H_{12}O_6)_n$ in powder form consisting of fibers with an average diameter of 10–20 nm, length of 300–900 nm and a crystallinity of about 92 %.

The initial components were taken in the appropriate proportions. One gram of the mixture was placed in 40 ml of distilled water and stirred for 30 min in an ultrasonic bath at a temperature of 50 °C. Then the mixture, which was a colloidal solution, was poured into a flask and stirred with a magnetic stirrer for 30 min. After that, the solution was again treated in an ultrasonic bath for 30 min at a temperature of 50 °C. The resulting substance was then dried in a drying cabinet at a temperature of 80 °C for 24 hours. At the final stage, the mixture was ground in a mortar and sifted through a sieve with a mesh size of 100 μm.

Samples in the form of a disk with a diameter of 10 mm and a thickness of 1.5 mm were obtained by compaction (pressure 180 MPa, compaction time 30 min). At the final stage, a conductive silver paste was applied to the surface of the samples to create the electrodes, followed by drying of the samples.

The temperature dependences of the dielectric constant (ε) in the temperature range of 100–300 K were obtained using an experimental setup based on an E7-20 LCR meter. The samples were placed in a measuring cell built into the cryostat, where during the experiment the temperature varied in the range of 100–300 K.

The measurements were carried out during heating at a rate of 2–3 K/min at a frequency of 1000 Hz. The temperature in the measuring cell was measured using a platinum resistance thermometer with an error of no more than ± 0.2 °C.

3. Experimental results

The temperature dependences of the dielectric constant of $(1-x)$ADP $- x$nC composites obtained during heating of the samples are shown in Figure 1. The obtained curves have the form typical for single-crystal ADP [15,16]. An abrupt increase in the dielectric constant is recorded in the vicinity of the Néel temperature (T_N), which slightly changes with a further increase in temperature. Some growth of ε of polycrystalline ADP for $x = 0.0$ above T_N, which was not observed for monocrystalline samples of ammonium dihydrogen phosphate [15,16], should be associated with the Maxwell-Wagner migration polarization caused by a thermally activated increase in the mobility of charge carriers in the intercrystalline the space of ammonium dihydrogen phosphate particles.

The nickel temperature values in the ADP particles in these composites vary slightly depending on the composition: $T_N \approx 151$, 151, 147, and 148 K for compositions with $x = 0.0$, 0.25, 0.5, and 0.75, respectively. Despite a certain variation in the values of T_N, one can see a tendency to decrease T_N in ammonium dihydrogen phosphate crystallites in the composite with an increase in the concentration of nanocrystalline cellulose.

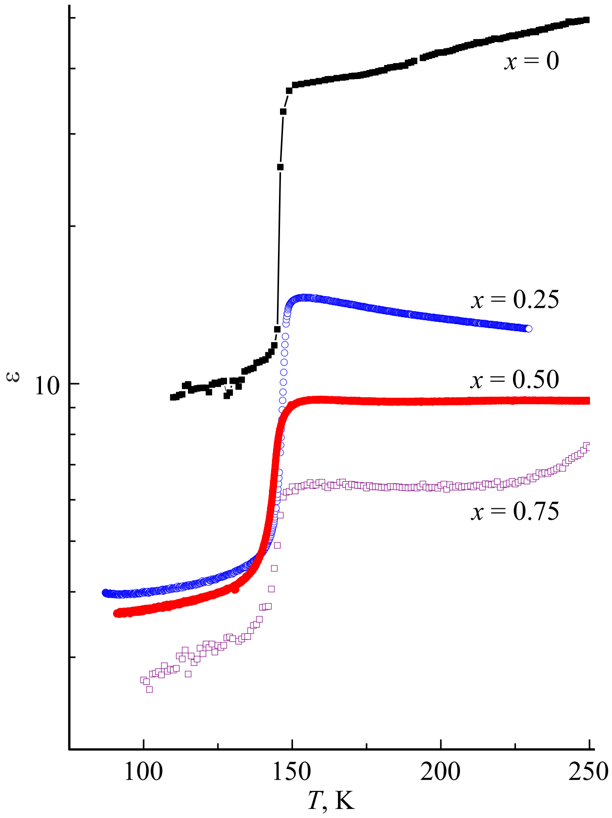

Figure 1. Dependencies $\varepsilon(T)$ for composites $(1-x)$ADP $- x$nC.

