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Changes in the spectral characteristics of the liquid crystalline active medium doped with multi-walled carbon nanotubes under the influence of nitrogen dioxide

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The paper examines the effect of nitrogen dioxide (NO_2) on the spectral characteristics of a liquid crystal mixture doped with multilayer nanotubes. The liquid crystal mixture was synthesized based on cholesteric liquid crystal BLO-61 and nematic 5CB (26%) with a wide range of mesophase existence temperatures, the concentration of nanotubes was up to 0.7%. It was established that the introduction of nanotubes into the mixture leads to a significant increase in the sensitivity of the mixture to inorganic substances due to increased absorption. An analysis of the change in the spectral properties of the mixture at different concentrations of nitrogen dioxide in the sensor volume was performed and the coefficient of spectral sensitivity was determined. The obtained results indicate the possible use of this mixture as a sensitive sensor element for the detection of nitrogen compounds in the future.

Keywords: optics, liquid crystal, nitrogen dioxide, LC sensors.

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Introduction

Today, threats of military conflicts are constantly increasing, as a result of which the problem of detecting ultra-small quantities of explosives at a distance or in difficult conditions is becoming urgent. Detection of traces of explosive substances is actively studied by scientists [1-3]. Serious danger is created by explosive substances, particularly hexane, petran, nitroglycerin, TNT, octogen, most of which contain nitro groups. Therefore, many known detection methods are not aimed at the search for specifically explosive substances, but at the detection of nitrogen-containing substances [4-5].

Nitrogen dioxide (NO_2) is an extremely toxic environmental pollutant. Prolonged exposure to NO_2 in high concentrations can lead to death [6].

Various technologies for detecting harmful gases have been developed, which are based on the use of various physicochemical signal transmission mechanisms, such as colorimetric, metal oxide, electrochemical, chemiluminescent, and semiconductor. Although some of these technologies have been developed and commercialized, they are limited in their application due to a lack of the necessary sensitivity, selectivity, or portability required to measure adverse NO_2 levels in complex occupational environments [7-8].

The development of new sensor technologies requires the creation of advanced material systems that demonstrate significant changes in their physical properties at appropriate concentrations of toxic gases. This will avoid the use of bulky and complex devices and reduce electricity consumption. Liquid crystal (LC) -based material systems can solve this problem, allowing for a reliable, lightweight, and sensitive sensor platform with minimal power consumption.

Liquid crystal optical gas sensors are characterized by short response time and high selectivity. Such sensors can measure in real-time, and are compact and efficient. The main sensitive element of such a sensor is a liquid crystal cell, the characteristics of which change as a result of gas adsorption on its surface. In this case, the change in the optical properties of the liquid crystal mixture under the action of the substance turns into a change in one of the parameters used to determine the concentration of such a gas [9-12]. Among such parameters can be transmission intensities, characteristics of phase transitions, and changes in spectral characteristics.

In our study, the main mechanism used for gas detection is the influence of their absorption maxima on the spectral characteristics of the liquid crystal cell. The absorption lines are specific for each of the gases, and the absorption bands in different parts of the spectrum have different characteristics. Gases of the NOx family, in particular NO_2, exhibit strong absorption in the near-ultraviolet and visible regions of the spectrum. The spectral characteristic of NO_2, in the visible region, is represented by a broad peak in the region of 300-450 nm [13]. Inorganic gases can be detected if their absorption lines lie within the wavelength range of the spectrometer, and are often detected by the minimum absorption [14-15].

To obtain spectral characteristics, the simplest configuration is a cell through which gas passes. Such a cell is connected by an optical fiber to the radiation source and the sensitive matrix of the spectrophotometer.

I. Sensitive element

Liquid crystals are currently used to create many sensors of chemical substances and sensors of physical quantities. However, the use of unmodified liquid crystal cells is sometimes not enough. Recently, the integration of nanoscale materials into liquid crystals has become a popular topic of research. The introduction of nanomaterials into liquid crystal mixtures leads to a change in their parameters. These changes in the properties of liquid crystal materials due to nanoparticle modification are the basis for creating new electronic components and expanding the capabilities of liquid crystal sensors.

