Semiconductor Physics, Quantum Electronics & Optoelectronics, 2016. V. 19, N 4. P. 399-403.
doi: https://doi.org/10.15407/spqeo19.04.399

PACS 61.30.Gd, 77.84.Nh

The non-linear dependence of 6CHBT liquid crystal conductivity on the concentration of gold nanoparticles

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Abstract. Within the frequency range $10^{-1}…10^{6}$ Hz at the temperature 293 K, the effect of gold nanoparticles on the dielectric properties of the planar-oriented nematic liquid crystal 6CHBT has been studied. The concentration of nanoparticles with the average diameter 3 to 5 nm was chosen as 0.01, 0.02 and 0.1 wt.%. It has been shown that for the frequencies less than 10 Hz, the dielectric properties of the samples can be described with the Debye dispersion. For the samples with the concentration of gold nanoparticles 0.1 wt.%, the time of relaxation has been estimated (4.7±0.5 s). It has been also shown that the conductivity of the liquid crystal depends non-linearly on the concentration of nanoparticles introduced into the liquid crystal. The greatest change in conductivity of the liquid crystal on the concentration of introduced gold nanoparticles has been obtained within the range of 0.01 to 0.02 wt.%. It has been assumed that the conductivity of 6CHBT that depends non-linearly on the concentration of introduced gold nanoparticles is caused by the competing processes of ion desorption from the gold nanoparticles and of nanoparticle aggregation.

Keywords: planar-oriented nematic liquid crystal, gold nanoparticles, conductivity, Debye dispersion.

Manuscript received 01.07.16; revised version received 15.09.16; accepted for publication 16.11.16; published online 05.12.16.

1. Introduction

Despite the chemical “inertness” of bulk gold, Au nanoparticles (ANP) are catalytically active and can capture impurities of various types. In the case of biological objects, these impurities may be, for example, cancer cells [1, 2]. Subsequently, these cells can be destroyed by heating the nanoparticles using the plasma resonance effect. It is clear that in most cases the concentration of nanoparticles should be sufficiently low in order to they can be easily excreted from the body due to immune processes. Therefore, the development of methods capable to estimate the ANP concentration in biological fluids has very important practical and scientific significance.

Since ANP can conduct electricity rather well, they have to increase the conductivity of body fluids. Therefore, measurement of fluid conductivity may be one of the methods to assess the content of a small amount of ANP. Most of biological fluids are rather complex systems. To somewhat reduce the number of problems arising in the course of analyzing the results of changes in the conductivity of biological systems under the influence of ANP at the initial stages of the study, it is purposeful to perform these experiments with simpler objects possessing the properties to similar to those of biological systems.

Liquid crystals (LC) can play the role of these biological objects. Therefore, these crystals were selected for analysis of the conductivity measurements in the presence of a small amount of ANP.

Analysis of publications on the ANP effects on properties of LC indicates that in most of cases studied were the optical properties of these mixtures. For example, in the work [3] it was shown that due to formation of oriented layers of the LC molecules around ANP, plasma levels are split. In the works [4, 5], being based on studies of the optical characteristics inherent to the mixture of ANP with LC, it was shown that aggregation of ANP can be reduced if using LC that has a smectic phase. The change in the optical or electro-optical properties of ferroelectric LC, when introducing ANP, was considered in [6-9]. The influence of ANP on non-linear optical properties of LC was studied in [10]. Studied in the work [11] was aggregation of ANP under the influence of electric field.

It was shown in [12] that the presence of a small amount of ANP in nematic LC 6CHBT affects the parameters of the Freedericksz transition in crossed electric and magnetic fields. It was shown that, even at low concentrations of ANP, there are significant changes in the magnitude of the voltage of the electric field and induction of magnetic field for Freedericksz transition. However, the mechanism of these changes has not been ascertained.

