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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

THE PHYSICAL PROPERTIES OF THE SYSTEMS OF LIQUID CRYSTAL-$BaTiO_3$ NANOPARTICLES

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GENERAL CHARACTERISTICS OF WORK

Relevance and currency of the research topic. It is known that molecules of some organic substances consisted of rodlike (calamitic) molecules orient in same direction at a certain temperature interval. This direction is called a director, and this state of matter is calledliquid crystal, since anisotropy belonging to crystals and viscosity doing to liquids in these systems are observed at the same time. Liquid crystals as being a specific condition of matter comprise the scientific interest. As the clear-cut examples of this realm are specifically the continuous increase of the scientific works and monographs, the existence of specialized scientific journals (Molecular Crystals and Liquid Crystals, Liquid Crystals), sequential organizations of the International, European and Asian Liquid Crystal Conferences every year. Nonetheless, the great interest to liquid crystals is correlated with their practical applications, mostly one in the display technique. Display systems set up basing on liquid crystals in contrast with other, possess a plenty of advantages: the simplicity of the production technology, low cost, having small sizes and very low energyconsumption. The continuous increase of the display technology's demands (the enhansing of the image quality, the decreasing of sizes and energy consumption etc.) require the continuous development of expluatation parameters of liquid crystals (usage durability, opration voltage, sweatching speed, contrast ratio etc.). One of the solutions of this problem is the purposeful synthesis of new liquid crystals of better material parameters that there has not been any progress in this sector. Other alternative approach is the constructivecombination of the properties of liquid crystals with other functional materials. For instance, the system used in flexable displays consists of micron-sized liquid crystal droplets dispersed in polymer medium. Conversely, submicron-sized particles of different properties (ferromagnet, ferroelectric, metal particles, and etc.) and carbon nanoparticles (nanotubes, fullerens, grafen) are dispercedin colloidal liquid crystal composits. Even the small amount of addition of above mentioned particles into liquid crystals can cause enormouschang in their properties and the creation of new effects in some cases. Speciallyinteresting effects happens in nematic liquid crystalsdopped

with ferroelectric barium titanat ($BaTiO_3$) particles. For example, by increasing the dielectric anisotropy of liquid crystals, ferroelectric particles decrease the threshold voltage of Frederix effect, increase the sweatching speed.Electromechanical effect with memoryis observed in the isotrope phase of liquid crystal-barium titanat colloid.

Thermotrop liquid crystals have other phases called cholesteric and smectic. In smectic liquid crystals,besides oforientational order, there is also translational order. The center of mass of molecules in smecticA liquid crystalsliesin equidistant ayersperpendicular to the director.Such a layered structure leads to lncreasingviscosity of smectic A liquid crystal by oneoretwo order. The high degree of viscosity causes the occurrence of the Frederix effect with memory, in its turn, the noted liquid crystals are added into the category of perspective materials useful for information recording and andstoring. Additionally, while preparing the colloid basing on nematic liquid crystals, stabilizer of 1-2 % (for example, oleic acid) is added to it to prevent the aggregation of particles. In most cases, stabilizer changes the material properties of liquid crystals in an undesirable manner, for instance, it constricts the temperature interval nematicliquid crystal phase. Since smectic A liquid crystal has a huge value of viscosity, when it is used as a matrix in liquid crystal-nonparticle systems, there is no need for stabilizer. Despite of these advantages, the threshold voltage of electro-optic effect in smecticA liquid crystals are considerably high (1-2 order) and has low speed in contrast with nematic liquid crystals.

Research objects and subjects. As a smectic A liquid crystal, 4-nitrophenil 4- desiloksibenzoat (named as 10NF) with positive dielectric anisotropy and 4-heksiloksibenzoic acid of 4-heksilokse 3-nitrobenzoy acid (C2) with negative dielectric anisotropy are used. Furthermore, in order to shift the smectic A phase of liquid crystal to low temperatures, nematic liquid crystal – 4,4-pentilsianobifenil (5CB) of low-teperature and positive dielectric anisotropy is added to it. As ferroelectric particles 100 nm, 200 nm, 300 nm, 400 nm, and 500 nm sized mono-disperse barium titanat ($BaTiO_3$) are used.

Aims and purpose of the research. To clarify the influence of various submicron-sized ferroelectric barium titanat particles on the physical properties of smectic A liquid crystals (dielectric permittivi-

ty, electrical conductivity, the temperature and enthalpy of phase transition) and, as a result find the possibilities of improvementthe parameters of electro-optic effect with memory happening in these systems (threshold voltage, swithingtime etc.). In order to achieve this purpose, the following problems are required to be solved:

1. The mastering of technological derivation of stable smecticAliquid crystal colloids on the basis of $BaTiO_3$ particles;

2. The improvement of the methods of homogeneous planar and homeotrop orientations of smecticA liquid crystal molecules in electro-optic cell;

3. The investigation of different sized $BaTiO_3$ particles' effect on the frequency dependence of dielectric permittivity and electrical current of smectic A liquid crystal of both positive and negative dielectric anisotropy;

4. The research of $BaTiO_3$ particles' effect on the electro-optic properties of smectic A liquid crystal;

5. The investigation of $BaTiO_3$ particles' effect on the thermal properties of smectic A liquid crystal.

Research methods. As practical research methods in the thesis, there has been used the low frequency dielectric spectroscopy method, i.e. capacity-frequency dependence of electro-optic cellss filled with colloids ofsmecticA liquid crystals of two different signed dielectric anisotropy and five different sized $BaTiO_3$ particles with the application of the of low frequency. The influence of submicron sized ferroelectric $BaTiO_3$ particles on planar-homeotrop and hometrop-planar transitions occurring in smectic A liquid crystal have been studied with the measurement method of the voltage-farad (C-V) and volt-lumen characteristics of the electro-optic cells. The effect of various sized BaTiO3 particles on phase transitions of smectic A liquid crystalshase been studied with differential scanning calorimetry and polarization microscopy methods.

Basic provisions for defense:

1. It has been clear that in liquid crystal colloidin case of external field absence ferroelectric $BaTiO_3$ particles with its main (polarization) axisorient in the same direction as that of the director, but not with dipole groups of liquid crystal molecules.

2. It has been shown that electro-optic effect in smectic A liquid

crystal with positive dielectric anisotropy happen at three stages: Firstly, $BaTiO_3$ particles inside liquid crystal turn by 90^o, then are polarised by transition from polidomenstate to monodomenstate, and finally turn liquid crystal molecules under the action of its local field.

3. 100 nm sized $BaTiO_3$ particles lead to abnormal changes in dielectric properties of smectic A liquid crystal at low frequencies. It is explained by contribution of those particles to conductivity characteristics of liquid crystal.

4. $BaTiO_3$ particles influence on the dielectric dispersion of smectic liquid A crystal and this effect depends on both the size of particles and the sign of dielectric anisotropy of liquid crystal.

5. The interaction of barium titanat particles with liquid crystal molecules have a significant impact on phase transitions in liquid crystal, especially from smectic A to isotrop liquid transition.

Scientific innovations. In the dissertation work, the following facts have been firstly identified:

1. $BaTiO_3$ particles increase the value of dielectric permittivity in both in planar and homeotrop textures of liquid crystals. This increase is mainly observed in the longitudinal component of dielectric permittivity. The more the size of $BaTiO_3$ particles, the more the increase in longitudinal component of dielectric permittivity.