Binary systems for primary transducers of optical sensors, for example, liquid crystal–nanoparticles, make it possible to create effective active environments in which the nanoparticle, interacting with the substance under study, provides modulation of the spectral characteristics of the liquid crystal [16-17].

The study of the influence of nano-sized particles on the electro-optical properties of liquid crystal materials opens up prospects for the creation of new nano-sized composites that can be used as active materials for electronic elements and devices.

Modification of the properties of liquid crystals to create optically sensitive media based on them for various types of optoelectronic devices is carried out mainly through the development of new multicomponent liquid crystal mixtures. However, this approach has practically exhausted itself, so in recent years considerable attention has been paid to composite systems based on liquid crystals with unique electro- and magneto-optical properties. It is promising to introduce objects with dimensions corresponding to the radius of action of intermolecular forces into an anisotropic medium, which ensures significant changes in all physical parameters of such composite materials.

As active elements of optical sensors based on liquid crystals, both native and induced cholesteric liquid crystals with a low content of nano-sized impurities are used. The choice of the cholesteric matrix for the development of sensitive media of the primary transducer of the optical gas sensor is due to its chemical stability and the stability of the mesophase at room temperature. [18-20].

As the basic liquid crystal matrix, an industrial mixture of cholesteric liquid crystals - BLO-61, which is characterized by minimal selective transmission at a wavelength, was chosen 390 nm, maybe 480 nm. The spectral characteristics of the BLO-61 liquid crystal are shown in Fig. 1. The essential advantages of this liquid crystal mixture are chemical inertness and the stability of the existence of the mesophase in the temperature range from 11 to 68 °C.

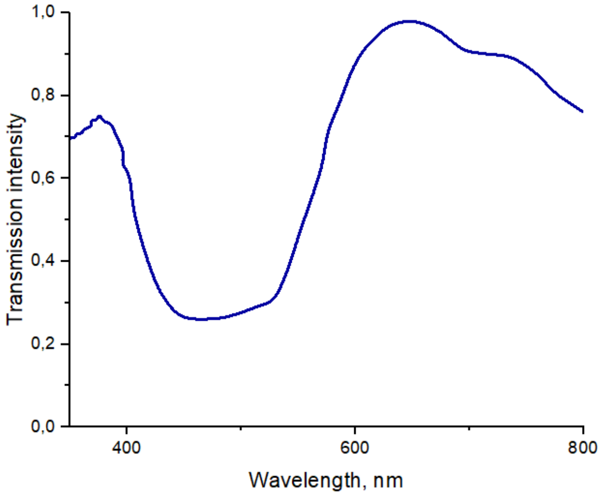

Fig. 1. Spectral characteristics of LC BLO-61

A nematic liquid crystal 5CB (4-n-pentyl-4-cyanobiphenyl) was used to obtain a cholesteric-nematic mixture.

The first stage of creating the studied nanocomposites consisted of adding nematic to the cholesteric liquid crystal to form a cholesteric-nematic mixture. The concentration of nematic was chosen to obtain the maximum selective reflection in the visible region and in this study is 25%.

To obtain a homogeneous mixture, the liquid crystal mixture was heated to an isotropic state, and after that, multi-walled nanotubes were added. The mixture was further homogenized in an ultrasonic bath for 1 hour. If necessary, the time of ultrasonic mixing can be increased. Effective formation of a homogeneous mixture is observed in the isotropic phase of the liquid crystal mixture. Due to this, homogeneous mixtures with low coagulation in the cholesteric-nematic mixture were obtained.

