

Optical-luminescent properties of liquid crystal systems with dispersed cerium oxide nanoparticles

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It is shown that suspensions of cerium oxide nanoparticles in the nematic 5CB phase undergo nonmonotonic changes in optical density with an increase in CeO₂ concentration with maximum transmission noted at a level of ~ 0.03 wt.%. With a further increase in the CeO₂ content above this threshold, as well as in the entire concentration range in the isotropic phase, the optical density increased as it could be expected. The luminescence of cerium oxide nanoparticles was of low intensity and was almost completely overlapped by the 5CB luminescence band. However, with other liquid crystal matrices, clear CeO₂ luminescence bands were observed at ~ 330 nm under excitation at ~ 270 nm for three samples of nanoparticles of different sizes and different manufacturers.

Keywords: cerium oxide nanoparticles, nematic 5CB phase, luminescence, liquid crystal matrices.

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Показано, що суспензії наночастинок оксиду церію у нематичній фазі 5CB зазнають немонотонні зміни оптичної щільності зі збільшенням концентрації CeO₂ з максимумом пропускання, зазначеним на рівні ~ 0,03 мас.%. При подальшому збільшенні вмісту CeO₂ вище цього порогу, а також у всьому діапазоні концентрацій в ізотропній фазі оптична щільність очікувано зростала. Інтенсивність люмінесценції наночастинок оксиду церію була досить низькою і майже повністю екранована смугою люмінесценції 5CB. Однак з іншими рідкокристалічними матрицями чіткі смуги люмінесценції CeO₂ спостерігалися близько ~ 330 нм при збудженні ~ 270 нм для трьох зразків наночастинок різного розміру і різних виробників.

Показано, что суспензии наночастиц оксида церия в нематической фазе 5CB претерпевают немонотонные изменения оптической плотности с увеличением концентрации CeO₂ с максимумом пропускания, отмеченным на уровне ~ 0,03 мас.%. При дальнейшем увеличении содержания CeO₂ выше этого порога, а также во всем диапазоне концентраций в изотропной фазе оптическая плотность ожидаемо возрастала. Интенсивность люминесценции наночастиц оксида церия была довольно низкой и почти полностью экранирована полосой люминесценции 5CB. Однако с другими жидкокристаллическими матрицами четкие полосы люминесценции CeO₂ наблюдались около ~ 330 нм при возбуждении ~ 270 нм для трех образцов наночастиц различного размера и различных производителей.

1. Introduction

Composite materials based on liquid crystals (LC) and other ordered soft matter systems with nanoparticles of different kinds dispersed therein are among the most popular objects of the modern materials science. Highly anisotropic carbon nanotubes can rather easily incorporate into the LC ordered structure, and a number of features that could be potentially promising for applications of such composites were described and analyzed [1–3]. To a lesser extent, the same can be said about disc-like exfoliated anisotropic particles of organomodified clays of laponite/montmorillonite type [4, 5]. Another class of nanoparticles that arouse much interest are nano-sized crystals of inorganic metal oxides, which are expected to substantially improve the performance of LC cells. In this respect, one should start with referring to a recent comprehensive review [6], where oxides of Mg, Zn, Al, Cu, Ni, Zr were shown to modify the LC parameters, in particular, those essential for functioning of LC electrooptic cells. (We do not mention here Fe, since ferroelectric particles in LC constitute a well-defined separate field [7, 8]). As an example, we would like to mention here some recent works on nematic dispersions of TiO₂ [9, 10], where clear effects of reduced response times, better contrast due to improved alignment, as well as lower Fredericksz transition thresholds were reported. As a particular feature, they have noted [10] a certain critical concentration of nanoparticles above which the effects of aggregation exerted their negative influence.

Our particular interest was focused on cerium oxide nanoparticles. Their dispersions in LC were reported, to our knowledge, in just two papers [11, 12]. The authors treated them as just another example of metal oxide nanoparticles, focusing on their obviously expected influence on electro-optical behavior. However, the presence of the aggregation-related concentration threshold has been also noted. In those papers, however, no attention was paid to luminescent properties of cerium oxide. (One could note some papers where luminescent properties of organic substances were shown to be dependent on the LC medium [13, 14], and similar effects could be expected in this case). So, our aim was to study dispersions of CeO₂ nanoparticles in LC matrices both from the viewpoint of temperature-dependent effects of their in-

corporation in the LC matrix and from the standpoint of luminescence, i.e., treating the ceria particles as a possible alternative to the well-known A^{II}B^{VI} quantum dots.

