PHYSICS AND CHEMISTRY OF SOLID STATE

V. 25, No. 1 (2024) pp. 109-113

Section: Technology

DOI: 10.15330/pcss.25.1.109-113

Vasyl Stefanyk Precarpathian National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА Т. 25, № 1 (2024) С. 109-113

Технічні науки

UDC: 681.325.2

ISSN 1729-4428 (Print) ISSN 2309-8589 (Online)

Z.M. Mykytyuk¹, Y.M. Kachurak¹, M.V. Vistak², I.T. Kogut³, R.L. Politanskyi⁴, O.Y. Shymchyshyn¹, I.S. Diskovskyi², P.V. Vashchenko⁵

Induced blue phase of cholesteric-nematic mixtures under the action of acetone vapors

¹Department of Electronic Engineering, Lviv Polytechnic Nationa University, Lviv, Ukraine, <u>vurii.m.kachurak@lpnu.ua</u> ²Danylo Halytsky Lviv National Medical University, Lviv, Ukraine, ³Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukraine, ⁴Yuriy Fedkovych Chernivtsi National University, Chernivtsi, Ukraine, ⁵Institute for Scintillation Materials, National Academy of Sciences of Ukraine, Kharkiv, Ukraine

Liquid crystals can exhibit structural orientational order. The creation of a mixture with the addition of chiral molecules to the nematic liquid crystal induces helical twisting, the axis of which is directed perpendicular to the cell surfaces. When some cholesteric mixtures with a sufficiently short spiral pitch (up to 400-500 nm) are heated to a temperature close to, but still lower than, the temperature of the main transition to the isotropic state, in some cases the so-called blue phases can be formed.

We carried out a study on the detection of structural manifestations of the blue phase under the action of vapors of chemical substances, in particular acetone. The main dependences of effect of acetone on the liquid crystal mixture depending on the concentration were also revealed. The two-stage phase transformation from cholesteric liquid crystal to the isotropic liquid via the intermediary blue phase could be clearly recorded by changes in optical transmission. Possible applications are discussed.

Keywords: liquid crystal; E7; gas sensor; blue phase; optical sensor.

Received 18 October 2023; Accepted 13 February 2024.

Introduction

Liquid crystals are characterized by birefringence (birefringence), as they have optical anisotropy. However, some liquid crystal mixtures, particularly in the cubic and blue phases, exhibit optical isotropy. In general, blue phases are characterized by the presence of twisting in two mutually orthogonal directions, which ultimately leads to the formation of doubly twisted cylinders [1]. The blue phases were shown to be promising for detection of organic vapors, showing some advantages as compared with conventional cholesterics, in particular, for detection of toluene, phenol and 1, 2 dichloropropane. [2, 3]

Cubic liquid crystal phases with representative threedimensional ordered supramolecular structures, such as interpenetrating networks and spheroids, are common in lyotropic liquid crystals and exist in some thermotropic

109

liquid crystals with amphiphilicity [4].

Among others, cholesteric and smectic blue phases are also presented. Cholesteric blue phases are of particular interest because they have a lattice whose structure is stabilized by lattice distortions and defects. Typically, blue phases exist in a narrow temperature range (less than 2 K) between the isotropic liquid and the chiral nematic phase. Blue phases consist of double twisted cylinders and are divided into three categories depending on the spatial structure of the cylinders: blue phase I (BPI), blue phase II (BPII), and blue phase III (BPIII).

The first and second types of blue phase have a highly ordered cubic structure. Cubic blue phases were actively studied until 1989 and were well studied [5, 6].

At the same time, today the structure of the blue phase of the third type has not been fully revealed. It is known that it has a very similar symmetry to the isotropic liquid crystal phase. Among the detailed reviews of blue phases,

325.2

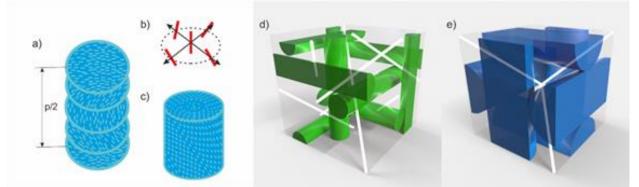


Fig. 1. a) cholesteric liquid crystal, with a characteristic spiral twist in the direction perpendicular to the axis of the predominant molecular orientation (director) b) schematic illustration of spiral twisting in two mutually perpendicular directions - a double-twisted cylinder is formed, shown in c). d) Structure of Blue phase I.
e) Structure of Blue phase II. Based on blue phases structure images from [9].

it is worth highlighting the following [7-8].