In addition to nematic and ferroelectric LC, we investigated the effect of ANP and other types of liquid crystals. For instance, studied in [13] was formation and behavior of surface plasmon resonance in thermotropic calamitic liquid crystals, and in [14] – strain in time of thermomechanical nematic liquid crystal elastomer. Effect of ANP on lyotropic liquid crystals similar to the body fluids was investigated in [15]. It was shown that lyotropic matrix induces aggregation of nanoparticles, which leads to a red shift of the surface plasmon resonance.

Performed in the work [16] was the study of cholesteric liquid-crystalline dispersion formed by double-stranded nucleic acid molecules of various families (DNA and poly(I)xpoly(C)). These samples are in fact already biological fluids. It was shown that embedding ANP leads to two effects: i) restructuring the spatial cholesteric structure of particles, ii) formation of ANP clusters.

From analysis of the above works, it follows that in none of them the task to determine the content of ANP distributed in the bulk, being based on the electrical properties of samples. Therefore, the aim of this study was to investigate the effect of small amounts of Au nanoparticles on the dielectric properties of nematic liquid crystals.

2. Materials and methods of research

In studying the impact of small amounts of ANP impurities on dielectric properties of LC, its conductivity is essential. Mixtures of nematic LC that are advantageously used in display technology have a relatively high conductivity. Therefore, for our study we chose a one-component nematic LC 6CHBT.

As ANP, we used gold nanoparticles functionalized with dodecanethiol with an average size of 3 to 5 nm (Sigma-Aldrich Co). In the initial state, ANP were dispersed in toluene with the concentration 2 wt.%. After that, ANP in toluene solution was introduced into LC, as a result of sonication and heating, the solvent was evaporated and the mixture of gold nanoparticles with 6CHBT was formed. For studies, except pure 6CHBT, we used the mixture of LC with ANP of the concentrations 0.01, 0.02 and 0.1 wt.%.

We filled the mixture of LC with ANP into cells of the sandwich type, which consisted of two glass plates coated with the optical ITO layer consisting of a mixture of indium and tin oxides, which that is electrically conductive and transparent in the visible spectral range. Before filling with the mixture, the cell capacitance was measured, and in this manner determined was its thickness. The test samples had the thickness 25 μm. To provide planar orientation of LC, a polyamide layer was deposited onto the electrodes (before making the cell). Further, this layer was mechanically rubbed in a certain direction. Observations under a polarizing microscope revealed that a small amount of ANP does not affect the homogeneity of planar orientation inherent to LC molecules.

Dielectric properties of the obtained samples were investigated within the frequency range $f = 10^{-1}\ldots10^{6}$ Hz by using the oscilloscopic method [17]. The amplitude of the measuring signal of triangular shape was 0.25 V. The measurements were performed at 293 K. The measurement error did not exceed 5%.

3. Experimental results and discussion

Fig. 1 shows the frequency dependence of the real component of the complex permittivity ε' of planar oriented: 6CHBT (*1*), 6CHBT+0.01 wt.% ANP (*2*), 6CHBT+0.02 wt.% ANP (*3*) and 6CHBT+0.1 wt.% ANP (*4*). From the analysis of the data obtained, it follows that the whole dielectric spectrum can be separated into three sections: **A**, **B** and **C**. In our previous studies [18, 19] and in [20], it was shown that each of these sections characterizes different processes.

Fig. 2 shows the frequency dependences of ε'' for 6CHBT (curve *1*) and for 6CHBT with various ANP concentrations (curves *2* to *4*). From the analysis of the data, it follows that within the frequency range 10 to