Some words should be said on CeO₂ luminescent properties in, so to say, non-LC conditions. Many papers describe synthesis of luminescent ceria nanoparticles, with particle size noted and XRD data presented. Just to note a recent example — 3–5 nm particle size, 413 nm photoluminescence (PL) maximum [15]. In [16], particles of 3.7 nm size were dispersed in methanol, with PL maximum recorded at ~ 350 nm, with a shift towards ~ 410 nm at higher concentration of nanoparticles. PL at 480 nm was recorded in [17] at 330 nm excitation, while the nanoparticle size variation from 5.8 nm to 11.5 nm (due to different soaking time in preparation) led to PL maxima within the 450–700 nm range, with ~ 600 nm being a certain statistical mode [18]. PL peaks at 490 nm and 610 nm were noted in [19], while PL maximum at 683 nm was obtained under 343 nm excitation [20]. This list can be easily extended, and a clear conclusion arises that no generally accepted view on PL of CeO₂ nanoparticles has emerged.

Therefore, our objective was a thorough investigation of optical properties in LC matrices doped with dispersed CeO₂ nanoparticles.

2. Experimental

In our experiments, we used the cholesteric mixture M5 that consisted of 30 % cholesteryl formate, 5 % cholesteryl butyrate and 65 % cholesteryl nonanoate. These cholesterol esters were obtained from Chemical Reagents Plant, Ukraine and used without further purification. The nematic 5CB (4-*n*-pentyl-4'-cyanobiphenyl) of 99,5 % purity was also obtained from Chemical Reagents Plant, Ukraine. The nematic mixture ZhK805 (50:50 % mixture of 4-butyl- and 4-hexyl-*trans*-cyclohexanecarboxylic acids) was obtained from NIOPIK, Russia. The components of the nematic mixture ZhK3105 (80 % *trans*-4-butylcyclohexanecarboxylic acid and 20 % decanoic acid), were obtained from Sigma-Aldrich and ISMA, NAS of Ukraine. The CeO₂ nanopowder, of particle sizes 25 and 50 nm, was obtained from Sigma-Aldrich, and 10 nm nanoparticles of cerium oxide were synthesized at ISMA, NAS of Ukraine. Optical transmission and selective reflection spectra were measured in sandwich-type LC cells (20 mm thickness) using a Shimadzu UV-2450 spectrophotometer (Japan) within

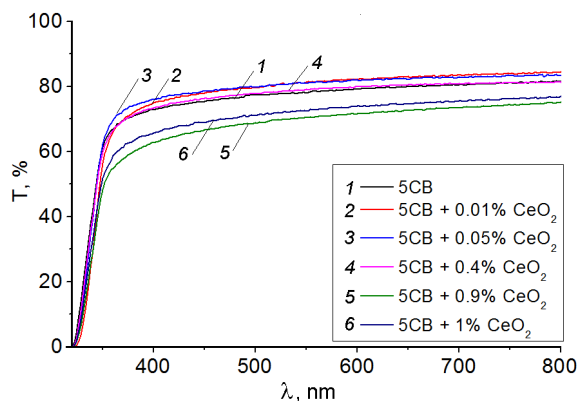


Fig. 1. Optical transmission spectra for suspensions 5CB + CeO₂ nanoparticles. Concentration rate of CeO₂ is from 0 % to 1.0 %, particle size 25 nm. The data are presented for 20 μm thick cells at 25°C.

300–900 nm spectral range. The luminescence study was carried out using a FLS920 Fluorescence Spectrometer (United Kingdom) with excitation at 275 nm. The LC+CeO₂ suspensions were obtained by adding the appropriate weights of cerium oxide to the LC hosts in the isotropic state with subsequent sonication (2–3 times for 30 sec) of the mixture using a UZD-22/44 ultrasonic disperser (Ukrrosprigor, Sumy, Ukraine).

3. Results and discussion

At the first stage of our work, we measured the optical transmission spectra of suspensions based on nematic liquid crystal 5CB doped with CeO₂ nanoparticles (Fig. 1). Such spectra were obtained over a wide temperature range, covering both the nematic and isotropic phases (the nematic to isotropic transition temperature for 5CB is 36°C). A characteristic feature of such optical transmission vs. temperature dependences, when there is a weakly first-order phase transition, is a sharp increase in the optical transmission value at the isotropic transition [21]. The magnitude of this "optical transmission jump" is a measure of the integration of nanoparticles into the orientationally ordered structure of the liquid crystal, and, as we can see (Fig. 2), the obtained data indicate a good distribution of CeO₂ nanoparticles in the volume of the LC matrix, which is expressed more clearly at higher nanoparticle concentrations.

