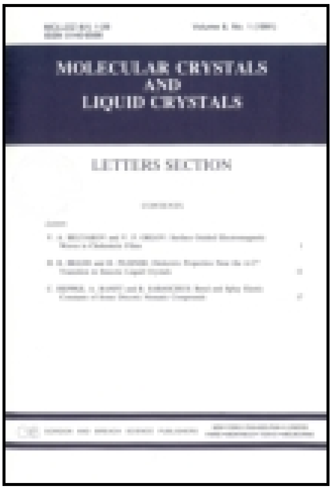

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Cholesteric Liquid Crystal Doped by Nanosize Magnetite as an Active Medium of Optical Gas Sensor

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A new approach to the creation of an active medium of optical gas sensors for the detection of carbon monoxide is proposed. The approach is based on the use of a liquid crystal host doped with iron compounds. Cholesteric liquid crystal CLC-2103L was doped by Fe_3O_4 magnetite nanoparticles with a concentration of 0.30-0.67% to develop the primary transducer of a carbon monoxide sensor. The proposed gas sensor registers the optical signal in the visible region of the spectrum, corresponding to the optical reflection by the helical structure of a cholesteric liquid crystal (CLC).

Keywords Cholesteric liquid crystal; carbon monoxide; magnetite; transmittance spectrum; sensor

Introduction

As usual, the gas sensors based on optical methods have a straightforward design and possess a higher sensitivity, selectivity, stability, and much longer lifetime than those based on non-optical methods. The response time of optical gas sensors is relatively short, which allows the on-line real-time detection [1]. The detection and the measurement of gas concentrations with the use of the optical absorption characteristics are important for monitoring a diversity of effects from industrial processes on environmental changes [2]. Optical gas sensors contain three major parts: a light source, gas chamber, and light detector (Fig. 1).

Spectroscopy is mostly used as one of the gas-sensing optical methods. There are several individual gas detection techniques including non-dispersive infrared spectrophotometry, tunable-diode laser spectroscopy, and photoacoustic spectroscopy [2]. However, their applications to gas sensors are seriously limited due to the miniaturization and a relatively high cost. Only a few commercial gas sensors are based on optical methods [2].

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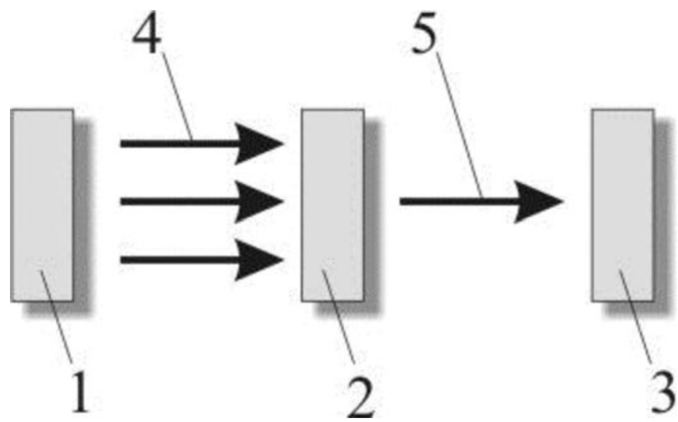

Figure 1. Schematic of a typical optical gas sensor: 1 – light source; 2 – gas chamber; 3 – light detector; 4 – input light; 5 – output absorbed light

Infrared (IR)-source gas sensors based on optical sensing principles are widely used, since each gas has its own IR absorption band to at a certain wavelength and, thus, the unique IR absorption attribute [3]. The optical detection of a gas, which is based on the IR absorption spectrum and currently occupies an important place in the gas detection technical field, is superior to the traditional detection methods by the accuracy, speed, and even security. When the IR source radiates a broad band including the wavelength absorbed by a detecting gas, the sample gas in the gas cell will absorb the radiation in its particular way. The optical filter is used to screen out all radiation except for the wavelength that is absorbed by the detecting gas. Therefore, the presence of the gas of interest can be detected and measured by an IR detector. This system is also known as a Non-Dispersive Infrared (NDIR) gas sensor [4].

In work [5], an analytical methodology to evaluate the response of a gas sensor based on correlation spectroscopy with the use of a Fabry–Perot interferometer was presented. The authors designed and tested three different gas sensors (CO, CO_2, and CH_4) based on correlation spectroscopy with a Fabry–Perot interferometer as a modulator, which is placed just in front of the optical detector and emits a converging beam. In work [6], a compact fiber-optics diode laser spectrometer is designed for the measurement of CO and CO_2 gas concentrations in the near infrared region around 1580 nm. We propose a novel optical method of detection of carbon monoxide (CO) that is not based on the detection of CO molecules by their absorption spectrum in the IR region [7].