10^3 Hz the ε″ magnitude decreases linearly with increasing the frequency *f*. This regularity corresponds to the condition that the resistance of the sample does not depend on the frequency and is equal to the resistance of the sample bulk. If we compare the analyzed section of the dielectric spectrum in Fig. 2 with the spectrum in Fig. 1, we see that it corresponds to the section **B**. For this section (as seen from Fig. 1), the value ε′ also does not depend on frequency. Therefore, this ε′ value is equal to the dielectric permittivity of the samples. As can be seen from Fig. 1, the ε′ value in LC in the presence of a small amount of ANP is insignificantly (within experimental errors) different from ε′ of 6CHBT. Therefore, for the section **B** of the dielectric spectrum, the dependence of ε″ on the availability and concentration of ANP was analyzed in more detail. For this analysis, the AC conductivity σ_{AC} is a more practically used parameter. As it is well known, it is related to ε″ through the equality

$$\sigma_{AC} = \varepsilon''\varepsilon_0\omega\,, \qquad (1)$$

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

The dependence of σ_{AC} on the ANP concentration is shown in Fig. 3. It follows from these data that the conductivity of the test samples depends non-linearly on the ANP concentration. The greatest changes in the conductivity are observed within the ANP concentrations of 0.01 to 0.02 wt.%. It may be caused by the complex nature of interactions between ions available in LC as well as ions that are introduced into LC together with ANP. If one adds to these processes the non-linear adsorption ones resulting in decreased concentration of nanoparticles in the sample bulk, it is obvious how it is difficult to describe this process as a whole. One of the probable mechanisms of reducing the ANP effect on the dielectric properties of LC in the concentration range of 0.02 to 0.1 wt.% is aggregation of nanoparticles.

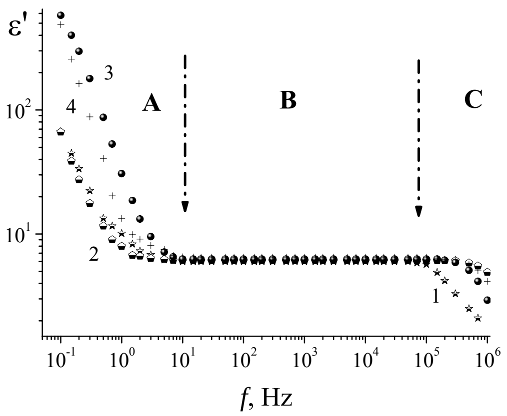

Fig. 1. The frequency dependences of the real part of the complex dielectric permittivity ε′ of nematic liquid crystal 6CHBT with different concentrations of gold nanoparticles: 0 (*1*), 0.01 (*2*), 0.02 (*3*), and 0.1 wt% (*4*). The sample thickness is 25 μm, temperature – 293 K.

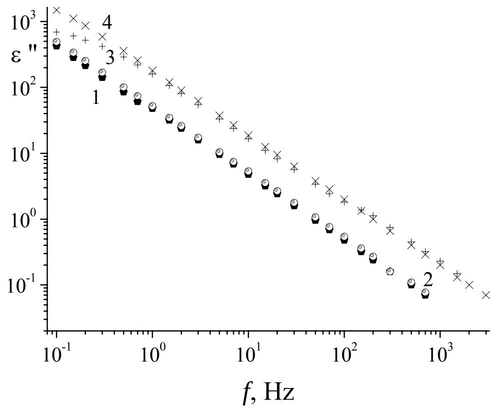

Fig. 2. The frequency dependences of the imaginary part of the complex dielectric permittivity ε″ of nematic liquid crystal 6CHBT with different concentrations of gold nanoparticles: 0 (*1*), 0.01 (*2*), 0.02 (*3*), and 0.1 wt% (*4*). The sample thickness is 25 μm, temperature – 293 K.

In this case, according to the data of Fig. 3, the conductivity does not practically change, which is caused by formation of ANP aggregates that obstruct desorption of ions from the surface of nanoparticles in LC. This aggregation also can occur most likely when the ANP concentration is less than 0.02, but probably its effectiveness is considerably lower. A similar non-linear dependence of the 6CHBT conductivity on the concentration of superionic Cu_6PS_5I nanoparticles was observed by us in the work [21], and this dependence was also explained by the complex nature of the processes of adsorption and desorption of ions on/from the surface of the nanoparticles.