The temperature dependences of the dielectric constant for $(1-x)$KDP $- x$nC composites are shown in Figure 2. They have a similar shape, which, due to the strong anisotropy of the dielectric properties of KDP, differs from the shape of the curves $\varepsilon_{11}(T)$ and $\varepsilon_{33}(T)$ observed for single crystal samples [15,16].

Near the Curie temperature of $T_C \approx 121$ K the dependences $\varepsilon(T)$ pass through a maximum similar to that observed in the case of a nominally pure potassium dihydrogen phosphate crystal ($x = 0.0$). A dielectric constant monotonously decreases above T_C.

The decrease of ε stops in the case of polycrystalline KDP ($x = 0.0$) above ≈ 215 K and an increase in the dielectric constant with temperature is observed. There is no such growth both in monocrystalline potassium dihydrogen phosphate [15,16] and in the studied $(1-x)$KDP $- x$nC composites. This increase can reasonably be attributed to the Maxwell-Wagner migration polarization like in case of $(1-x)$ADP $- x$nC compositions. It should be noted that the contribution of this mechanism to the dielectric response in both the $(1-x)$KDP $- x$nC and $(1-x)$ADP $- x$nC systems decreases with increasing nanocrystalline cellulose content.

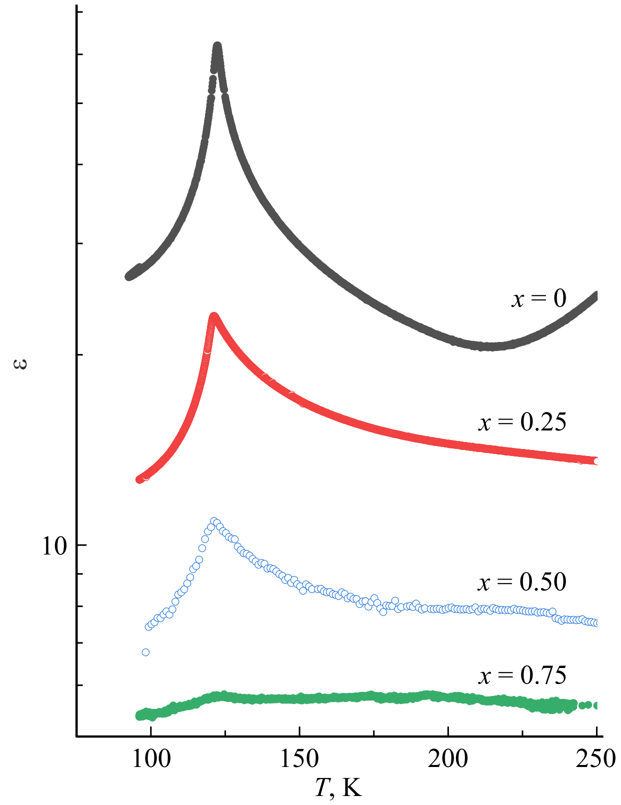

Figure 2. Dependencies $\varepsilon(T)$ for composites $(1-x)$KDP $- x$nC.

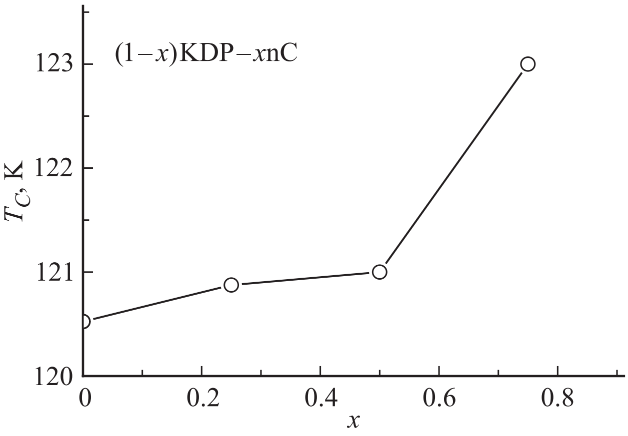

Figure 3. Concentration dependence of the Curie temperature in KDP crystallites in the composite $(1-x)$KDP $- x$nC.

Studies of the temperature dependences of the tangent of the dielectric loss angle $(\mathrm{tg}\,\delta)$ of both composites — $(1-x)$KDP $- x$nC and $(1-x)$ADP $- x$nC revealed their monotonous growth at temperatures above $\approx 220{-}250$ K, obviously, due to the Maxwell-Wagner relaxation polarization. At temperatures below ≈ 200 K, the measured values of $\mathrm{tg}\,\delta$ are small and are characterized by a large spread of „experimental points". For this reason, they are not discussed in this paper.

