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Influence of superionic nanoparticles Cu₆PS₅I on dielectric properties of nematic liquid crystal 6CHBT

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Abstract. Within the frequency range $10 \dots 10^6$ Hz, the influence of Cu₆PS₅I nanoparticles on the dielectric properties of planar oriented liquid crystal 6CHBT has been studied. It has been shown that nanoparticles lead to an increase in conductivity, but the conductivity dependence on concentration is non-monotonic function. It has been suggested that the reason of non-monotonic dependence of conductivity of 6CHBT on the concentration of nanoparticles is significant influence of ion adsorption on the nanoparticle surface and increase in the viscosity of liquid crystal when introducing nanoparticles.

Keywords: nematic liquid crystal, superionic nanoparticle, dielectric properties.

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1. Introduction

Nowadays, the practical use of liquid crystals (LC) is mainly associated with manufacture of displays. In this direction, a significant amount of researches was performed, which allowed to create the most effective devices of information displays. Studies show that relatively soon the liquid crystal display can be replaced by electroluminescent displays, as they do not require backlighting and can be flexible. However, a large number of research laboratories work on expanding the functionality of LC.

One of the promising methods of expanding the functionalities of LC is introduction of nanoparticles. The analysis of publications shows that a lot of studies

with using different types of nanoparticles are already performed. The most promising direction to modify functionalities of LC is ferroelectric nanoparticles [1-7]. One of the features of these nanoparticles is the presence of a strong local electric field. As it was shown in [1], the presence of the electric field results in the capture of ions and reduction of the LC conductivity.

Reducing the control voltage when cholesteric LC operates as an optical element and increasing anisotropy of the permittivity were just explained by the presence of strong electric fields around the nanoparticles [2]. Almost 3-fold increase in anisotropy of the permittivity after introduction of BaTiO₃ was obtained in the paper [3]. It was shown that this introduction into nematic LC leads to manifestation of the electromechanical memory

effect in the isotropic phase [4] and to reduction of the Fredericks threshold [5] as well as to changes in thermodynamic and dielectric properties of LC [6]. In the paper [7], it was found that after introducing the ferroelectric nanoparticles into nematic LC, elasticity constants of LC are reduced, while the permittivity and rotational viscosity of LC are increased. The theoretical explanation concerning some of the above effects was grounded in the paper [8].

Nanoparticles of superionic conductors with the argyrodite structure, in particular $\text{Cu}_6\text{PS}_5\text{I}$, can significantly expand the LC functional properties. They are characterized by high electrical conductivity, have ferroelastic and nonlinear optical properties [9, 10]. At room temperature, the crystals $\text{Cu}_6\text{PS}_5\text{I}$ form a cubic crystal lattice (space group $F\bar{4}3m$) [9]. Observed at low temperatures in the $\text{Cu}_6\text{PS}_5\text{I}$ crystals are two phase transitions (PT), one of which is superionic and ferroelastic PT of the first order at $T_I = (144\dots169)$ K, the other one – structural PT of the second order at $T_{II} = (269\pm 2)$ K [11, 12]. As it was noted in [12], when $T_I < T < T_{II}$ the $\text{Cu}_6\text{PS}_5\text{I}$ crystals belong to a cubic system (space group $F\bar{4}3c$), while at $T < T_I$ – to monoclinic (space group Cc).

The aim of this paper was to study the influence of $\text{Cu}_6\text{PS}_5\text{I}$ nanoparticles on dielectric properties of nematic LC 6CHBT.

2. Materials and methods of the research

We performed the research of dielectric properties of nematic liquid crystal 6CHBT with and without impurity of $\text{Cu}_6\text{PS}_5\text{I}$ nanoparticles in the sandwich-type cells with transparent ITO electrodes. The concentration of nanoparticles with an average size of 35 nm in LC equaled to 0.01, 0.05 and 0.1 mg/ml. To create a planar orientation of LC molecules, a polymer layer was deposited on electrodes and appropriately treated. The cell thickness was 10 μm . The LC cell was filled by using the capillary method at the temperature 5...10 $^\circ\text{C}$ higher than that of the phase transition nematic-isotrop.

The dielectric properties of the prepared sandwich cells were studied within the frequency range 10 to 10^6 Hz at 293 K by using the oscilloscopic method [13]. The amplitude of the measuring signal with the sinusoidal shape was 0.25 V. Assuming that the equivalent circuit of measuring cell is the resistance and capacitor connected in parallel, we determined the values of resistance R and capacitance C of samples at different frequencies and, being based on these values and geometric cell size, we determined the imaginary (ϵ'') and real (ϵ') components of the complex dielectric conductivity, respectively.