To present and analyze the obtained data, we assumed that for the optical transmission of CeO₂ suspensions, the Bouguer-Lambert-Beer (BLB) law must be followed at least approximately [22, 23]. Henceforth,

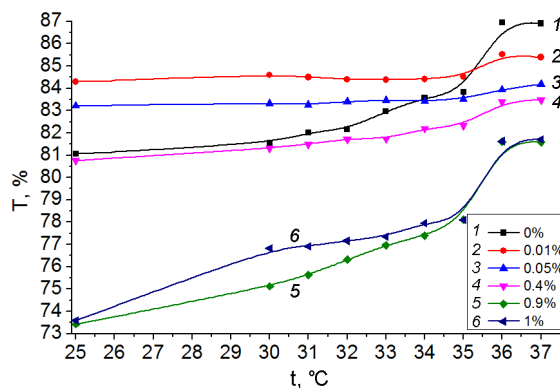


Fig. 2. Optical transmission as a function of temperature for 5CB + CeO₂, particle size 25 nm. The data are presented for cells 20 μm thick at the wavelength of 800 nm.

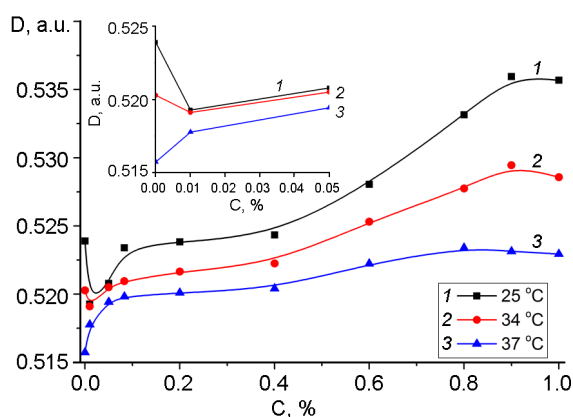


Fig. 3. Optical densities D versus concentration, C , of CeO₂ in 5CB at three different temperatures: 25°C and 34°C (nematic phase), and 37°C (isotropic phase). The thickness of cell, l , was 20 μm, particle size 25 nm.

all graphs and discussions will be given for the values of $D = -\lg(T/100)$. Under the conditions of the BLB law, one could expect linear dependences $D = \epsilon cl$, where c is the concentration of CeO₂, l is the thickness of the cell, and ϵ is the effective extinction coefficient as a certain characteristic of CeO₂ in the dispersed state.

On the dependence of the optical density of 5CB + CeO₂ suspensions (Fig. 3) on the concentration of cerium oxide nanoparticles, an anomalous extremum in the region of low concentrations can be observed. The decrease in optical density with the addition of CeO₂ in the concentration range of 0.01 to 0.05 wt. % or less is a rather unexpected result. With a further increase in the concentration of cerium oxide in the LC matrix, the increase in optical density is close to linearity (until aggregation processes start at higher concentrations).

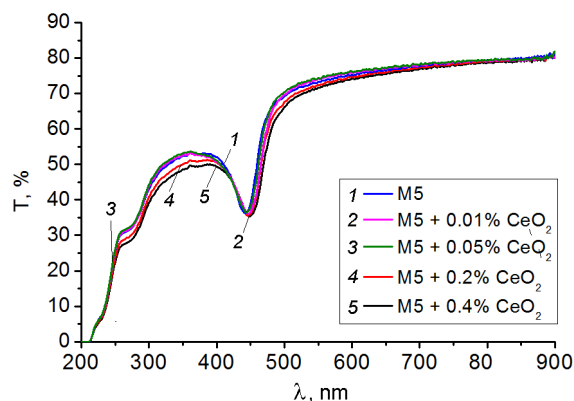


Fig. 4. Optical transmission spectra for suspensions M5 + CeO₂ nanoparticles. Concentration rate of CeO₂ is from 0 % to 0.4 %.

To understand the nature of this phenomenon and to determine the factors affecting the orientational ordering (and the observed effect), similar measurements were performed for 5CB + CeO₂ systems at temperatures that corresponded to the isotropic state of the matrix. This excluded the possibility of the orientational ordering effects in the optical properties of the suspension. As it can be seen, at 37°C addition of CeO₂ to the LC matrix at concentrations both below and above 0.05 wt. % leads to an increase in optical density because the nanoparticles of cerium oxide contribute to the processes of absorption and scattering of light and thus increase the optical density of the entire system.