2. $BaTiO_3$ particles impact on the dielectric permittivity dispersion of C2 liquid crystal. $BaTiO_3$ particles shift the dispersionof transverse component of dielectric permittivity of C2 liquid crystal observed at high frequencies (10^5 Hz) to low frequency range, and the shifts value is almost independent of particlesize.

3. The weak dispersion of longitudinal component of dielectric permittivity of C2 liquid crystal observed at low frequencies (10^2 Hs) shifts toward high frequencies under the influence of $BaTiO_3$ particles. The more the size of $BaTiO_3$ particles, the more this shift value is.

4. $BaTiO_3$ particles significantly decrease the threshold voltage of planar-homeotrop transition occurring in smectic A liquid crystal (10NF+5CB) with positive dielectric anisotropy. The effect is explained by the creation of local electric field around polarized $BaTiO_3$ particles, but not with the increasing of dielectric anisotropy of liquid crystal.

5. $BaTiO_3$ particles decrease the threshold voltage of homeotrop-planar transition of C2 liquid crystal with negative dielectric anisotropy minimum twice. This result also can be explained within the framework of local field conception.

6. Ferroelectric $BaTiO_3$ particles increase planar-homeotrop and homeotrop-planar transition speed by an order. This is explained by the fact the particles act as a nucleation centers from wich the transition begins.

7. $BaTiO_3$ particles increase the temperature of smectic A-isotrope phase transition. The more the size of particles, the more this increase. In the case of 500 nm-sized $BaTiO_3$ particles, this increase is about 5.5^oC. $BaTiO_3$ particles also increase the enthalpy of smectic A-isotrop phase transition. This increase is more for middle sized (200-400 nm) particles.

8. In case of small sized (100 nm, 200 nm) $BaTiO_3$ particles, crystal-smectic A phase transition temperature increase by a small value. Conversely, it weakly decreases in in case of big sizes (300-500 nm). It is possible to tell similar results about transition enthalpy.

Theoretical and practical significance of the research.

1. Colloids prepared in the basis of smectic A liquid crystals possess high stability and the stabilizers are not required in their preparation.

2. In contrast with puresmecticA liquid crystals, colloids prepared in the basis of smectic A liquid crystals and $BaTiO_3$ particles have more usage parameters (low control voltage and high transition speed).

3. $BaTiO_3$ particles allow to expand smectic A liquid crystal temperature intervalsignificantly.

4. The achieved practical results may assist the progression and development of the theory of similar colloids.

Approbation and application. The results of the researches in the dissertation work have been discussed in the following international and republic conferences and printed: «Opto-, nanoelektronika, kondensə olunmuş mühit və yüksəkenerjilər fizikası» Beynəlxalq konfransı (Bakı, 25-26 dekabr 2015); The 26^{th} International Liquid Crystal Conference (Kent State University, USA, July 31-August 5, 2016); «Fizikanın actual problemləri» IX Respublika elmi konfransı

(Bakı, 22 dekabr 2016); «Modern Trends in Physics» International Conference (Baku, 20-22 April 2017); International Scientific Conference of Young Researchers (Baku, 05-06 may 2017); The 14th European Conference on Liquid Crystals Moscow State University (Russia, June 25-30, 2017); «Modern Trends in Physics» International Conference (Baku, May 1-3, 2019).

The dissertation comprises 10 articles and 7 theses, and all have been printed in local and foreign articles. Out of these, three articles have been done in impact-factorized journals of Clarivate Analytics (Web of Science) and Scopus database. Out of theses, the two were discussed and printed in international and European conferences.

Name of the organization where the dissertation work is executed. The dissertation work was accomplished at the departments of «Chemical Physics of Nanomaterials» of Baku State University.

Structure, volume and main content of dissertation work. Dissertation work is posted on 160 pages as a whole. It consists of an introduction, including 61 figures, 7 tables, 5 chapters, a conclusion, practical recommendations, references include 3 works in Russian, 134 works in English and 13 works in Azerbaijani. The volume of the dissertation (with the exception of gaps and pictures in the text, tables, graphs, appendices and list of reference) – 164210 characters (introduction – 13924, Chapter I – 39013, Chapter II – 24858, Chapter III – 35142, Chapter IV – 30980, Chapter V – 18759, Result – 1498 characters).

CONTENT OF THE DISSERTATION WORK

In the introduction the actuality of the topic is emphasized; the purpose and scientific progress of the work and main scientific items presented for the defence are noted.

In the first chapter the information about physical properties of liquid crystals and ferroelectrics is noted. The dispersion methods of ferroelectric particles in liquid crystal matrix and the summary of broad spectrum of books and reviewusabout physical properties of obtained colloids are emphasized. The controversial results about the effect of ferroelectric $BaTiO_3$ particles on the physical properties of liquid crystal have been analyzed, and the causes of these contraries

have been clarified.

In the second chapter the detailed information the structural and physical properties about the substances used in the research. Smectic A liquid crystals of two different dielectric anisotropy and $BaTiO_3$ferroelectric particles have been described. Smectic A liquid crystal of positive dielectric anisotropy consists of two components: 4-nitrophenyl 4'-deciloksybenzoat (a conventional name 10NF) and 4-ciano 4'-pentilbiphenyl(a conventional name 5CB) inmole ratioof 1:1. The produced mixture has

Crystal 32.5 ^{o}C*Smectic A* 47 ^{o}C*Nematic* 54 ^{o}C*Isotropic liquid*

phase transitions and anisotropy of dielectric permittivity $\Delta\varepsilon = +13{,}8$. The other liquid crystal with negative dielectric anisotropy used in the research is one component of 4-hexyloxyphenyl ether of 4-hexyloxy-3-nitrobenzoic acid (a conventional name is C2) has the following phases:

Crystal 30.5^{o}C *Smectic A* 71^{o}C *Isotropic Liquid*

The dielectric anisotropy of C2 is $\Delta\varepsilon = -8{,}6$.

100 nm, 200 nm, 300 nm, 400 nm and 500 nm sized monodisperse $BaTiO_3$ particles were used in the research. The size of the particles were checked with Jeol JSM 767-F Scanning Electron Microscope. The dispersion of $BaTiO_3$ particles in liquid crystal was performed in ultrasound shaker. The measurement of dielectric and electro-optic properties of liquid crystal was done with the electro-optic cell. To analyze the structures and forms of the pure liquid crystal and liquid crystal+$BaTiO_3$ colloids curried of and in the thesis, complex physical methods were applied: scanning electron (SEM), differential scanning calorimetric (DSC), low frequency dielectric spectroscopy, capacity-voltage (C-V) measurement method.

In the third chapter the impact of different submicron sized barium titanat ($BaTiO_3$) particles on the dielectric properties of smectic A liquid crystal of positive and negative dielectric anisotropy is studied. The method of low frequency dielectric spectroscopy was applied. The weight fraction of barium titanat particles in colloid is 1 %, the corresponding volume fraction is 0.17%. The dielectric measurements are done in the electrooptic cells of d=17 μm thickness and around working area of 50 mm^2 at the temperature 32^{o}C. The IET-

1920 RLC meter provides to measure the capacity (C) of the electro-optic cell filled with liquid crystal, resistivity (R) and loss factor (D) at [20 Hz; 1 MHz] frequency interval. The amplitude of sinusoidal test signal applied to the gap is selected to be 1 V. The electro-optic cell is considered as parallel connected capacitor and resistor. The real and imaginary parts of dielectric permittivity can be calculated using the formulas[1]

$$\varepsilon' = \frac{\varepsilon}{\sqrt{1+D^2}}, \ \varepsilon'' = \varepsilon' \cdot D \qquad (1)$$

The value of the longitudinal components of above noted physical quantities are derived in the homeotrop orientation ($\varepsilon'_{\parallel}, \varepsilon''_{\parallel}$) and the transverse ones of them are done in the planar ($\varepsilon'_{\perp}, \varepsilon''_{\perp}$) orientation. The impact of $BaTiO_3$ particles on dielectric properties of liquid crystal of positive dielectric anisotropy are illustrated in Figures 1 and 2.