The obtained by us non-linear dependence of LC conductivity on the presence of small concentrations of ANP should be considered when developing the methods for estimation of nanoparticle concentrations by using the conductivity change not only in LC, but in other liquids and particularly in body fluids.

It follows from the analysis of dielectric spectra in Fig. 1 that in the section **A** the ε′ value is much higher than the dielectric permittivity of the sample bulk part, which was estimated using the analysis of the dielectric spectrum in the section **B**. As we have shown in [19], the reason for this effect is uneven distribution of the electric field in the sample (at low frequencies the electric field is mainly applied to the near-electrode layer with a small thickness). Therefore, changes in the ε′ value for low frequencies characterize the change in the parameters of the near-electrode layers.

As one of the characteristics of the near-electrode layer, we can take the ε′ value at the lowest frequency. The dependence of ε′ on the ANP concentration for the frequency 10^{-1} Hz is shown in Fig. 4. It is seen that since the ANP concentration is close to 0.02 wt.% there observed a significant (almost 9-fold) change in the ε′

value. The small difference between the ε′ values for 6CHBT and 6CHBT+0.01 wt.% ANP as well as for the mixtures LC+ANP with the concentrations of 0.02 and 0.1 wt.% gives the reason to assume that the parameters characterizing the near-electrode layer are non-linearly dependent on the ANP concentration. Thus, not only the parameters of the bulk part of the sample, but also the parameters for the near-electrode layer of these samples are not linearly dependent on the nanoparticle concentration.

Adsorption of nanoparticles on the electrode surface can be considered as one of the main reasons for changes in the parameters of near-electrode layers in the presence of a small amount of ANP. Therefore, being based on the data obtained, it can be assumed that the concentration of ANP adsorbed on the electrode surface is a non-linear function of their concentration.

The dielectric spectrum in the section **A** is caused by the relaxation process of a certain type. To establish the mechanism of this process, the dependence ε″(ε′) (Cole–Cole diagram) was analyzed. For all the samples, except 6CHBT+0.1 wt.% ANP, the experimental values form only a small section of the arc, from which it was difficult to plot the whole Cole–Cole diagram. Therefore, the detail analysis of the Cole–Cole diagram was performed only for the samples 6CHBT+0.1 wt.% ANP.

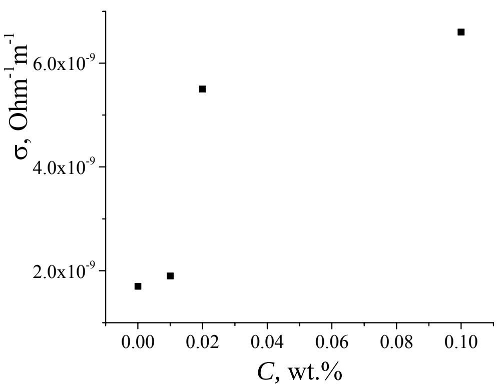

Fig. 3. The dependence of the conductivity of the liquid crystal 6CHBT of the concentration of gold nanoparticles.

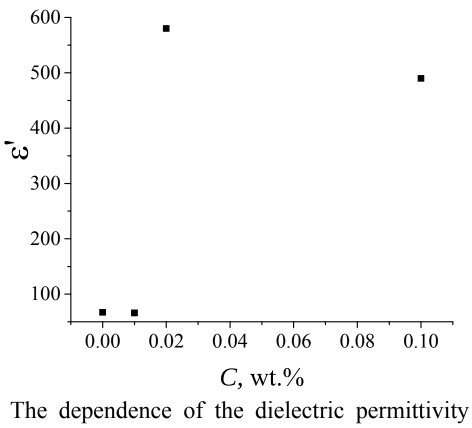

Fig. 4. The dependence of the dielectric permittivity of the liquid crystal 6CHBT on the concentration of gold nanoparticles at the frequency 10^{-1} Hz.