Since all other experimental conditions were the same, the reason for the appearance of an anomalous minimum of optical density should be the presence of liquid crystal ordering of the investigated suspensions. Since CeO₂ nanoparticles participate in light absorption and scattering of the system regardless of its physical state, it can be concluded that at low concentrations, namely 0.05 wt. % or less, this contribution is insignificant, but these dopant concentrations are sufficient to reduce the orientation of the LC system, which leads to a decrease in the optical density of the suspension.

A similar effect was observed for LC + CNT systems [24], where the addition of small concentrations of dopant led to the suppression of director fluctuations with an increased optical transmission.

At the same time, lower rate of the optical density increase when the CeO₂ concentration reaches the value of about 1 wt. % indicates the beginning of the aggregation process. One can say that in suspensions

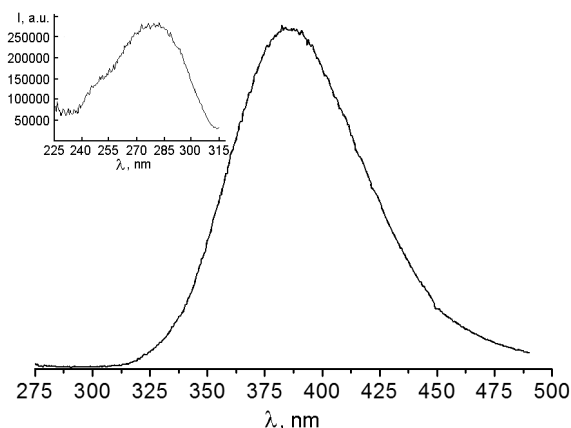


Fig. 5. Photoluminescence spectra of 5CB. The excitation spectrum is shown in Inset.

5CB + CeO₂ in the range up to 1 wt. %, no tendencies to aggregation are observed.

The mixture of cholesterol esters M5 was used to study the interaction of CeO₂ with cholesteric liquid crystal (CLC) medium. As in the case of nematic LCs, the results of the temperature dependences of the optical transmission indicate good integration of CeO₂ nanoparticles into the LC matrix. The increase in the concentration of CeO₂ did not affect the position of the maximum selective reflection λ_{max} of CLC (Fig. 4).

From the obtained set of results, it can be concluded that CeO₂ as a dopant for LC systems has a significant impact on characteristics of the system even at relatively low concentrations and opens new opportunities for the use of systems based on them.

The next step of our studies was to measure the luminescence of the dopants in LC matrices. But 5CB, as it known, has its own wide band in the visible range, which makes it an inappropriate choice for these tasks (Fig. 5), it was necessary to select the LC a mixture that would not overlap the CeO₂ luminescence band.

So, our next step was to use a nematic mixture that would have no luminescence band in the range of eventual CeO₂ luminescence.

The nematic mixture ZhK805 (50:50 % mixture of 4-butyl- and 4-hexyl-*trans*-cyclohexanecarboxylic acids — 4CHCA and 6CHCA), and as well as a mixture of cholesterol esters M5 were used. The excitation wavelength was 275 nm (Fig. 5).

As a result, it was possible to obtain a clear luminescence band of CeO₂ with a maximum of 330 nm in the nematic liquid crystal matrix ZhK805 (Fig. 6). In the literature, the luminescence of CeO₂ was characterized by emission bands at ~ 390 nm

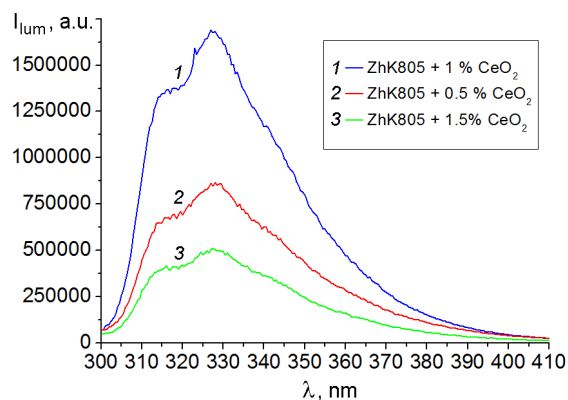


Fig. 6. Luminescence spectra of ZhK805 + CeO₂, particle size 25 nm.