As it is could be observed in Figure 3, BaTiO3 particles don't have a considerable impact on the transversal component of dielectric permittivity of smectic A liquid crystal. This indicates that polar axes of BaTiO3 particles orient the same direction as the director of liquid crystal while passing from colloid isotropic phase to liquid crystal nemati core smectic A phase

Due to the less amount of $BaTiO_3$ particles in colloid, the following equations of the longitudinal and transversal components of dielectric permittivity of colloid are accepted to be correct

$$\varepsilon_{\parallel}^{colloid} = \varepsilon_{\parallel}^{LC} + f\varepsilon_{\parallel}^{FNP} \text{ and } \varepsilon_{\perp}^{colloid} = \varepsilon_{\perp}^{LC} + f\varepsilon_{\perp}^{FNP} \qquad (2)$$

and $\varepsilon_{\parallel}^{FNP} \sim 10^3$ and $\varepsilon_{\perp}^{FNP} \leq 100$ are considered for $BaTiO_3$ particles, this corresponds to the experimental results.

At low frequencies of sinusoidally changing electric field liquid crystal molecules have time to follow the direction of the field. Molecules cannot follow the rapid change rate of the direction of the electric field at high frequencies ($10^5 Hz$ and more), as a result dielectric permittivity starts to decrease (Figure 2). If ferroelectric barium

[1]Feldman Yu. Dielectric relaxation phenomena in complex systems / Yu. Feldman, Yu.Gusev, M.Vasiliyeva. – Kazan: Kazan University, – 2012, – 134p.

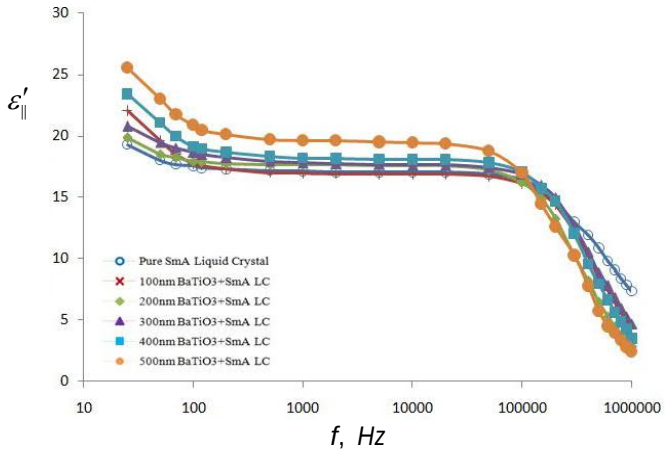

Figure 1. The frequency dependence of dielectric permittivity longitudinal component real part of pure liquid crystal (10NF+5CB) and its colloids of different sized $BaTiO_3$ particles

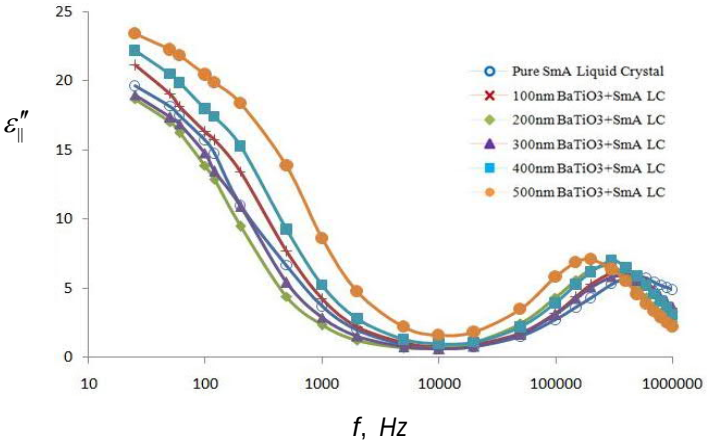

Figure 2. The frequency dependence of longitudinal component of imaginary part of dielectric permittivity of pure liquid crystal (10NF+5CB) and its colloids of different sized $BaTiO_3$ particles

titanat particle is considered as a dipole of radius R, the electric field created by it at distance *r* away from its center reads as below.[2]

[2]Matveev A.N. Electricity and Magnetism. – Moscow: Mir Publishers, – 1986, – 448p.

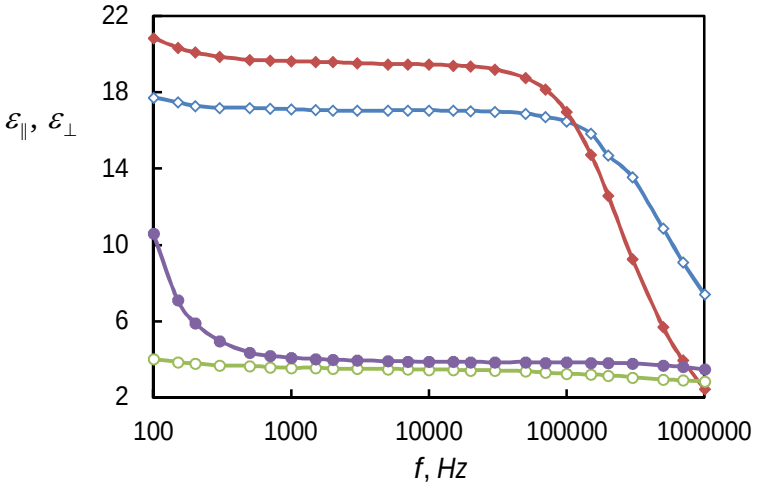

Figure 3. The dielectric permittivity – frequency dependence of the pures mectic A liquid crystal (10NF+5CB) and collide (10NF+5CB+$BaTiO_3$ (500 nm): empty rhombus 10NF+5CB $\varepsilon_{\parallel}$, full rhombus 10NF+5CB+$BaTiO_3$; $\varepsilon_{\parallel}$; empty circle 10NF+5CB $\varepsilon_{\perp}$ full circle 10NF+5CB+$BaTiO_3$ $\varepsilon_{\perp}$;

$$E_{FNP} = \frac{P_S \cdot R^3}{3\varepsilon_0 r^3}(3\cos^2\theta + 1). \qquad (3)$$

Equation (3) indicates that the more the size of particle, the more intense the local field created by it. This field hinders the rotation of liquid crystal molecules when external electric field changes direction. Lack of dielectric dispersion till 1*MHz* in transversal component is explained as both lack of strong dipole group perpendicular to long axis of liquid crystal molecules, and easy rotation of molecules around its long axis.

The following results have been obtained from the experiments done in smectic A phased – liquid crystal of negative dielectric anisotropy (Figure 4 and 5).

The addition of $BaTiO_3$ particles to smectic A liquid crystal significantly increases longitudinal component of dielectric permittivity, and the more the size of particles, the more this increase is detected. It does not change the transversal component of dielectric permittivity.