It follows from these data that the dependence ε″(ε′) for the sample 6CHBT+0.1 wt.% ANP can be approximated by a semi-circle with a small error. According to the theory [20], the relaxation process of this type is described by the Debye equation:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau}, \qquad (2)$$

where ε* is the complex dielectric permittivity, ε_∞ and ε_s are the values of the dielectric permittivity at the frequencies $f = \infty$, and $f = 0$ Hz, respectively, τ is the dielectric relaxation time.

From the parameters in the equation (2), the most informative is the time of dielectric relaxation. We have estimated its value as 4.7±0.5 s.

In the section **C** of dielectric spectrum, changes in the parameters of dielectric processes under the influence of nanoparticles were significantly lower than those in the sections **A** and **B**. That's why they have not been analyzed in detail in this paper. The relaxation process that occurs in this frequency range is characteristic for any polar liquids and is caused by the transition from the dipole and electron polarization (at lower frequencies) to the purely electron polarization (at higher frequencies). The reason for this effect is that the molecules (and, hence, their dipole moments) have no time to oscillate under the field action for the period close to that of alternating electric field.

4. Conclusions

It has been experimentally shown that the presence of gold nanoparticles with the concentrations of 0.01 to 0.1 wt.% in nematic liquid crystal 6CHBT leads to changes in the parameters of near-electrode layers and bulk part of the sample, which considerably exceed the error of measuring these parameters.

In general, the presence of nanoparticles in LC leads to increasing the conductivity value. However, this dependence (as well as that of the near-electrode layer parameters) on the concentration of nanoparticles is non-linear. In the presence of 0.1 wt.% ANP, the conductivity of the mixture of liquid crystal and ANP is increased almost by 4 times. Moreover, the maximum changes in the value of conductivity occur within the concentration range of 0.01 to 0.02 wt.% ANP.

One reason of the non-linear dependence of the parameters of near-electrode and bulk properties of the sample on the nanoparticle concentration may be aggregation of nanoparticles, the efficiency of which considerably increases beginning from the ANP concentrations higher than 0.02 wt.%.

The non-linear dependence of the conductivity on the concentration of gold nanoparticles revealed in the mixture of liquid crystal and ANP can be characteristic for biological objects. Therefore, when developing the methods to control nanoparticles in biological systems, which are based on conductivity measurements, one should take into account that, even at low concentrations of nanoparticles, the conductivity can be a non-linear function of the concentration typical to introduced impurities.