Blue phases are potentially useful for applications in display devices, but the main difficulty for their implementation is very low temperature ranges. However, today, in work [9], polymer-stabilized blue phases were demonstrated, in which the temperature range was extended to more than 60 K. They demonstrate fast electro-optical switching with a response time of 10^{-4} s with a stabilized blue phase.

Stabilized blue phases of liquid crystal mixtures can also be used to detect substances. [2,10-15]

Thus, studies demonstrate the use of the blue phase of a liquid crystal mixture for the detection of xylene, heptane, cyclohexane, dichloromethane, and ethyl alcohol [10]. Another study demonstrates sensitivity for the detection of toxic organics, including toluene, phenol, and 1,2 dichloropropane.

Another study demonstrates the use of blue phase manifestations of a liquid crystal mixture of E7 nematic and S811 impurity to detect biopolymers [15]. The scheme of the experiment is similar to our previous works, however, the degrees of the reverse transition of the mixture after heating, with manifestations of the blue phase, and a more complex approach to the construction of a liquid crystal cell were used.

Based on these data, which indicate the possibility of using blue phases for the detection of vapors of organic substances, the purpose of this work was to use liquid crystal compositions in which the formation of blue phases (BP) is possible in a certain temperature range. In our previous work [16] it was noted the presence of certain anomalies in the change in the transmission intensity of individual color lines at temperatures when the cholesteric phase of certain mixtures transitioned into the blue phase (BP). A detailed analysis of the physicochemical mechanisms of such behavior was provided by us in [17], where, based on a number of comparative experiments, it was clearly shown the equivalence of the action of volatile organic substances absorbed by the liquid crystal (LC) phase and the same substances introduced into the LC composition as a common impurity component. The development of these works with the use, along with model ethanol, of other typical volatile organic compounds seemed very natural.

I. Methodology of the experiment

A cholesteric-nematic mixture of nematic E7 and cholesteric impurity CB15 was used in the study to detect acetone vapors. The concentration of cholesteric impurity in the mixture was 38%. The temperature characteristics of this mixture show a transition to an isotropic state at a temperature of about 34-36 degrees Celsius, therefore, at room temperature, about 20 degrees, the transition does not occur.

In the process of research, the prepared mixture was applied in a thin layer on spectrally transparent glass, which was placed in a closed container with a photoemitter and photoreceiver, as well as a container with acetone.

As a result of the evaporation of acetone, its concentration in the closed volume increased over time, which contributed to the transition of the liquid crystal cell to an isotropic state. The preliminary goal of the study was to determine the time dependencies for testing the possibilities of creating an acetone sensor based on a liquid crystal cell.

The measuring stand consists of a photoemitter and a photoreceiver. The photoemitter is represented by an LED, and the photoreceiver is an array of photodiodes, with photodiodes sensitive to three spectral components. The gradual phase transition of the liquid crystal mixture causes a corresponding change in the intensity of light transmission, which, accordingly, causes a change in the intensity on the photodiode, which is reflected in the graphs.

II. The results of the experiment and their discussion

As a result of the experiment, we revealed the manifestation of a blue phase for this liquid crystal mixture, when it transitions into an isotropic state under the action of acetone. It can be clearly seen that for all three cases of acetone introduction (Fig.3, a,b,c) the process is realized in two stages. At first, with small quantities of absorbed acetone, the transmission intensity

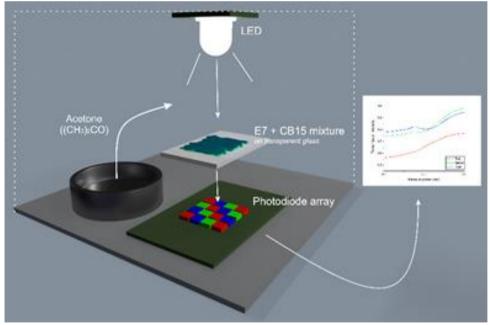


Fig. 2. Schematics of the experimental setup.