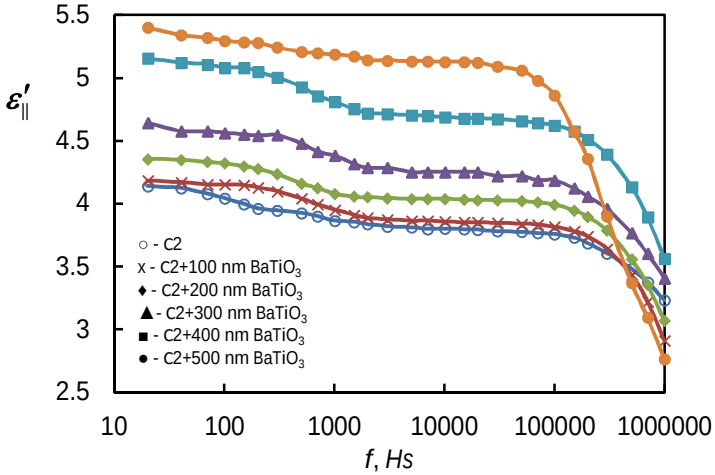

Figure 4. The frequency dependence of real part longitudinal component of dielectric permittivity of pure (C2) liquid crystal and its colloids of different sized $BaTiO_3$ particles

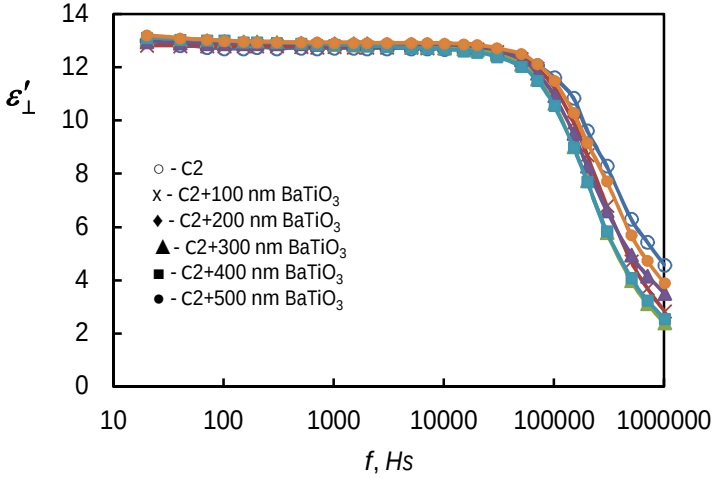

Figure 5. The frequency dependence of real part of transversal component of dielectric permittivity of pure (C2) liquid crystal and its colloids of different sized $BaTiO_3$ particles

This change also is explained as a result coupling of spontaneous polarization of $BaTiO_3$ particles with the director field of liquid crystal

C2.[3] Intermolecular anisotropic interaction, occuring in isotropic liquid-crystal phase transition and being responsible for liquid crystal phase, slightly polarize polidomen barium titanate particles and orient them along the director. If barium titanate particles are accepted have volume fraction of $f \approx 0{,}0017$, value in the polar direction of dielectric permittivity of $\varepsilon_{\parallel}^{FNP} \sim 10^2 \div 10^3$ and its perpendicular component's value of $\varepsilon_{\perp}^{FNP} \sim 10^1 \div 10^2$ in Equation 2, the experimental results have a qualitative explanation.

The frequency dependence of imaginary part ($\varepsilon_{\parallel}''$) of longitudinal component of dielectric permittivity of pure smectic A liquid crystal and its colloids are illustrated Fig. 6. The weak dispersion is observed in all low frequencies (100-1000 *Hz* frequency interval) with exception of colloid mixed with 100 nm sized $BaTiO_3$ particles. It is explained as polar $-C-NO_2$ and $-COOH$ groups are not exactly perpendicular to the long axis of liquid crystal molecules. For instance, while reviewing the structure of C_2 molecule, it is possible to observe polar nitrophenol group $-C-NO_2$(having a dipole moment of $p \approx 4$ *debay* = $1.3\times10^{-29} Kl\cdot m$) forms an angle 60^o with the long axis of molecule. This means that the parallel component of the dipole moment of group exists to that:

$$p_{\perp} \approx p\cos 60^o \approx 4 \cdot \frac{1}{2} debay = 2\, debay\,.$$

Similar facts can be noted about polar carboxyl group $-COOH$: ($p \approx 1{,}6$ *debay*$=5{,}3\cdot10^{-30} Kl\cdot m$). The relaxation frequency (the frequency corresponding to maximum of dielectric loss) shifts to high frequency region when $BaTiO_3$ particles are added to liquid crystal. The more the size of particles, the more this slide is observed.

The dispersion of transersal component ($\varepsilon_{\perp}$) of dielectric permittivity is associated with freezing rotayion of strong $-C-NO_2$ and weak $-COOH$ transversal dipole groups around long axis liquid crystal molecules. It is easy for molecules to rotate around long axis. Consequently, the dispersion of transversal component of dielectric

[3]Al-Zangana, A comparison between size dependent paraelectric and ferroelectric $BaTiO_3$ nanoparticle doped nematic and ferroelectric liquid crystals / S.Al-Zangana, M.Turner, I.Dierking // Journal of Applied Physics, – 2017. v.121, 085105, – p.1-12.

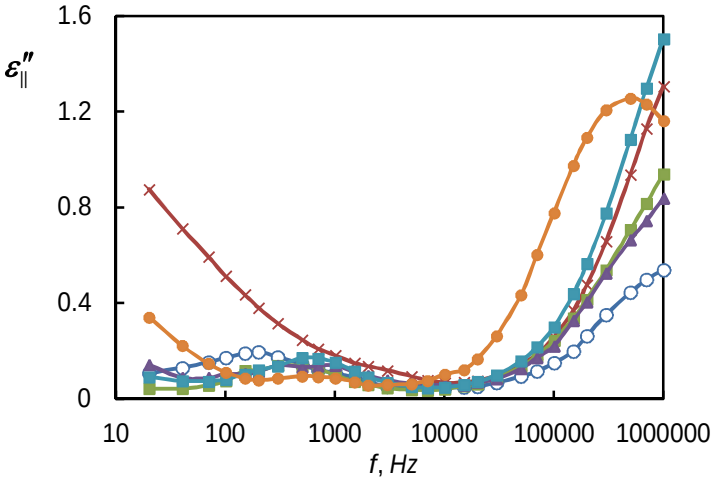

Figure 6. The frequency dependence of imaginary part of longitudinal component of dielectric permittivity of pure (C2) liquid crystal and its colloids of different sized $BaTiO_3$ particles