The toxic effect of carbon monoxide causes a severe poisoning. This effect is mortally dangerous to human life and health. The carbon monoxide detection is a complicated task, because this gas has no odor or color and is not absorbed by the well-known sorbents (e.g., by conventional masks). This is impossible to sense this gas in the environment without special means. At the breathing, this highly toxic gas gets into blood and binds to hemoglobin by 200-500 times faster than oxygen. This causes the oxygen deficiency and the irreversible damage of brain, lungs, and heart. This situation encourages the researchers to develop and to improve CO sensors of various types: from colored indicators and electrochemical cells to solid-state sensors, which use oxide semiconductor materials [8, 9] or organic compounds (e.g., dendrymers [10]) as sensitive primary transducers. Liquid crystals (LCs) are perspective materials for the detection of hazardous gases due to the high sensitivity to a change of their molecular ordering under the external influence. Such changes can be easily detected optically, because LCs possess a large optical anisotropy. When the CO molecules are absorbed by a liquid crystal material, its optical properties are changed, but LCs do not exhibit a high selectivity toward carbon monoxide.

We propose a new approach to the design of CO sensors. It is based on the determination of the optical properties of LCs doped with iron compounds such as magnetite nanoparticles. Therefore, such gas sensor can detect the optical signal in the visible spectrum region, corresponding to the optical reflection of the helical molecular structure of CLC.

The sensitivity of magnetite to carbon monoxide was used to design a high-selectivity gas sensor. Such high sensitivity is explained by the presence of iron atoms in the oxidation state +2 and +3, as in case of a hemoglobin molecule. It is well known that the doping of a liquid crystal with Fe_3O_4 nanoparticles allows one to manipulate the magnetic and electric properties of LCs and their molecular orientation in external electric or magnetic fields [11, 12]. Magnetite nanoparticles are important in structural liquid crystal transitions. The significant Fe_3O_4 effect on the nematic LC anchoring energy was established. However, the influence of Fe_3O_4 magnetite nanoparticles on the cholesteric LC optical characteristics under the action of carbon monoxide remains not studied.

The aim of the present paper is to study the effect of magnetite nanoparticles on the sensitivity of the optical characteristics of a cholesteric liquid crystal to carbon monoxide.

Experimental

The thermally stable cholesteric mixture CLC-2103L was selected as a liquid crystal host. It was doped with Fe_3O_4 magnetite nanoparticles to 0.30-0.67% concentrations with the aim to develop the primary transducer of an optical sensor of carbon monoxide. Fine-grained magnetite was synthesized by means of the method of alkaline hydrolysis of iron (II) and iron (III) salts and stabilized by sodium oleate (OlNa), as described in [9]. According to X-ray diffraction (DRON-2M, FeKα-radiation) studies, obtained magnetite is characterized by enhanced diffraction peaks, which are inherent in semiamorphous Fe_3O_4 samples. X-ray analysis confirmed the existence of a cubic phase with spinel-type structure [9], the *Fd-3m* space group, and the value of lattice parameter $a = 8.3490$ (3) Å for Fe_3O_4 nanoparticles. The average grain size was 75.5 (± 7.3) Å, as calculated from X-ray analysis. The stabilization of nanoparticles with OlNa caused some increase of the size of Fe_3O_4 domains to 89.4 (±5.7) Å.

Carbon monoxide was produced by a chemical reaction based on the chemical decomposition of formic acid (HCOOH) in the presence of the concentrated sulfuric acid. The molecules of sulfuric acid take away the water molecules from HCOOH with the formation of chemically stable hydrates. The common reaction scheme is as follows:

$$HCOOH \xrightarrow{(H_2SO_4)_{conc.}} CO + H_2O.$$

Spectral studies of CLC-2103L doped with magnetite nanoparticles are carried out in the wavelength range 200-900 nm at temperatures of 293-326 K with the carbon monoxide concentrations from 20 to 150 mg/m^3. These CO concentrations were chosen with regard for the maximally allowable concentrations (according to hygienic standards GN 2.2.5.1313-03