3. Experimental results and analysis

Fig. 1 shows the frequency dependence of ϵ' (1) and ϵ'' (2) for planar oriented LC 6CHBT. As can be seen

from the data, observed is the inverse dependence of ϵ'' on frequency f (the resistance value is independent of frequency) and the ϵ' value does not practically depend on f . Thereof, we can conclude that within the studied frequency range the electrode phenomena have no effect on the frequency dependences of ϵ' and ϵ'' [14]. It is important to note that we observed similar frequency dependences of ϵ' and ϵ'' for 6CB with impurity of nanoparticles $\text{Cu}_6\text{PS}_5\text{I}$.

Fig. 2 shows the frequency dependences of ϵ' with the concentration of impurity $\text{Cu}_6\text{PS}_5\text{I}$: 0 (1) 0.01 (2) 0.05 (3) and 0.1 mg/ml (4). Analyzing the data, we can conclude that the dependence $\epsilon'(f)$ caused by the near-electrode phenomena in LC with nanoparticles $\text{Cu}_6\text{PS}_5\text{I}$ begins at higher frequencies than that in LC without impurities.

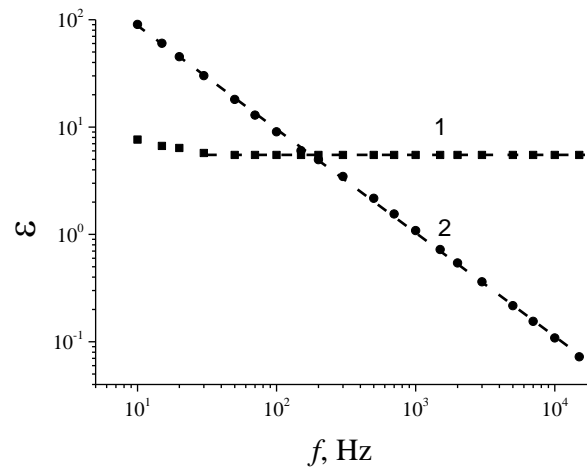


Fig. 1. Frequency dependences of the real ϵ' (1) and imaginary ϵ'' (2) components of complex dielectric conductivity for planar oriented liquid crystal 6CHBT. The sample thickness was 10 μm . The temperature was close to 293 K.

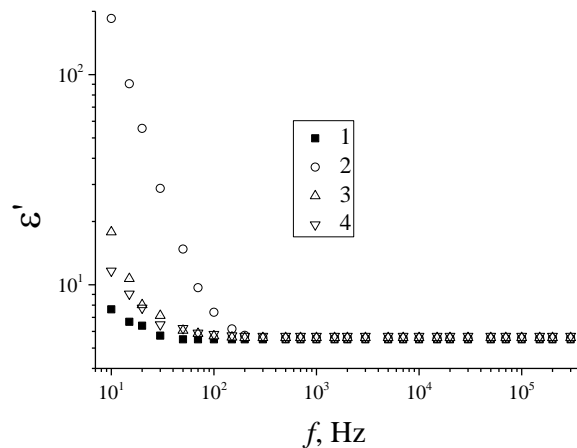


Fig. 2. Frequency dependences of the real component of complex permittivity ϵ' for LC 6CHBT with the impurity $\text{Cu}_6\text{PS}_5\text{I}$ concentrations: 0 (1) 0.01 (2) 0.05 (3) and 0.1 mg/ml (4). The sample thickness was 10 μm , the temperature – 293 K.

It should be noted that the influence of $\text{Cu}_6\text{PS}_5\text{I}$ nanoparticles on the ϵ' value of LC in the range of frequencies $f < 10^2$ Hz is non-monotonic depending on the concentration of this impurity. Maximum change in the ϵ' value is observed at the lowest concentrations of the used ones of $\text{Cu}_6\text{PS}_5\text{I}$ nanoparticles, which is equal to 0.01 mg/ml. As shown in [14], the dispersion shift of the ϵ' value may be caused by the increase in conductivity of LC when introducing the impurity.

According to the ϵ'' values, the experimentally obtained value of conductivity can be estimated from the relation

$$\sigma = \epsilon_0 \omega \epsilon'',$$

where ϵ_0 is the vacuum electric constant, and $\omega = 2\pi f$ is the cyclic frequency.