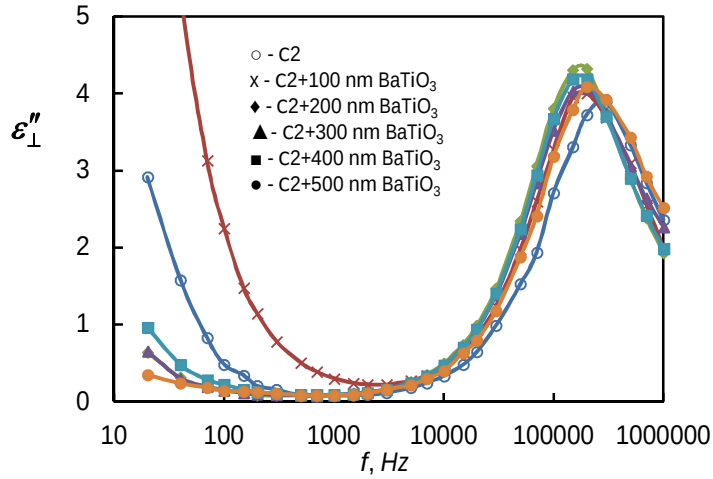

Figure 7. The frequency dependence of imaginary part of transversal component of dielectric permittivity of pure liquid crystal (C2) and its colloids of different sized $BaTiO_3$ particles

permittivity happens at high frequencies. The relaxation frequency shifts to low ones after adding $BaTiO_3$ particles to liquid crystal. These particles (expect 100 nm sized ones) decrease the imaginary

part of longitudinal component of dielectric permittivity (or dielectric losses) at low frequencies. Its cause is polarized particles' trapping of ions of local electric field. The more the frequency increases, the less this effect is, since the polarization of particles in the reverse direction is getting difficult in case the direction of electric field oppositely changes. Conversely, 100 nm-sized $BaTiO_3$ particles at low frequencies increase dielectric losses. It is related to both weak polarization of such sized particles and weak detection of «ion trap» effect. Also, since the size of these particles is relatively close to that of molecules of smectic A liquid crystal, as a result of this effect, material parameters of liquid crystal can change significantly, for example, translation viscosity can do. This, in its turn, results in sharp rise of electric current and dielectric losses.

In the fourth chapter the impact of ferroelectric $BaTiO_3$ particles on threshold voltage and other electro-optic properties of liquid crystal of both positive ($\varepsilon_{\parallel} > \varepsilon_{\perp}$) and negative ($\varepsilon_{\perp} > \varepsilon_{\parallel}$) dielectric anisotropy is studied by using on volt-farad (C-V) characteristics.

When the sign of anisotropy of dielectric permittivity of liquid crystal and its colloids are positive, electro-optic effects are in planar-homeotrop phase transition. The threshold voltage (U_{th}) is derived from C-V characteristic of electro-optic cell since effective dielectric permittivity (ε_{eff})of liquid crystal increases during the planar-homeotrop transition, in accordance with the equation

$$C = \varepsilon_0 \varepsilon_{eff} \frac{S}{d}. \qquad (4)$$

This increases electric capacity of cell. As a threshold voltage is taken the voltage at which the electric capacity of the cell starts to increase. Visually the threshold voltage can be obtained in polarization microscope as a voltage of planar texture disrupting. But, because this method is not so much accurate, it is advisable to measure threshold voltage with the application of farad-volt or volt-lumen characteristics.

The dependence of effective dielectric permittivity of pure smectic A liquid crystal and colloids prepared with that liquid crystal and different sized ferroelectric $BaTiO_3$ particles on bias voltage applied to eletrooptic cell is illustrated in Figure 8. As expected, addition of

$BaTiO_3$ particles slightly increases the value of latitudinal component ($\varepsilon_\perp$) of dielectric permittivity of liquid crystal. The weak maximum ($U_{\max}$) inherent in the pure liquid crystal is observed at low voltages ($U < 10V$) in all colloids. Namely, the weak increase of dielectric permittivity is firstly observed, later its decreases. Then, from a certain voltage (U_{th}) the dielectric permittivity begins to increase again due to the planar-homeotrop transition and this increase has considerably a sharp feature.

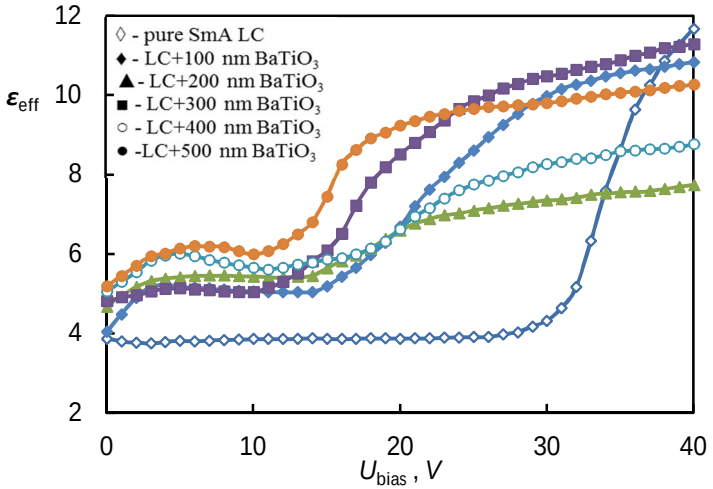

Figure 8. The bias voltage dependence of effective dielectric permittivity of pure smectic A liquid crystal and its colloids

The results derived from the figure can be generalized in the table 1.

Table 1. The threshold voltage and maximum voltage values of planar-homeotrop transition of puresmectic A liquid crystal and its colloids

Sample	**Pure SmA**	**SmA+ $BaTiO_3$ (100 nm)**	**SmA+ $BaTiO_3$ (200 nm)**	**SmA+ $BaTiO_3$ (300 nm)**	**SmA+ $BaTiO_3$ (400 nm)**	**SmA+ $BaTiO_3$ (500 nm)**
$\varepsilon_\perp$	3.9	4.0	4.6	4.8	5.0	5.2
U_{max}		3	5	6	6	6
U_{th}	26	14	14	10	11	18

As shown in the table,

1) the addition of $BaTiO_3$ particles to liquid crystal increases the transversal component of dielectric permittivity;

2) The weak maximum observed in the dependence $\varepsilon_{\perp}(U)$ of colloids with particle sizes greater than 200 *nm* has unchanged for sizes 300, 400 and 500 *nm*;

3) $BaTiO_3$ particles sharply decreases the threshold voltage of smectic A liquid crystal, and this decrease is clearly observed in 300 and 400 nm sized particles.

The review modern theories about the structure and properties of $BaTiO_3$ particles reveals that ferroelectric particles consist of a tetragonal core and cubic layer of about 5 *mkm* thickness (core-shell model)[4].

Submicron $BaTiO_3$ particles possess monocrystal and polidomen structure in the case of absence of electric field. The value (ε_c^{FP}) of dielectric permittivity in the direction of ***c*** axis along which spontaneous polarization exists is much more than that (ε_a^{FP}) in the direction of *a* axis. While colloid is passing from isotropic phase into smectic A one, c axis of segnetoelectric $BaTiO_3$ particles orients chaotically and their contribution to dielectric permittivity is considered as average value $f \cdot \frac{1}{3}\left(2\varepsilon_a^{FP} + \varepsilon_c^{FP}\right)$. When bias voltage is applied to electrooptic cell, torque rotating $BaTiO_3$ particles is generated due to the action of electric field and particles orient with their c axis in the direction of electric field. As a result, the contribution of these particles to dielectric permittivity increases and it reaches maximum ($U_{\max}$) at a certain value of voltage since the orientation of particles with its *c* axis in the field direction is completed.