Due to their large effective surface area, carbon nanotubes can absorb chemical substances, which makes it possible to increase the absorption of substances by the cell due to their use, and, accordingly, to increase the sensitivity of the liquid crystal cell [21-23]. So, at work [24] doping of the mixture was used to significantly increase the sensitivity of the liquid crystal cell to NO_2 multi-walled nanotubes, with a weight concentration of 0.7%.

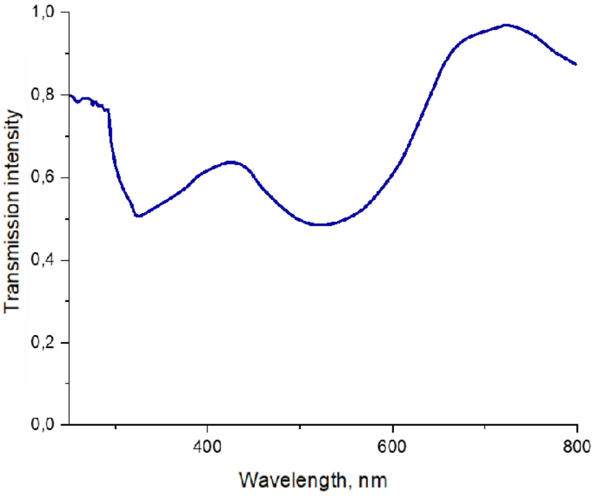

Fig. 2. Transmission spectrum of the cholesteric-nematic mixture with a concentration of 5CB – 25%.

In fig. 3 shows the spectral characteristics of a cholesteric-nematic mixture with a 5CB nematic concentration of 25% and an admixture of carbon nanotubes of 0.45 and 0.7 wt.%.

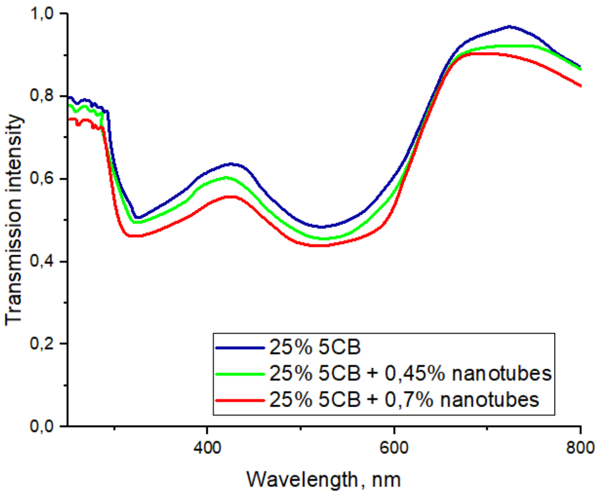

Fig. 3. Spectral characteristics of a nanocomposite based on a cholesteric nematic mixture, with a 5CB nematic concentration of 25% and an admixture of multi-walled carbon nanotubes.

II. Experiment

The spectrum of the nematic liquid crystal of the 5CB impurity is characterized by an absorption minimum at a wavelength of 360 nm, which is close to the wavelength of the maximum absorption of the NO_2 spectrum in the visible region. Therefore, the use of liquid crystal 5CB as an active element of the NO_2 optical sensor is expedient.

During the interaction of nitrogen dioxide with the 5CB liquid crystal, the spectral characteristics of the liquid crystal change, as shown in Fig. 4.

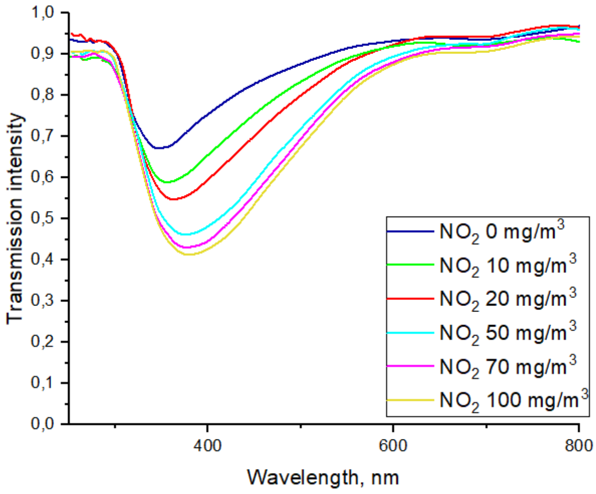

Fig. 4. Changes in the spectral characteristics of the nematic liquid crystal 5CB under the influence of NO_2.