References

1. S.S. Agasti, A. Chompoosor, C.-C. You, P. Ghosh, C.K. Kim, V.M. Rotello, Photoregulated release of caged anticancer drugs from gold nanoparticles // *J. Am. Chem. Soc.* **131**(16), p. 5728-5729 (2009).
2. B. Kang, M.A. Mackey and M.A. El-Sayed, Nuclear targeting of gold nanoparticles in cancer cells induces DNA damage, causing cytokinesis arrest and apoptosis // *J. Am. Chem. Soc.* **132**(5), p. 1517-1519 (2010).
3. S.Y. Park, D. Stroud, Surface-enhanced plasmon splitting in a liquid-crystal-coated gold nanoparticle // *Phys. Rev. Lett.* **94**, p. 217401 (2005).
4. R. Pratibha, K. Park, I.I. Smalyukh, W. Park, Tunable optical metamaterial based on liquid crystal-gold nanosphere composite // *Opt. Exp.* **17**, p. 19459-19469 (2009).
5. D.F. Gardner, J.S. Evans, I.I. Smalyukh, Towards reconfigurable optical metamaterials: Colloidal nanoparticle self-assembly and self-alignment in liquid crystals // *Mol. Cryst. Liq. Cryst.* **545**, p. 3[1227]–21[1245] (2011).
6. R. Pratibha, K. Park, W. Park, I.I. Smalyukh, Colloidal gold nanoparticle dispersions in smectic liquid crystals and thin nanoparticle-decorated smectic films // *J. Appl. Phys.* **107**, 063511 (2010).
7. J. Prakash, A. Choudhary, A. Kumar, D.S. Mehta, A.M. Biradar, Nonvolatile memory effect based on gold nanoparticles doped ferroelectric liquid crystal // *Appl. Phys. Lett.* **93**, 112904 (2008).
8. A. Kumar, J. Prakash, D.S. Mehta, A.M. Biradar, W. Haase, Enhanced photoluminescence in gold nanoparticles doped ferroelectric liquid crystals // *Appl. Phys. Lett.* **95**, 023117 (2009).
9. S. Kaur, S.P. Singh, A.M. Biradar, A. Choudhary, K. Sreenivas, Enhanced electro-optical properties in gold nanoparticles doped ferroelectric liquid crystals // *Appl. Phys. Lett.* **95**, 023120 (2009).
10. A. Acreman, M. Kaczmarek, G. D'Alessandro, Gold nanoparticle liquid crystal composites as a tunable nonlinear medium // *Phys. Rev. E*, **90**, 012504 (2014).
11. L.-H. Hsu, K.-Y. Lo, S.-A. Huang, C.-Y. Huang, and Ch.-S. Yang, Irreversible redshift of transmission spectrum of gold nanoparticles doped in liquid crystals // *Appl. Phys. Lett.* **92**, 181112 (2008).
12. P. Kopčansky, N. Tomašovicova, M. Koneracka et al., Structural phase transition in liquid crystal doped with gold nanoparticles // *Acta Physica Polonica A*, **118**(5), p. 988-989 (2010).
13. A.Choudhary, G. Singh, A.M. Biradar, Advances in gold nanoparticle – liquid crystal composites // *Nanoscale*, **6**, p. 7743-7756 (2014).
14. R. Montazamia, C.M. Spillmann, J. Naciri, B.R. Ratna, Enhanced thermomechanical properties of a nematic liquid crystal elastomer doped with gold nanoparticles // *Sensors and Actuators A*, **178**, p. 175-178 (2012).
15. M. Lenart, R.F. Turchiello, G.F. Goya, S.L. Gomez, Enhanced thermal lens effect in gold nanoparticle-doped lyotropic liquid crystal by nanoparticle clustering probed by Z-scan technique // *Braz. J. Phys.* **45**, p. 213-218 (2015).
16. Y.M. Yevdokimov, S.G. Skuridin, V.I. Salyanov, V.I. Popenko, V.M. Rudoy, O.V. Dement'eva, E.V. Shtykova, A dual effect of Au-nanoparticles on nucleic acid cholesteric liquid-crystalline particles // *J. Biomat. and Nanobiotech.* **2**, p. 461-471 (2011).
17. A.J. Twarowski, A.C. Albrecht, Depletion layer in organic films: Low frequency measurements in polycrystalline tetracene // *J. Chem. Phys.* **70**(5), p. 2255-2261 (1979).
18. A.V. Koval'chuk, Relaxation processes and charge transport across liquid crystal – electrode interface // *J. Phys.: Condensed Matter*, **13**, N 24, p. 10333-10345 (2001).
19. A.V. Koval'chuk, Low and infra-low dielectric spectroscopy liquid crystal-solid state interface. Sliding layers // *Ukr. J. Phys.* **41**(10), p. 991-998 (1996).
20. E. Barsukov, J.R. Macdonald, *Impedance Spectroscopy. Theory, Experiment and Applications.* New Jersey, John Wiley & Sons Inc., 2005.
21. I.P. Studenyak, P.Yu. Demko, A.V. Bendak et al., Influence of superionic nanoparticles Cu_6PS_5I on dielectric properties of nematic liquid crystal 6CHBT // *Semiconductor Physics, Quantum Electronics & Optoelectronics*, **18**, N 2, p. 205-208 (2015).