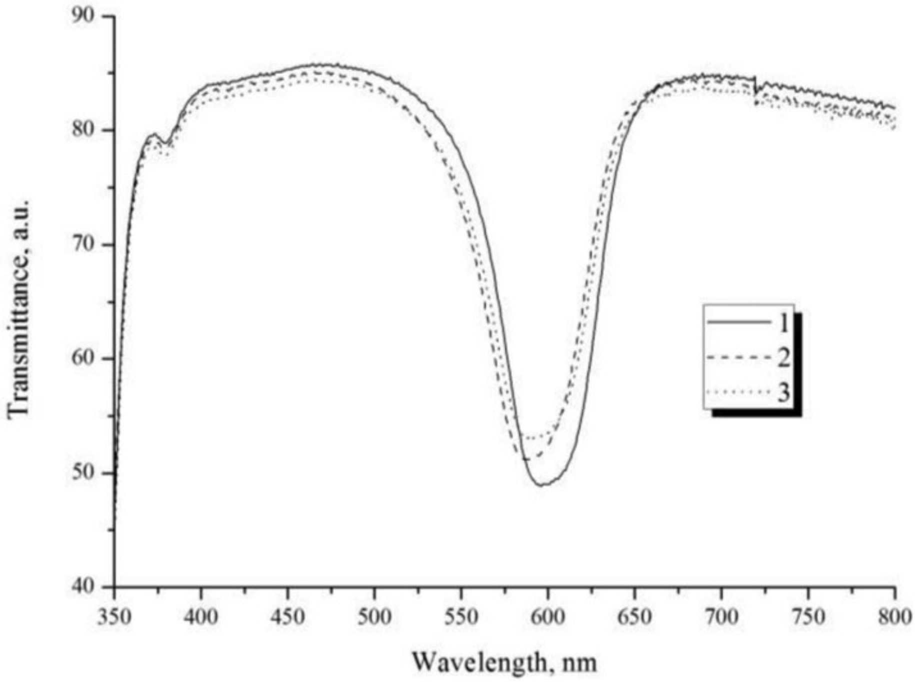

Figure 2. Optical transmission spectra of undoped CLC-2103L (1) and CLC-2103L doped with 0.63% (2) and 0.30% (3) Fe_3O_4 magnetite.

(Ukraine), the values of 20 mg/m^3 and 150 mg/m^3 correspond, respectively, to maximally allowable concentrations at the working area and at one breathing).

The typical liquid crystal cell was used in studies. One glass plate was replaced by an optically transparent porous material. The LC cell was placed in an experimental chamber (volume is 0.5×10^{-3} m^3), which was filled by carbon monoxide at the corresponding concentration. The gas concentration was determined from the initial concentrations of chemical reaction reactants. After the action of carbon monoxide in the experimental chamber, the liquid crystal cell was placed in a spectrophotometer. Our LC cell was at the action of carbon monoxide up to 10 min.

Results and Discussion

The optical transmittance spectrum of CLC-2103L (Fig. 2, curve 1) is characterized by one intensive band with a minimum at 597 nm (at room temperature). In case of the LC host doped with magnetite, we observed a shift (18-20 nm) of the transmission minimum to the short wavelength range (Fig. 2, curves 2 and 3). Moreover, the shift magnitude increases with the magnetite concentration in the LC host. Such shift can be explained by the existence of the adsorption interaction between LC and magnetite. The most essential shift was observed for the 0.63% Fe_3O_4 magnetite concentration in the LC host, which was the reason to choose this mixture for studies.

For the studies of sensitive properties of CLC-2103L doped with Fe_3O_4 magnetite, the liquid crystal cell was subjected to the action of carbon monoxide. As shown in Fig. 3,a,

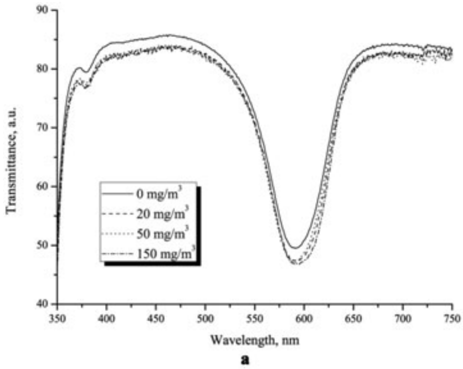

Figure 3. Optical transmission spectra of undoped CLC-2103L (a) and doped with (0.63%) Fe_3O_4 magnetite (b) at different carbon monoxide concentrations (the reaction time is 5 min).

there are no significant changes in the optical transmission spectra of undoped CLC-2103L at the action of carbon monoxide.