A slight increase in the Curie temperature in ferroelectric inclusions is recorded with an increase in the concentration of x in the $(1-x)$KDP $- x$nC composite (Figure 3). This turned out to be somewhat unexpected, since due to the difference in temperature coefficients of linear expansion, KDP crystallites experience compressive pressure from the matrix, which should lead to a decrease in T_C [15]. (TKL of cellulose is of the order $10^{-4}\,\mathrm{K}^{-1}$ [17,18], and of the order $10^{-5}\,\mathrm{K}^{-1}$ [16].)

Compressive pressure is also experienced by ADP crystallites in the $(1-x)$ADP $- x$nC composite. It may cause a slight decrease in their phase transition temperature.

The qualitative difference in the effect of the matrix on the temperature shift T_C and T_N in the studied materials is apparently due to the action of the electrostatic field $E_{=}$. According to Ref. [15] the field $E_{=}$ increases the ferroelectric phase transition temperature in KDP by $\Delta T \approx 0.47E_{=}$ (ΔT, K; $E_{=}$, kV/cm), but it does not affect T_N in ammonium dihydrogen phosphate.

It is difficult to accurately determine the field strength $E_{=}$ induced by the pyroelectric effect in cellulose [19], but it is possible to estimate the order of its magnitude. According to Ref. [19] polarization P attributable to the presence of cellulose in the composition of wood (birch) at $T = 140$ K is about $10^{-6}\,\mathrm{C/m^2}$.

The field $E_{=}$ can be estimated in a composite by using the formula $E_{=} = \sigma/2\varepsilon_0$, valid for an infinitely large charged plane, where the surface charge density $\sigma = P$, ε_0 is the absolute electric constant. The estimated electrostatic field strength is 0.56 kV/cm less than the values $E_{=} = 4{-}6$ kV/cm required to shift T_C by $2{-}3$ K. At the same time, it is close to these values and may increase with more accurate calculations of the pyroelectric-induced field, taking into account its significant heterogeneity. In addition, it should be borne in mind that nanocrystalline cellulose has a higher pyroelectric coefficient compared to wood [19].

Let us consider the effect of the composition of composites on their dielectric permittivity (Figure 1 and Figure 2). It is possible to see a regular decrease in the dielectric response in both materials as the concentration of x increases in them, which is illustrated in Figures 4 and 5.

The obtained dependences $\varepsilon(x)$ are essentially nonlinear. However, they are „straightened" when plotted in semi-logarithmic coordinates: $\lg \varepsilon$ from x, (insets in Figures 4 and 5). This type of concentration dependence of the dielectric constant corresponds to the Lichtenecker model [20], according to which the total contribution of the components of a binary mixture to the total dielectric constant is determined by the ratio:

$$\lg \varepsilon = \lg \varepsilon_A - x(1-k)\lg(\varepsilon_B/\varepsilon_A), \tag{1}$$

where ε_B and ε_A are the values of the dielectric constant of the individual components of the composite, k is a constant that takes into account the different nature of the mating components.

In the framework of this model, dielectric spheres polarized in a local electric field are considered. For well-dispersed composites $k = 0.3$, however, in our case, the optimal approximation of experimental data by the ratio (1) was achieved at $k \approx 0$.

It should be noted, however, that the dielectric constant of compounds with $x = 0$ is noticeably higher than the values predicted by the Lichtenecker model (insets in Figures 4 and 5). This is probably attributable to the noticeable contribution of migration polarization to the dielectric response of polycrystalline ADP and KDP samples, which is noticeably attenuated, as noted above, in composites.

4. Conclusion

The results of the experiments showed that the presence of nanocrystalline cellulose leads to a slight decrease in the temperature of the antisegnetoelectric phase transition in ammonium dihydrogen phosphate particles in the $(1-x)\mathrm{ADP}-x\mathrm{nC}$ composite. A slight increase in the Curie temperature is observed in KDP inclusions in the $(1-x)\mathrm{KDP}-x\mathrm{nC}$ composite, probably caused by the action of an electric field resulting from the pyroelectric effect in nanocrystalline cellulose.