The decrease of dielectric permittivity is explained as nonlinear dependence of polarization of ferroelectric particles on the electric field. In reality, as the voltage applied to electrooptic cell, polarization of ferroelectric particles approaches its saturation value, i.e. the increase rate of polarization (P/E), being dependent on of electric

[4]Sedych P. Size Effects in Fine Barium Titanate Particles / P. Sedych, D. Michel, E.V. Charnaya // Ferroelectrics, -2010. v.400, -p.135–143.

field, weakens. It leads to the decrease of dielectric permittivity of ferroelectric particles and as a whole colloid, respectively thanks to the following equation

$$\varepsilon^{FP} = 1 + \frac{P}{\varepsilon_0 E} \tag{5}$$

and Equation 2. The sharp increase of dielectric permittivity of both colloid and clean smectic A liquid crystal at high voltages, as noted above, is related to the planar-homeotrop phase transition. A result of this transition, dielectric permittivity (ε^{LC}) of liquid crystal increases three times and this causes sharp rise of effective dielectric permittivity of colloid due to equation (2). Electric field created by polarized $BaTiO_3$ particles near its' surfacecan be written as below:

$$E_{loc} \sim \frac{P}{\varepsilon_0 \varepsilon^{LC}} = \frac{\varepsilon_0(\varepsilon^{FP} - 1)E_0}{\varepsilon_0 \varepsilon^{LC}} = \frac{(\varepsilon^{FP} - 1)E_0}{\varepsilon^{LC}}. \tag{6}$$

Since the values of ε^{LC}, ε^{FP} and E_0 quantities are 10, 10^3 and $10^6 V/m$, respectively, the calculated local field is $E_{loc} \sim 10^8 \ V/m$, and this is sufficient to rotate liquid crystal molecules around $BaTiO_3$ particles. As a result, $BaTiO_3$ particles play an essential role at the beginning of planar-homeotrop phase transition at less voltages.

The threshold voltage of homeotrop-planar phase transition in smectic A liquid crystal of negative dielectric anisotropy cannot be detected with volt-farad characteristic because the possible highest applicable biasvoltage in E7-20 imitancemeter is 120 *V*, nevertheless, it cannot cause homeotrop-planartransition. Therefore, threshold voltage in these systems can be detected visually in polarization microscope. The volt-lumen characteristic of electro-optic cell can be used to get more exact value. The results are generalized in Table 2. Rise time in the table was determined from time dependence of light transmittance, when irect voltage is applaide to electrooptic cell (Figure 9).

The items noted in the table are evaluated as below:

1) the addition of $BaTiO_3$ particles to smectic A liquid crystal decreases the threshold voltage of homeotrop-planar phase transition and this deceasee is getting more and more as the size of particles is increasing.

Table 2. The values of threshold voltage and transition corresponding to clean smectic A liquid crystal and its colloids for the homeotrop-planar transition

Sample	Pure SmA	SmA+ $BaTiO_3$ (100 nm)	SmA+ $BaTiO_3$ (200 nm)	SmA+ $BaTiO_3$ (300 nm)	SmA+ $BaTiO_3$ (400 nm)	SmA+ $BaTiO_3$ (500 nm
U_{th},V	230	220	180	160	145	135
τ,s	1,6	1,3	0,18	0,22	0,28	0,35

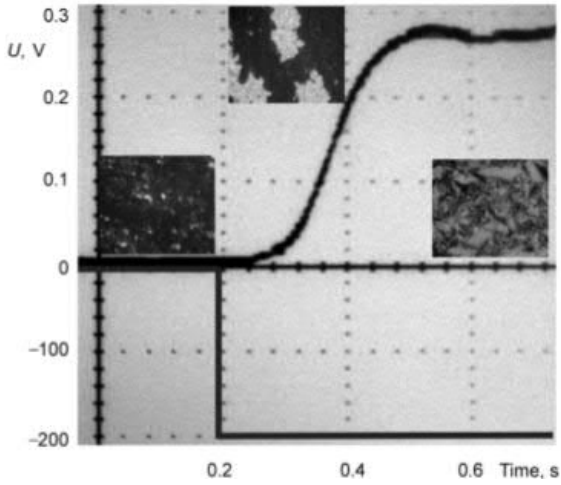

Figure 9. Time dependence of transmittance of the homeotrop-planar phase transition

2) except of 100 nm sized particles, $BaTiO_3$ particles decrease homeotrop-planar transition rise time. This effect is maximum (9 times more) in case of 200 nm sized $BaTiO_3$ particles. As the size of particles is increasing, this effect weakens slightly.

The experimental results noted above can be explained with current theories. Hopeotrop-planar transition occuring in smectic A liquid crystal of negative dielectric anisotropy reveals itself as nucleation, growing and covering ofdefects under influence of external electric field. In accordance withParodi's theory, the threshold voltage of this transition is determined as[5]

[5]Blinov L.M. Electrooptic Effects in Liquid Crystal Materials / L.M.Blinov, V.G. Chigrinov // Springer Verlag, New York,-1994.-p.464.

$$U_{th}^2 = \frac{W_a d}{2\varepsilon_0 |\Delta\varepsilon| l}. \quad (7)$$

Here, W_a is the sum of elastic forces related to the distortion of smectic structure, and l is the length of molecule. As we could see in Table 2, $BaTiO_3$ particles decrease the absolute value of dielectric anisotropy of C2 liquid crystal. Because of equation (7), the threshold voltage of homeotrop-planar transition should increase. Nonetheless, experimental results indicate the opposite one. This controversy means either inapplicability of Parodi's equation in colloid case, or sharp decrease of W_a in the equation. When 100 V voltage is applied to electro-optic cell the electric field

$$E_{ext} = \frac{U}{d \cdot \varepsilon_\perp} \approx \frac{100\,V}{2 \cdot 10^{-5} m \cdot 5} = 10^6 \frac{V}{m} = 10 \frac{kV}{cm} \quad (8)$$

acts on $BaTiO_3$ particles. This field is satisfactory to polarize ferroelectric particles. If these particles are accepted to be spherical, their induced dipole moment is

$$p = \frac{4\pi R^3}{3} \cdot P_S \approx \frac{4 \cdot 3 \cdot (10^{-7} m)^3}{3} \cdot 0{,}1 \frac{C}{m^2} = 4 \cdot 10^{-22} C \cdot m. \quad (9)$$

The size (radius) of particles and the vale of spontaneous polarization were takenas R=100nm=$10^{-7}m$, is 0, 1C/m, respectively.

The electric field strengscreated by ferroelectric particle in the r distance away from it is determined with Eq (3). The intensity if this field along the oplar axes of polarized particles ($\theta = 0$) close to their surface (r = 0,5mkm) is denied as

$$E_{FNP} \approx \frac{p}{4\pi\varepsilon_0 r^3} \approx \frac{4 \div 10^{-22}}{4 \cdot 3 \cdot 10^{-11} \cdot (5 \cdot 10^{-7})^3} \approx 6 \cdot 10^6 \frac{V}{m} = 6 \frac{V}{mkm} \quad (10)$$

This is considerable to rotate liquid crystal molecules. So, in contrast with smectic liquid crystal C2, less threshold voltage of homeotrop-planar transition in $BaTiO_3$ colloid is subject to the local field created by $BaTiO_3$ particles. As the size of particles increases, their dipole momentum increase and local field near the surface is much more due to Equation (9) and this causes homeotrop-planar transition at less voltages.