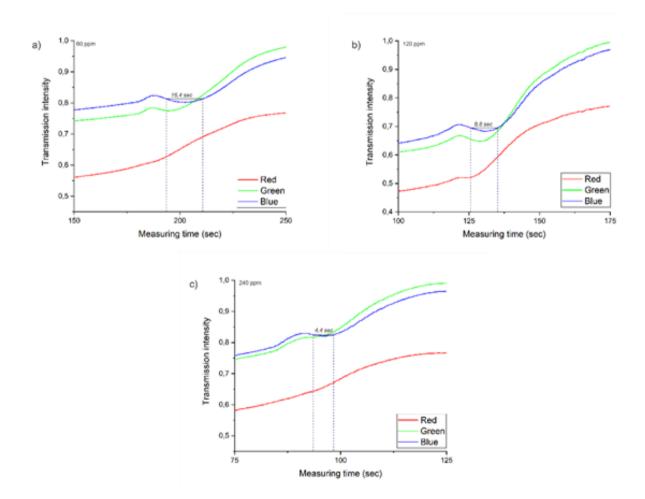


Fig. 3. Graphs of the dependence of the half-width of the existence of the blue phase, with an increase in the concentration of acetone in the measuring container, 240 ppm (a), 120 ppm (b), 60 ppm (c).

decreases due to the formation of the blue phase. Under further action of absorbed acetone, the transformation to the isotropic phase occurs, evidenced by the renewed increase in optical transmission. In addition, we carried out similar measurements of the optical transmission vs. temperature, which also demonstrated a two-stage transformation (cholesteric – blue phase – isotropic), in the same way as it was described in [17] for ethanol.

To register and process the results of measuring the concentration of acetone vapors, it seems promising to adapt also a hybrid microsystem for biomedical applications [18] using an integral primary signal converter from a photodetector based on a highly sensitive CMOS operational amplifier and its elements [19, 20].

In order to identify the dependencies between the concentration of acetone vapors in the capacity of the test device and the time of manifestation of the blue phase of the liquid crystal cell, additional graphs were constructed. These graphs reflect the dependence of the half-width of the temporal manifestation of the blue phase, for the measured blue component of the spectrum, on the concentration of acetone. Among the measured concentrations are 0.4 ml (240 ppm), 0.2 ml (120 ppm), 0.

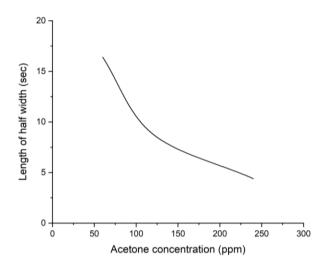


Fig. 4. Summary graph of the dependence of the duration of the half-width of the blue phase on the acetone concentration.

The process of detecting the phase transition of the blue phase takes place at a constant temperature of 20 degrees Celsius. Acetone introduced into a container with a liquid crystal cell is gradually evaporated, which increases the concentration of acetone vapors in the closed volume. The transition of the cell occurs gradually, and according to the results of the experiment, the transition time depends on the concentration of acetone. In particular, we can state that when the concentration of acetone increases from 60 ppm to 120, and then to 240 ppm, the interval of existence of the blue phase is 32, 16, and 8 seconds, respectively.

Since a similar phase transition occurs when the temperature changes, the use of such a system in environments with a change in temperature may give false indicators. In particular, when the ambient temperature increases, the rate of transition to the isotropic state will be higher than at the same concentration of acetone and a stable temperature.

Conclusions

The liquid crystalline blue phase, which arises as a result of the action on a mixture of liquid crystals of acetone, shows a direct dependence of duration on the concentration of acetone. The phase transition itself in this case is similar to the temperature transition. The direct relationship between the concentration of acetone vapors and the duration of the phase transition of the used cell allows for the possibility of using such a system as a sensor. The two-step character of the observed changes in optical transmission allows the designing of a vapor sensor tuned for a certain threshold value of the effective amount of vapor. However, based on previous works, it can be asserted about the existing cross-sensitivity of such a system to other substances, in particular alcohols, and some other organic substances. The disadvantage of using such a cell as a sensor or detector is also a serious temperature dependence. If the liquid crystal mixture is doped with gold nanoparticles or carbon nanotubes, it is also possible to detect some inorganic substances, preliminary studies indicate sensitivity to CO₂, NO.