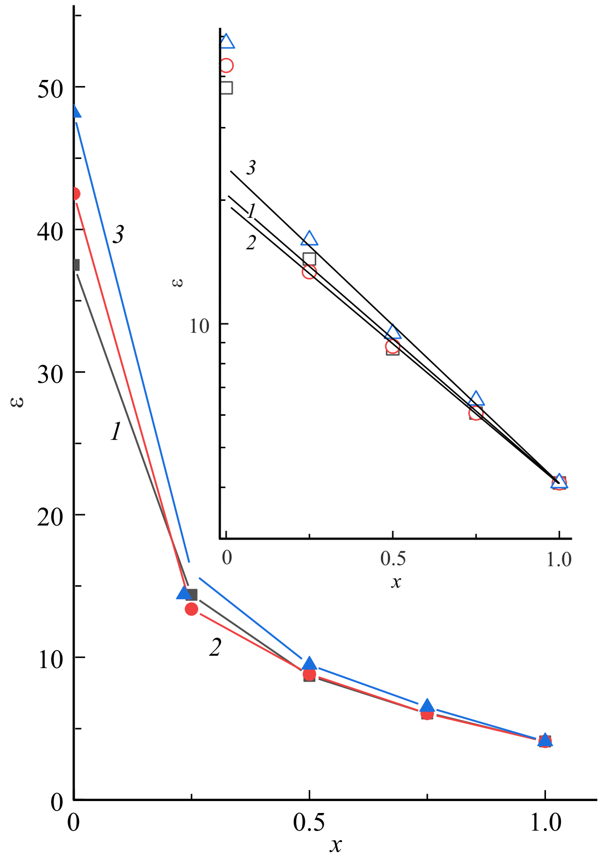

Figure 4. Concentration dependences of the dielectric constant of a composite $(1-x)\mathrm{ADP}-x\mathrm{nC}$ at temperatures of 150 (*1*), 200 (*2*) and 250 K (*3*). The same dependencies in semi-logarithmic coordinates are shown in the insert.

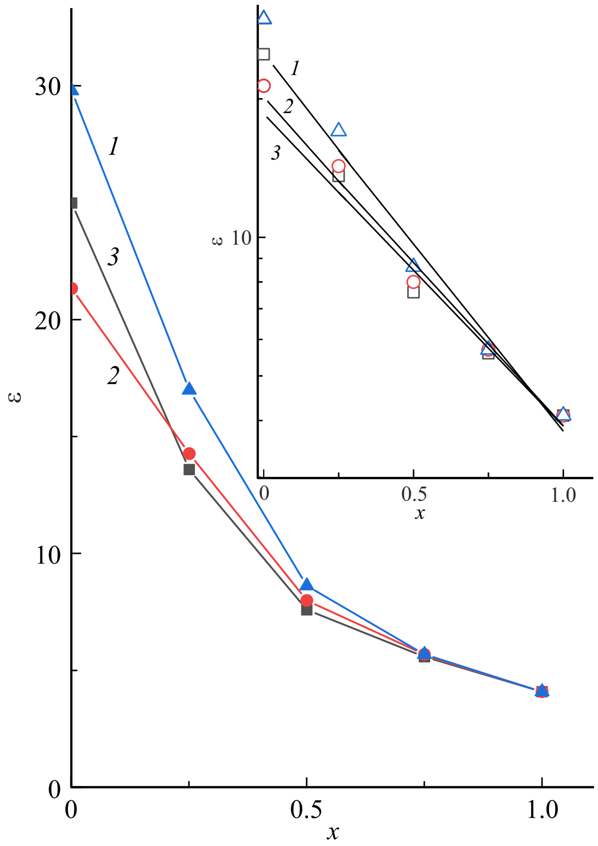

Figure 5. Concentration dependences of the dielectric constant of a composite $(1-x)\mathrm{KDP}-x\mathrm{nC}$ at temperatures of 150 (*1*), 200 (*2*) and 250 K (*3*). The same dependencies in semi-logarithmic coordinates are shown in the insert.

A weakening of the contribution of Maxwell-Wagner polarization to the dielectric response of the studied composite materials was found in comparison with polycrystalline ADP and CDP due to the blocking of the surface conductivity of the crystallites of these salts by nanocrystalline cellulose particles.

It has been found that the concentration dependences of the dielectric permittivity of $(1-x)\mathrm{KDP}-x\mathrm{nC}$ and $(1-x)\mathrm{ADP}-x\mathrm{nC}$ composites can be approximated using the Lichtenecker model.

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Conflict of interest

The authors declare that they have no conflict of interest.

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