It has been emphasized above that homeotrop-planar transition happening in electrooptic cell starts as a nucleus in some defects, this

process continues until these sites complete to cover each other. It is clear that transition timedepends on the number of nuclei and the increase rate of their walls. When $BaTiO_3$ particles are added to smectic A liquid crystal, these particles play a role as defects where nuclei exist. Consequently, homeotrop-planar transition rate of C2+$BaTiO_3$ colloid increases in comparision with clean C2 liquid crystal (transition time decreases). The other factor impacting on transition time is the rate of increasing of nucleus' wall, and this depends on the difference ($U - U_{th}$) of applied external voltage and threshold one: the more this difference, the more the rate of nucleus grow and the less transition time. So, transition time from homeotrop phase to planar one depends on the number of $BaTiO_3$ particles and the local field strength created by them.Decreasing size of particles at the same value of volume fractionhas two effects: 1. their number increases and this has a positive effect on transition rate; 2. local field created by $BaTiO_3$ particles weakens and this has a negative effect on transition rate. Table 2 demonstrates that the former plays an essential role in the two opposite factors. The exception in 100 *nm* sized $BaTiO_3$ particles (less transition rate) is related to weak (dearth of) ferroelectric property of these particles.

In the fifth chapter the impact of different sized $BaTiO_3$ particles on phase transitions of smectic A liquid crystals measured by the DSC method is studied. In case of 10NF+5CB and its colloids, peaks corresponding to transitions smectic A-nemaric and nematic-isotropic liquidcover each other in most casesit is difficult to distinguish them from each other. Therefore, the focus here is mostly on the liquid crystal C2 with negative permittivity.

The results of measurements done in smectic A phased liquid crystal C2 are illustrated in Figures 10, 11. The derived facts can be noted as below: crystal – smectic A phase transition temperature (T_{CA}) of $BaTiO_3$ particles of small sizes (100 nm, 200 nm) increases. This decreases for particles of big sizes (300-500 nm). $BaTiO_3$ particles increase smectic A-isotropic phase transition temperature (T_{AI}) (thermal stability of smectic A phase) and this increase if getting higher as the size of particles is increasing. Similarly, interpretation is valid for crystal -smectic A phase transition enthalpy (ΔH_{AI}). $BaTiO_3$ particles slightly increase smectic A-isotropic phase transition

being weak first order phase transition, i.e. it increases ΔH_{AI} phase transition enthalpy a bit.

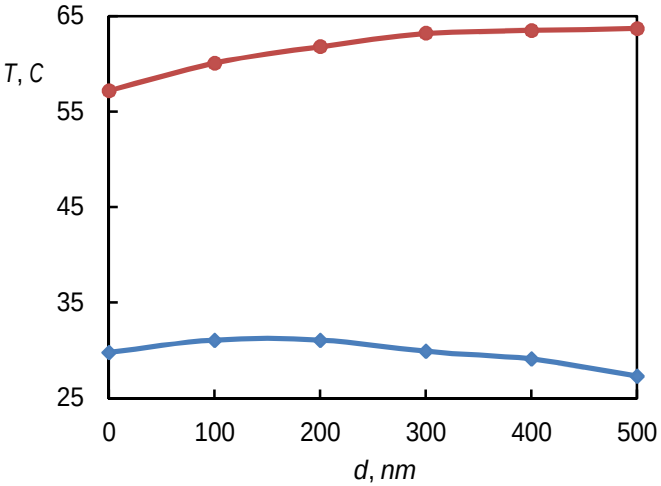

Figure 10. The dependence of phase transition temperature of smectic A liquid crystal on the size of added $BaTiO_3$ particles: circles – T_{AI} smectic A-isotropic phase transition temperature, rhombuses – T_{CA} crystal-smectic A phase transition temperature.

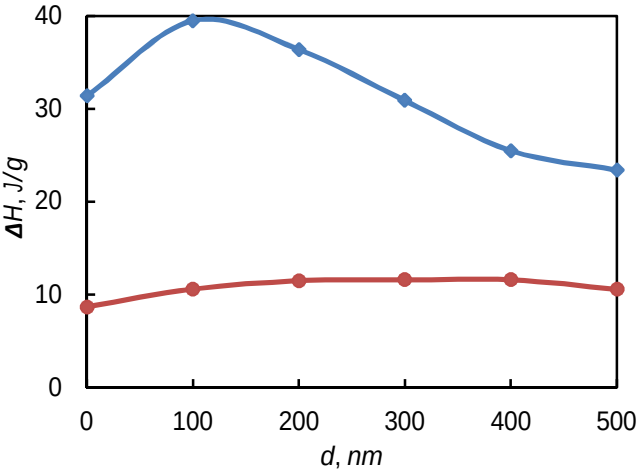

Figure 11. The dependence of phase transition enthalpies of smectic A liquid crystal on the sizes of $BaTiO_3$ particles: circles – ΔH_{AI} smectic A-isotropic phase transition enthalpies, rhombuses – ΔH_{CA} crystal-smectic A phase transition enthalpies

Nematic phase does not exist in our searched liquid crystal, smectic A phase directly converts into isotropic phase, therefore, transition occurs as a sufficient strong first type phase transition ΔH_{AI} = 8.7 J/g. Since $BaTiO_3$ particles amplify smectic A-isotropic phase transition (increase the transition enthalpy) and increase thermic stability (T_{AI}) of smectic A phase, it is explained by the increasingof orientation order parameter. As noted in the previous chapters, ferroelectric $BaTiO_3$ particles orient with their polar axes (main direction of spontaneous polarization) parallel to the optical axis (director) of liquid crystal. As a result, $BaTiO_3$ particles get a certain dipole moment. The local electric field created by these dipoles increase order parameter of liquid crystal. So, this increases both smectic A-isotropic phase transition temperature and transition enthalpy.The more the size of particles, the more the values of noted physical quantities since their dipole moments increase. The downwards shifting of crystal-smectic A phase transition by $BaTiO_3$ particles can be explained as weakening of interaction required for crystal - smectic A transition of ferroelectric particles.

$BaTiO_3$ particles added to a positive dielectric anisotropic liquid crystal (5CB+10NF) shift the crystal-smectic A phase transition temperature downward, albeit weakly, but increases the nematic-isotropic phase transitiontemperature. As for liquid crystal used in the experiment, it can be said that the crystal-smectic phase A transition is a type I strong phase transition. The smectic A-nematic transition is very weak first order or second orderphasetransition. In our experiments, the peak corresponding to this transition was observed only in colloid with particles of 500 nm. Nematic - isotropic transition is a weak type I phase transition. The increase in temperature of the nematic-isotropic phase transition can be explained by the formula.[6]

$$T_{NI} = 1.03 \times \frac{\phi_{NP} \Delta\varepsilon P^2}{135 k_B \rho_{LC} \varepsilon_0 \varepsilon^2} \qquad (11)$$

ϕ_{NP} is the volume fraction of ferroelectric particles, P- spontaneus

polarization, ρ_{LC}-density of liquid ctystal. Since larger particles have greater spontaneous polarization, they increase the nematic-isotropic phase transition point more strongly[6].

MAIN RESULTS

1. It has been clarified that submicron sized $BaTiO_3$ particles independently upon the sign of dielectric anisotropy increases considerably only longitudinal component of dielectric permittivity of smectic A liquid crystal. The more the size of $BaTiO_3$ particles, the more this increase is detected. This result is interpreted as the interaction of polar axis of $BaTiO_3$ particles with the director of liquid crystal.

2. $BaTiO_3$ particles shift the dispersion of dielectric permittivity of smectic A liquid crystal of both positive and negative dielectric permittivity, observed at high frequencies (10^5 Hz), towards low frequency region. This shift is explained as the result of counter action of local electric field created by $BaTiO_3$ particles to the rotation of molecular dipoles.