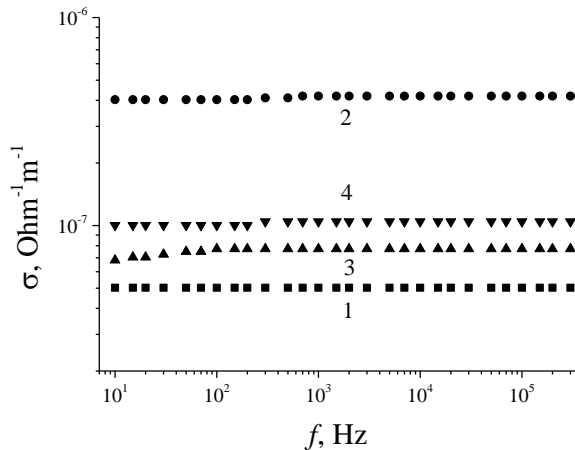


Fig. 3. Frequency dependences of the conductivity for LC 6CHBT with the impurity $\text{Cu}_6\text{PS}_5\text{I}$ concentrations: 0 (1) 0.01 (2) 0.05 (3) and 0.1 mg/ml (4). The sample thickness was 10 μm , the temperature – 293 K.

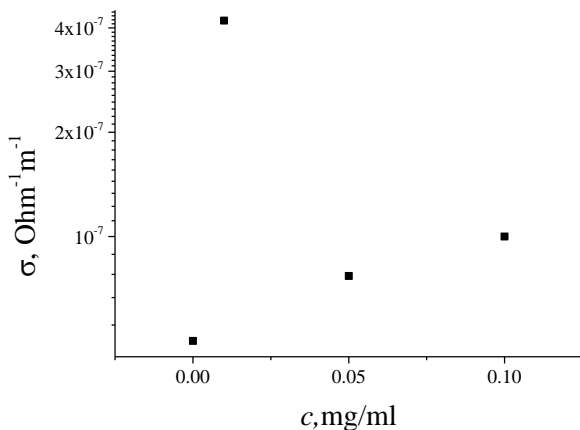


Fig. 4. Dependence of the conductivity for LC 6CHBT on the concentration of $\text{Cu}_6\text{PS}_5\text{I}$ nanoparticles.

Fig. 3 shows the frequency dependences of conductivity for planar oriented 6CHBT with the concentration of $\text{Cu}_6\text{PS}_5\text{I}$ impurity: 0 (1) 0.01 (2) 0.05 (3) and 0.1 mg/ml (4). As it was predicted when analyzing the concentration dependences of ϵ' , the value of conductivity σ for 6CHBT is also nonmonotonously dependent on the concentration of nanoparticles $\text{Cu}_6\text{PS}_5\text{I}$. To easier analyze this effect, presented in Fig. 4 is the concentration dependence of conductivity of 6CHBT, which is plotted on some of the data used for plotting Fig. 3. Namely, the value of conductivity LC bulk is determined in that frequency range where the σ value does not depend on the frequency f .

As can be seen from Fig. 4, the largest change in conductivity of 6CHBT occurs when the selected concentration of nanoparticles is lowest (0.01 mg/ml). With further increasing the nanoparticle concentration, the decrease of the conductivity is observed, and then we see a small increase at the maximum of the selected concentrations (0.1 mg/ml). From the results obtained, it can be assumed that for the system “nematic liquid crystal 6CHBT – nanoparticles $\text{Cu}_6\text{PS}_5\text{I}$ ”, there are several mechanisms of influence of nanoparticles on the LC conductivity. In one of these mechanisms, the nanoparticles increase the LC conductivity due to introducing ions additional to ions existing in LC. However, if the main process was only such a mechanism of conduction change under the influence of nanoparticles, the conductivity with increasing concentration must constantly grow.

For an explanation of the data, one should take into account the existence of a process that leads to a reduction of LC conductivity when introducing nanoparticles. One of these processes can be adsorption of ions that carry a charge in LC on the surface of the nanoparticles. In addition, the LC conductivity when introducing nanoparticles can be reduced owing to increasing the LC viscosity (in this process the ion mobility is reduced). According to the obtained experimental data, one cannot be uniquely said what mechanism of these mechanisms for reducing the conductivity with introducing nanoparticles is the main. It is clear that the conductivity may decrease due to the action of each of the above mechanisms of change in the 6CHBT conductivity when introducing $\text{Cu}_6\text{PS}_5\text{I}$ nanoparticles.

4. Conclusions

It has been shown that introduction of the nanoparticles $\text{Cu}_6\text{PS}_5\text{I}$ within the concentration range 0.01...0.1 mg/ml leads to the increase in the value of the real component of complex permittivity ϵ' at low frequencies and in conductivity over all the range of frequencies. However, the concentration dependence of the ϵ' and σ values is not monotonous.

The reason for the non-monotonic dependence of permittivity and conductivity on the concentration of $\text{Cu}_6\text{PS}_5\text{I}$ nanoparticles can be not only increase in these

values with introducing the nanoparticles, but also decrease due to adsorption of ions on the surface of the nanoparticles and increase in LC viscosity with increasing the nanoparticle concentration.

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