From fig. 4, it can be concluded that as a result of the interaction with nitrogen dioxide, there is a shift of the spectral minimum of the transmittance of the 5CB liquid crystal to the long-wave region of the spectrum. Such a change in spectral characteristics occurs as a result of the interaction of 5CB molecules with NO_2 molecules. The minimum transmission wavelength of the liquid crystal changes from 360 to 384 nm when the gas concentration changes from 0 to 100 mg/m^3. The minimum concentration of NO_2 to change the spectral characteristics of 5CB is 10 mg/m^3. The dependence of the absorption maximum shift on the concentration of nitrogen dioxide is shown in Fig. 5.

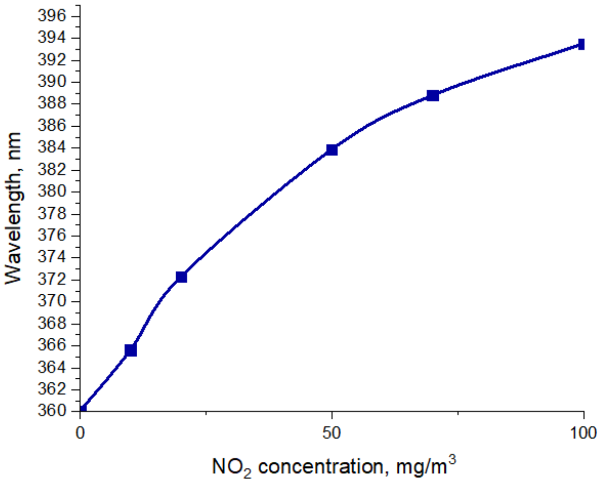

Fig. 5. Variation of the absorption maximum of 5CB as a function of NO_2 concentration.

Depending on the concentration of 5CB nematic in the cholesteric-nematic mixture, we can observe differences between the changes in the spectral characteristics of nanocomposites under the influence of NO_2. Spectral characteristics of nanocomposites based on cholesteric-nematic mixture with a concentration of 5CB 25% and an admixture of multi-walled nanotubes 0.7% under the action of nitrogen dioxide are shown in Fig. 6 and 7, respectively. We can state that the addition of multilayer nanotubes to the liquid crystal mixture increases the shift of spectral characteristics and allows the detection of lower concentrations of NO_2. When the liquid crystal sensitive element interacts with gas, two transmission minima shift in opposite directions, and at high concentrations of nitrogen dioxide, the two peaks merge into one broad one.

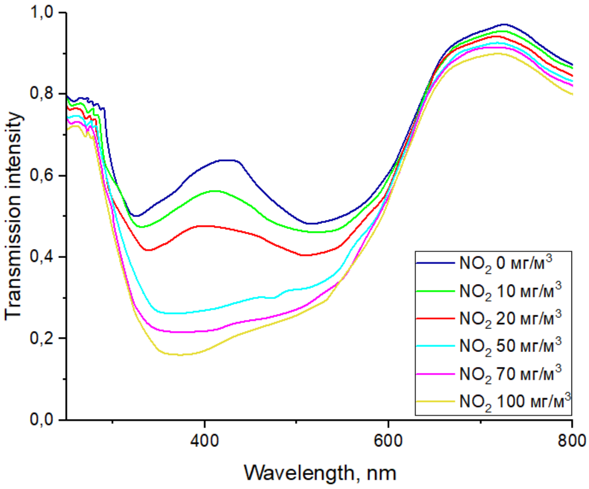

Fig. 6. Transmission spectrum of a liquid crystal mixture with a concentration of 5CB nematic 25% under the action of NO_2.