3. It has been clarified that $BaTiO_3$ particles decrease the threshold voltage of Frederix transition (both planar-homeotrop and homeotrop-planar) observed in smectic A liquid crystal (10 NF+5CB and C2) by twice. This drop is interpreted as creation of local field around polarized $BaTiO_3$ particles, not as increase of dielectric anisotropy of liquid crystal.

4. $BaTiO_3$ particles increase the rate of Frederix transition observed in liquid crystal by one order, and it is explained by the fact that the $BaTiO_3$ particles play the role of centres from witch the transitionbegins.

5. $BaTiO_3$ particles increase smectic A-isotropic phase transition temperature by some degree, and weakly impact on crystal-smectic A phase transition temperature. As a result, it is possible to expand smectic A phase temperature interval by adding of $BaTiO_3$ particles.

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[6]Lin, Y. On the phase transitions of 8CB/Sn2P2S6 liquid crystal nanocolloids / Y. Lin, R. Douali, F. Dubois // The European Physical Journal E, – 2015. v.38, 103, – p.1-8

Published scientific works on the topic of the dissertation:

1. Humbatov, Sh.A. The study of BaTiO3 nanoparticles effect on threshold properties of Liquid Crystal 5CB / Sh.A. Humbatov, M.A.Ramazanov, A.R. İmamaliyev // Molecular Crystals and Liquid Crystals, – 2017. 646, – p.263-267.

2. Hümbətov, Ş.Ə., $BaTiO_3$ hissəciklərinin smektik A maye kristalının faza keçidlərinə təsirinin tədqiqi / Ş.Ə. Hümbətov, M.Ə.Ramazanov, A.R. İmaməliyev, Z.Ə. Ağamalıyev, M.N.Mirzəyev // – Bakı: AJP Fizika jurnalı, – 2017. XXIII, №2, – s.15-19.

3. İmaməliyev, A.R., Əks işarəli dielektrik anizotropiyalı smektik A maye kristalların dielektrik xassələrinə $BaTiO_3$ hissəciklərinin təsirinin öyrənilməsi / A.R. İmaməliyev, M.Ə. Ramazanov, Ş.Ə.Hümbətov // – Bakı: Bakı Universitetinin Xəbərləri, fizikariyaziyyat elmləri seriyası, – 2017. №4, – s.139-145.

4. İmaməliyev, A.R. Müxtəlif ölçülü $BaTiO_3$ hissəciklərinin smektik a maye kristalın astana xassələrinə təsiri / A.R. İmaməliyev, M.Ə.Ramazanov, Ş.Ə. Hümbətov [və b.] // AJP Fizika jurnalı, – Bakı: –2018. XXIV, №4, – s. 27-30.

5. Ramazanov, M.A. Effect of Barium Titanate Particles on Dielectric and Electro-Optical Properties of a Smectic-a Liquid Crystal / M.A.Ramazanov, A.R. Imamaliyev, S.A. Humbatov [et al.] // Russian Physics Journal, – 2018. v.60, – p.1659-1666.

6. Imamaliyev, A.R. Effect of ferroelectric BaTiO3 particles on the threshold voltage of a smectic A liquid crystals / A.R. Imamaliyev, M.A. Ramazanov, S.A. Humbatov // Beilstein Journal of Nanotechnology, – 2018. 9, – p.824-828.

7. Imamaliyev, A.R. Influence of size of small ferroelectric barium titanate particles on dielectric properties of smectic a liquid crystal with a positive dielectric anisotropy / A.R. Imamaliyev, M.A. Ramazanov, Sh.A. Humbatov [et al.] // Journal of Low Dimensional Systems, – Baku: – 2019. 3(2), – p.19-22.

8. Hümbətov, Ş.Ə. Mənfi dielektrik anizotropiyalı smektik a maye

kristalin dielektrik xassələrinə barium titanat hissəciklərinin ölçü effektinin təsiri // – Bakı: AJP Fizika jurnalı, – 2019. XXV, №2, – s. 50-56.

9. Hümbətov, Ş.Ə. $BatiO_3$ hissəciklərinin müsbət dielektrik anizotropiyalı smektik a maye kristalin faza keçidlərinə təsiri // – Bakı: AJP Fizika jurnalı, – 2019. XXV, №4, – s. 44-49.

10. İmaməliyev, A.R., Mənfi dielektrik anizotropiyali smektik a maye kristalin elektro-optik xassələrinə $BaTiO_3$ hissəciklərinin ölçü effektinin təsiri / A.R. İmaməliyev, M.Ə. Ramazanov, Ş.Ə.Hümbətov [və b.] // – Bakı: AJP Fizika jurnalı, – 2020. XXVI, №3, –s. 13-18.

11. Ramazanov, M.Ə., İmaməliyev, A.R., Hümbətov, Ş.Ə., 5CB nematik maye kristalının astana gərginliyinə BaTiO3 nanohissəciklərinin təsiri // Fizika Problemləri İnstitutunun yaradılmasının 10 illiyinə həsr olunmuş «Opto-, nanoelektronika, kondensə olunmuş mühit və yüksək enerjilər fizikası» Beynəlxalq konfransı, Bakı: – 25 – 26 dekabr, – 2015, – s. 76-78.

12. Humbatov, Sh.A., Ramazanov, M.A., Imamaliyev, A.R. The study of $BaTiO_3$ nanoparticles effect on threshold properties of Liquid Crystal 5CB // 26th International Liquid Crystal Conference, Kent State University, USA, – 31 July – 5 August, – 2016.

13. Ramazanov, M.Ə., İmaməliyev, A.R., Hümbətov, Ş.Ə., Mirzəyev, M.N. Smektik A fazalı maye kristalda faza keçidlərinə $BaTiO_3$ nanohissəciklərinin ölçü effektinin təsiri / Fizikanın aktual problemləri» IX Respublika elmi konfransı, Bakı, – 22 dekabr, – 2016. -s.181-183.

14. Гумбатов, Ш.А., Рамазанов, М.А., Имамалиев, А.Р., Ибрагимов, Т.Д., Агамалиев, З.А. Влияние частиц титаната бария на диелектрические свойства смектическово А жидкого кристалла // Proceedings of International Conference «Modern Trends in Physics», – Baku: – 20 – 22 April, – 2017, – p. 89.

15. Hümbətov, Ş.Ə., Ramazanov, M.Ə., İmaməliyev, A.R., Ağamalıyev, Z.Ə., İbrahimov, T.C. Seqnetoelektrik barium ti-

tanat hissəciklərinin smektik A maye kristalının dielektrik xassələrinə təsiri / I International scientific conference of young researchers dedicated to the 94th Anniversary of the National leader of Azerbaijan Heydar Aliyev, – Baku: Baku Engineering University, – 05 – 06 May, – 2017, – s.77-78.

16. Ramazanov, M.A., Imamaliyev, A.R., Humbatov, Sh.A. Effect of ferroelectric $BaTiO_3$ particles on threshold voltage of smectic A liquid crystal // 14^{th} European Conference on Liquid Crystals, Moscow State University, Moscow, Russia, – 25 – 30 June, – 2017.

17. Humbatov, Sh.A., Imamaliyev, A.R.,Ramazanov, M.A., Bayramov G.M. Size effect of small ferroelectric $BaTiO_3$ particles on dielectric properties of a smectic A liquid crystal with negative dielectric anisotropy / International Conference «Modern Trends in Physics», –Baku:–1–3May, –2019. –p.61-62.

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