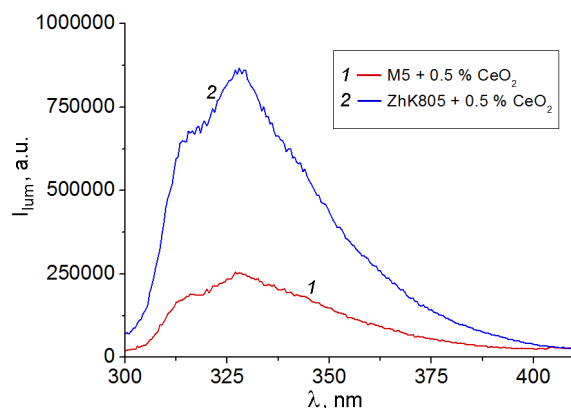


Fig. 7. Luminescence spectra of ZhK805 + CeO₂ and M5 + CeO₂, particle size 25 nm.

and, as shown in [16], where methanol was used as a medium for nanoparticles, the luminescence maximum could be shifted to the low-wavelength region. To ensure that this band does not come from the components of the used matrix, our studies were also carried out with M5 used as LC matrix (Fig. 7).

Since the main result (photoluminescence peaked at ~ 330 nm) was reproduced for several LC matrices and for three different types of CeO₂ nanoparticles which it in good agreement with our data of optical transmission studies, we conclude that CeO₂ dispersed in common thermotropic LC media demonstrates rather reproducible behaviour. This fact, in our opinion, opens new prospects for inorganic nanoluminescent phosphors dispersed in liquid crystals. Such composite materials can be promising for various optical and optoelectronic applications.

However, in spite of the good optical properties of the ZhK805 LC matrix, it has one significant drawback, namely, too high ($>90^\circ\text{C}$) temperature of the nematic-isotropic phase transition. This makes it im-

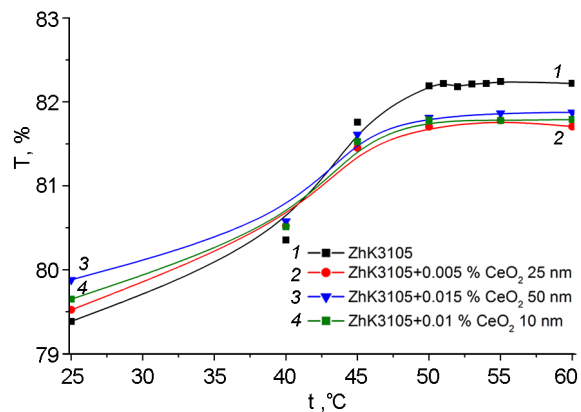


Fig. 8. Optical transmission as a function of temperature for ZhK3105+CeO₂, particle size 10 nm, 25 nm, 50 nm. The data are presented for 20 μm thick cells for the wavelength of 800 nm.

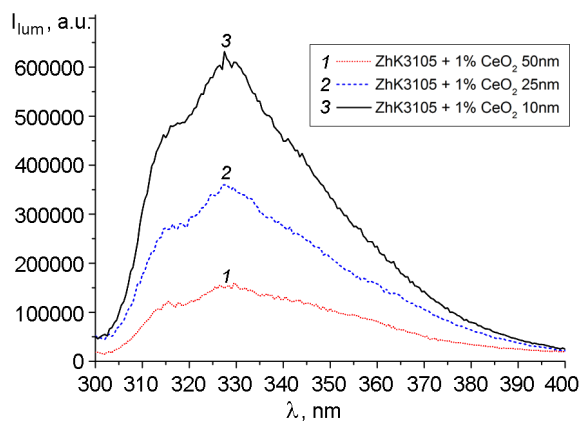


Fig. 9. Luminescence spectra of ZhK3105 + CeO₂, particle size 10 nm, 25 nm, 50 nm.

possible for us to study the behavior of matrices doped with cerium oxide nanoparticles in an ordered and isotropic state. Therefore, in order to study phase transitions in LC composites doped with CeO₂, without losing the possibility of detecting the luminescence of dopants, an LC composition ZhK3105 based on 4CHCA (80 %) and decanoic acid (20 %) was chosen. As shown for compositions containing CeO₂ in the size range from 10 nm to 50 nm (Fig. 8), no significant differences could be noted, and the luminescence band was observed in the same wavelength region as for other types of LC matrices, i.e., ~ 330 nm (Fig. 9).

4. Conclusions

To conclude, we can say that cerium oxide nanoparticles can both decrease the optical density of the LC matrix and increase it depending on the concentration range, which makes it possible to use this effect in various

applications of LC cells. It has been shown that when CeO₂ nanoparticles (10–50 nm) are introduced into a LC medium with the intrinsic luminescence band not shielding the CeO₂ band, under sufficient excitation energy (275 nm) cerium oxide displays photoluminescence with a maximum at ~ 330 nm, which is reproducible in different LC matrices.

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