In another case, we observe the significant changes in the optical transmission spectrum of CLC-2103L doped with Fe_3O_4 nanoparticles (Fig. 3b). When the carbon monoxide concentration increases, there are the significant changes in the transmittance minimum position and the shapes of spectral lines: the half-widths of spectral lines and their ratios

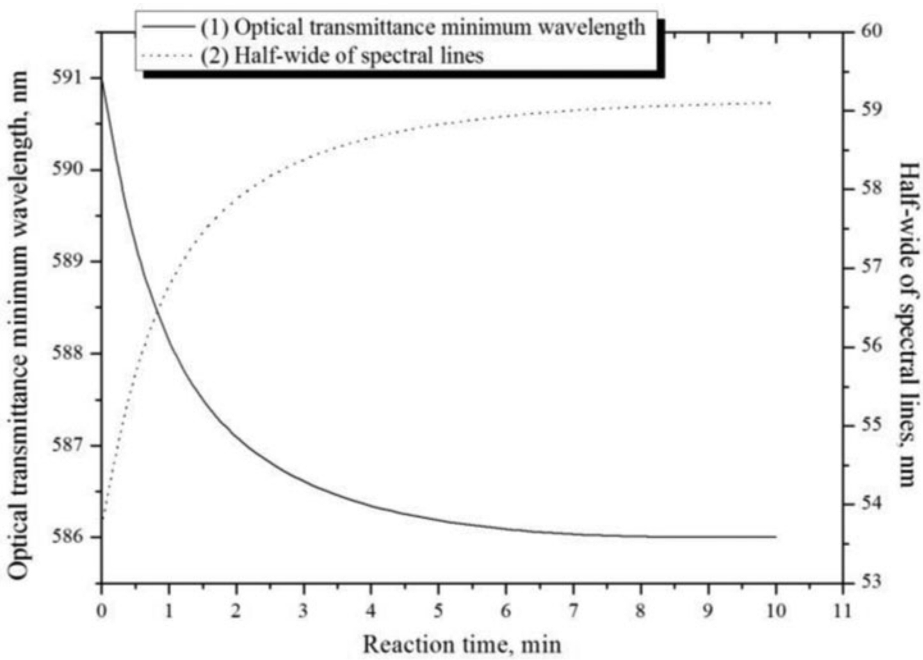

Figure 4. Dependences of the optical transmittance minimum wavelength (1) and the half-width of spectral lines (2) on the reaction time at a carbon monoxide concentration of 100 mg/m^3 for CLC-2103L doped with (0.63%) Fe_3O_4 magnetite.

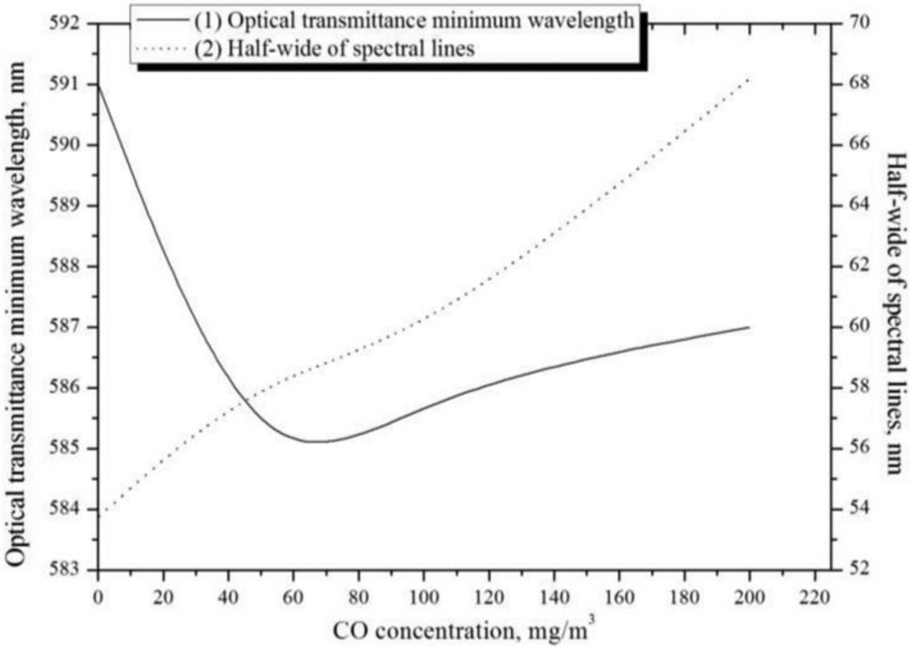

Figure 5. Dependences of the optical transmittance minimum wavelength (a) and the half-width of spectral lines (b) on the carbon monoxide concentration for CLC-2103L doped (0.63%) with Fe_3O_4 magnetite.

to the transmittance minimum wavelength are changed. The dependences of these optical parameters are almost linear over a wide range of CO concentrations.