Mykytyuk Z.M. – Dr.Sc., Prof.; Kachurak Y.M. – postgraduate; Vistak M.V. – Dr.Sc., Prof.; Kogut I.T. – Dr.Sc., Prof.; Politanskyi R.L. – Dr.Sc., Prof.; Shymchyshyn O.Y. – PhD, associate professor; Diskovskyi I.S. –candidate of medical sciences, teacher; Vashchenko R.V. – postgraduate.

- M.A. Bedolla Pantoja, Y. Yang, & N.L. Abbott, *Toluene-induced phase transitions in blue phase liquid crystals*. Liquid Crystals, 46 (13-14), 1925 (2019); <u>https://doi.org/10.1080/02678292.2019.1633432</u>.
- [2] B. Gurboga, E. Kemiklioglu, Optical sensing of organic vapor using blue phase liquid crystals. Liquid Crystals, 49(11), 1428 (2022); <u>https://doi.org/10.1080/02678292.2022.2038294</u>.
- [3] Y. Yang, Y.K. Kim, X. Wang, M. Tsuei, & N.L. Abbott, Structural and optical response of polymer-stabilized blue phase liquid crystal films to volatile organic compounds. ACS Applied Materials & Interfaces, 12(37), 42099 (2020); https://doi.org/10.1021/acsami.0c11138.
- [4] A. Yoshizawa, *Material design for blue phase liquid crystals and their electro-optical effects*. RSC advances, 3(48), 25475 (2013); <u>https://doi.org/10.1039/c3ra43546f</u>.
- [5] V.A. Belyakov, & V.E. Dmitrienko, *The blue phase of liquid crystals*. Soviet Physics Uspekhi, 28(7), 535 (1985); https://doi.org/10.1070/PU1985v028n07ABEH003870.
- [6] S. Meiboom, J.P. Sethna, P.W. Anderson, & W.F. Brinkman, *Theory of the blue phase of cholesteric liquid crystals*. Physical Review Letters, 46(18), 1216 (1981); <u>https://doi.org/10.1103/PhysRevLett.46.1216</u>.
- [7] P.P. Crooker, Blue phases. Chirality in liquid crystals, 186 (2001).
- [8] P. Oswald, P. Pieranski, Nematic and cholesteric liquid crystals: concepts and physical properties illustrated by experiments. CRC press, (2005); <u>https://doi.org/10.1201/9780203023013.</u>