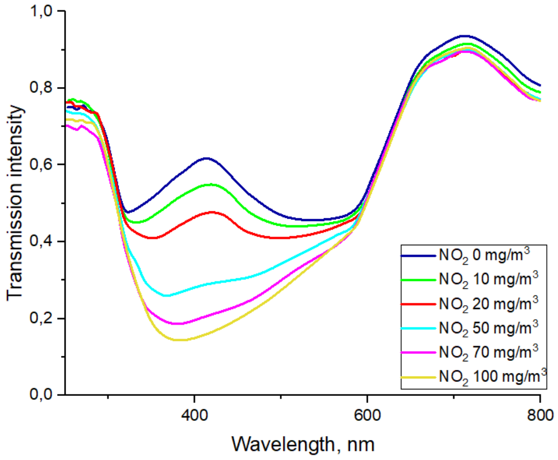

Fig. 7. Transmission spectrum of a liquid crystal mixture with a concentration of 5CB nematics of 25% and doped with multi-walled nanotubes under the influence of NO_2.

An experiment to study the spectral characteristics of the nematic liquid crystal 5CB under the influence of SO_2 and NO_2 demonstrates its interaction with nitrogen dioxide, and the strengthening of such interaction due to the creation of a cholesteric-nematic mixture with the cholesteric BLO-61, and the subsequent further increase in sensitivity after doping the mixture with multilayer nanotubes with a concentration of 0.7%.

The coefficient of spectral sensitivity of 5CB nematic to NO_2 is 0.38 nm/mg/m^3. The use of a cholesteric-nematic mixture based on BLO-61 and 25% 5CB increases the coefficient of spectral sensitivity almost twice. When multi-walled nanotubes are added to the liquid crystal mixture, the maximum sensitivity to nitrogen dioxide is achieved, which is close to 5 nm/mg/m^3. This increase in spectral sensitivity is explained by the fact that the coefficient of spectral sensitivity is determined not only by the specific surface area of carbon nanotubes but also by the curvature of their surface. In multi-walled nanotubes, the surface curvature is much smaller than in single-walled ones, so molecules are more easily absorbed on them, which leads to an increase in the coefficient of spectral sensitivity.

Conclusion

As a result of the research, the interaction of nematic liquid crystal 5CB and mixtures based on it, doped with multilayer nanotubes and nitrogen dioxide was studied. The graphs obtained demonstrate a significant increase in spectral sensitivity to NO_2 when 0.7 % multi-walled nanotubes are added to the liquid crystal mixture. Further prospects of the research consist in expanding the list of NOx compounds for interaction with a liquid crystal sensitive element doped with nanotubes. As well as the search for new liquid crystal mixtures, which, due to their characteristics, could demonstrate better sensitivity to NOx compounds.

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Зміна спектральних характеристик рідкокристалічного активного середовища допованого багатошаровими вуглецевими нанотрубками під дією нітроген діоксиду

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В роботі досліджено вплив діоксиду азоту (NO_2) на спектральні характеристики рідкокристалінчної суміші, легованої багатошаровими нанотрубками. Рідкокристалічну суміш синтезовано на базі холестеричного рідкого кристалу BLO-61 та нематика 5CB (26%) із широким діапазоном температур існування мезофази, концентрація нанотрубок становила до 0,7%. Встановлено, що введення нанотрубок в суміш призводить до істотного збільшення чутливості суміші до неорганічних речовин за рахунок збільшення абсорбції. Проведено аналіз зміни спектральних властивостей суміші при різних концентраціях діоксиду азоту в об'ємі сенсора та визначено коефіцієнт спектральної чутливості. Отримані результати вказують на можливе використання цієї суміші як чутливого елемента сенсора для виявлення азотних сполук у майбутньому.

Ключові слова: оптика, рідкі кристали, діоксид азоту, рідкокристалічний сенсор.