It was established by experimental studies that, at the action of carbon monoxide on the LC host doped with magnetite, the reaction time is small and does not exceed 1-1.5 min. When the reaction time increases, the optical response time dependences are not changed significantly (Fig. 4, curve 1). When the reaction time is above 5 min, the small decrease is observed in optical response time dependences. Such experimental results proclaim the high sensitivity of our primary transducer based on an LC host doped with magnetite to the gas as compared with the well known gas sensors on semiconductor materials base [8, 9].

The optical transmittance minimum wavelength is decreased sharply (8-10%) at the carbon monoxide concentrations from 0 to 70 mg/m^3 (Fig. 5, curve 1) and does not change strongly up to a CO concentration of 150 mg/m^3. Curve 2 in Fig. 5 illustrates the half width of an optical line versus the carbon monoxide concentration. This curve is linear in the full interval of studied CO concentrations.

As was described above, the optical transmission spectra in the cholesteric liquid crystal doped with magnetite are changed at the action of carbon monoxide. These changes can be explained by the interaction between magnetite nanoparticles and carbon monoxide molecules. At the same time, the shape and the symmetry of nanoparticles can affect their electronic properties and, respectively, the mechanism of interaction with carbon monoxide [14].

Magnetite (or iron (II, III) oxide) reacts actively with carbon monoxide molecules. During this reaction, iron oxide is reduced into pure iron, which is accompanied by the formation of carbon dioxide by the reaction

$$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2.$$

However, the course of this reaction with the formation of final products is unrealistic in the LC environment of magnetite nanoparticles. It can be assumed that the CO molecule, competing with the liquid crystal molecules in the adsorption on the surface of magnetite nanoparticles, can form relatively stable coordination bonds with the surface of magnetite, as well as with functional groups of the LC. This leads to a violation of the order of the cholesteric crystal, which leads to a change in the transmission spectrum of the LC - magnetite composite. The higher the concentration of CO, the more noticeable are these changes.

Conclusion

We propose a new active medium of optical sensors for the detection of a carbon monoxide concentration that is based on the registration of optical transmission spectra in the visible wavelength range. As the primary transducer of an optical gas sensor, the CLC-2103L cholesteric liquid crystal host doped with Fe_3O_4 magnetite nanoparticles is used. We have found a significant shift of the optical transmittance minimum and an increase of the half-width of spectral lines for the proposed active medium that depend on the CO concentration. These changes in the optical spectra are explained by a violation of the order of the cholesteric crystal in the LC – magnetite composite. Moreover, the higher the concentration of CO, the more noticeably magnetite interacts with carbon monoxide.

References

[1] Sitian, C., Hong, L., Sha, H., Daqiang, Z. & Huansheng, N. (2012). *Sensors*, *12*, 9635.
[2] Hodgkinson, J., & Tatam, R. (2013). *Meas. Sci. Technol.*, *24*, 1.
[3] Zheng, H. (2008). In: Proceedings of International Workshop on Education Technology and Training and Geoscience and Remote Sensing (ETT and GRS), Shanghai, China, 21–22 December, 175.
[4] Baetz, W., Kroll, A., & Bonow, G. (2009). In: Proceedings of IEEE International Conference on Robotics and Automation (ICRA), Kobe, Japan, 12–17 May, 2773.
[5] Vargas-Rodrígueza, E., & Ruttb, H. N. (2009). *Sensors and Actuators B*, *137*, 410.
[6] Engelbrecht, R. (2004). *Spectrochimica Acta Part A*, *60*, 3291.
[7] Pulido, C., & Esteban, Ó. (2013). *Sensors and Actuators B*, *184*, 64.
[8] Youssefa, S., Podlecki, J., Habchi, R., Brouche, M., Foucarana, A., Bouvier, D., Brillouet, N., & Coudray, P. (2012). *Sensors and Actuators B*, *173*, 391.
[9] Yamazoe, N., Sakai, G., & Shimanoe, K. (2003). *Catalysis Surveys from Asia*, *7*, 1.
[10] Kooa, B. W., Songa, C. K., & Kimb, C. (2001). *Sensors and Actuators B*, *77*, 432.
[11] Arantes, F. R., Figueiredo Neto, A. M. & Cornejo, D. R. (2011). *Journal of Applied Physics*, *109*, 07E315.
[12] Mitróová, Z., Koneracká, M., Timko, M., *et al.* (2010). *Physics Procedia*, *9*, 41.
[13] Aksimentyeva, O. I., Opaynych, I. Ye., Dyakonov, V. P., Piechota, S., Zakordonskyi, V. P., Demchenko, P. Yu., & Szymczak, H. (2012). *Physics and Chemistry of Solid State*, *13*, 2, 438.
[14] Mpourmpakis, G., Andriotis, A. N., & Vlachos, D. G. (2010). *Nano Lett.*, *10* (3), 1041.