- [9] H. Kikuchi, M. Yokota, Y. Hisakado, H. Yang, , & T. Kajiyama, *Polymer-stabilized liquid crystal blue phases*. Nature materials, 1(1), 64 (2002); <u>https://doi.org/10.1038/nmat712</u>.
- [10] D.S. Hou, L. Zheng, D.P. Sun, X. Zhou, J.L. Zhu, & W.M. Han, Polymer-stabilized blue phase liquid crystal sensor for sensitive and selective detection of organic vapors. Liquid Crystals, 49(2), 201 (2022); https://doi.org/10.1080/02678292.2021.1951381.
- [11] Z. Hotra, Z. Mykytyuk, O. Sushynskyy, O. Hotra, O. Yasynovska, P. Kisała, *Sensor systems with optical channel of information transferring*. Przeglad Elektrotechniczny, 86 (10), 21(2010)/
- [12] W. Wójcik, Z. Mykytyuk, M. Vistak, G. Barylo, R. Politanskyi, I. Diskovskyi, I. Kremer, M. Ivakh, W. Kotsun, Optical sensor with liquid crystal sensitive element for amino acids detection Przeglad Elektrotechniczny, 96 (4), 178 (2020). <u>https://doi.org/10.15199/48.2020.04.37</u>.
- [13] Z. Mykytyuk, I. Kremer, M. Ivakh, I. S. Diskovskyi, and S. V. Khomyak, Optical sensor with liquid crystal sensitive element for monitoring acetone vapor during exhalation, Mol. Cryst. 721, 24 (2021); https://doi.org/10.1080/15421406.2021.1905273.
- [14] W. Wojcik, M. Vistak, Z. Mykytyuk, R. Politanskyi, I. Diskovskyi, O. Sushynskyi, I. Kremer, T. Prystay, A. Jaxylykova, I. Shedreyeva, *Technical solutions and SPICE modeling of optical sensors*, Przeglad Elektrotechniczny, 96 (10), 102 (2020);. <u>https://doi.org/10.15199/48.2020.10.18</u>.
- [15] M.J. Lee, C.H. Chang, & W. Lee, Label-free protein sensing by employing blue phase liquid crystal. Biomedical Optics Express, 8(3), 1712 (2017). <u>https://doi.org/10.1364/BOE.8.001712.</u>
- [16] Z. Mykytiuk, H. Barylo, I. Kremer, M. Ivakh, Y. Kachurak, & I. Kogut, Features of the transition to the isotropic state of the liquid crystal sensitive element of the gas sensor under the action of acetone vapor. Physics and Chemistry of Solid State, 23(3), 473 (2022); <u>https://doi.org/10.15330/pcss.23.3.473-477</u>.
- [17] I.A. Gvozdovskyy, Y.M. Kachurak, P.V. Vashchenko, I.A. Kravchenko, Z.M.Mykytyuk, Liquid crystal sensors for detection of volatile organic compounds: comparative effects of vapor absorption and temperature on the phase state of the sensor material. Functional Materials, 30(2), 303 (2023); <u>https://doi.org/10.15407/fm30.02.303</u>.
- [18] B. S. Dzundza, I.T. Kohut, V.I. Holota, L.V. Turovska, M.V. Deichakivskyi, *Principles of construction of hybrid microsystems for biomedical applications*. Physics and Chemistry of Solid State, 23(4), 776 (2022); <u>https://doi.org/10.15407/fm30.02.303</u>.
- [19] I. Kogut, B. Dzundza, V. Holota, O. Bulbuk, V. Fedoriuk, & L. Nykyruy, *Modeling of integrated signal converters for biomedical sensor microsystems*. Physics and Chemistry of Solid State, 24(3), 515 (2023); https://doi.org/10.15330/pcss.24.3.515-519.
- [20] I.T. Kogut, A.A. Druzhinin, V.I. Holota, 3D SOI Elements for System-on-Chip Applications. Advanced Materials Research, 137 (2011); <u>https://doi.org/10.4028/www.scientific.net/amr.276.137.</u>

3.М. Микитюк¹, Ю.М. Качурак¹, М.В. Вісьтак², І.Т. Когут³, Р.Л. Політанський⁴, О.Й. Шимчишин¹, І.С. Дісковський², П.В. Ващенко⁵

Індукована блакитна фаза холестерико-нематичних сумішей під дією парів ацетону

¹Кафедра електронної інженерії, Національний університет «Львівська політехніка». Львів, Україна. <u>yurii.m.kachurak@lpnu.ua</u>

²Львівський національний медичний університет імені Данила Галицького, Львів, Україна. ³Прикарпатський національний університет імені Василя Стефаника, Івано-Франківськ, Україна.

⁴Чернівецький національний університет імені Юрія Федьковича, Чернівці, Україна.

⁵Інститут сцинтиляційних матеріалів, Національна Академія Наук України, Харків, Україна

Рідкі кристали можуть демонструвати структурний орієнтаційний порядок. Створення суміші з додаванням хіральних молекул до нематичного рідкого кристалу викликає спіральне закручування, вісь якого спрямована перпендикулярно до поверхні рідкокристалічної комірки. При нагріванні деяких холестеричних сумішей з досить коротким кроком спіралі (400-500 нм) до температури, близької, але все ж нижчої від температури основного переходу в ізотропний стан, у деяких випадках виникає так звана блакитна фаза. В роботі проведено дослідження щодо виявлення структурних проявів блакитної фази під дією парів хімічних речовин, зокрема, ацетону. Виявлено також основні залежності впливу ацетону на рідкокристалічну суміш залежно від концентрації. Двоступінчасте фазове перетворення від холестеричного рідкого кристалу до ізотропної рідини через проміжну блакитну фазу можна було чітко зафіксувати змінами в оптичному пропусканні. Можливі додатки обговорюються.

Ключові слова: рідкий кристал; Е7; газовий сенсор; блакитна фаза; оптичний сенсор.