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Influence of gold nanoparticles on the electro-optical properties of a nematic liquid crystal

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Received December 27, 2024
Revised January 29, 2025
Accepted February 28, 2025

The influence of gold nanoparticles on the electro-optical properties of the nematic liquid crystal ZhK-1289 has been thoroughly investigated. A concentration-dependent shift in the clearing temperature was observed, with a concentration of 0.03 wt% resulting in a decrease of 1 K, while an increase to 0.03 wt% led to a reduction of 7 K. Analysis of the electro-optical dispersion parameters revealed that the most significant change in refractive index anisotropy occurs within the wavelength range of 590−700 nm. Furthermore, the incorporation of gold nanoparticles was found to lower the Frederiks threshold voltage by as much as 15%. These findings underscore the potential of gold nanoparticles to enhance the performance of liquid crystal-based devices, particularly in display technology, antennas, and biosensors.

Keywords: electro-optical properties liquid crystals, gold nanoparticles, dispersion of the anisotropy of the refractive index.

DOI: 10.61011/EOS.2025.03.61162.14-25

Introduction

The application of liquid crystal (LC) materials has been actively expanding in recent decades. In particular, for a long time, displays has been produced on the basis of LC materials [1–4]. Currently, new application areas are being actively developed: phase shifters for 5G antennas [5,6], liquid crystal lenses [7,8], electronic paper [9–11], and systems for pathogen detection and quality control [12–15].

Expanding applications of LC materials require improving the performance and efficiency of the developed liquid crystal-based devices. Two key approaches are used to improve performance: development of new LC materials and matrix modification using nanoscale particles. The second approach has been actively developed over the last decades [1,2,16–26].

Analysis of literature data shows that the effect of nanoparticles on the properties of LC composites significantly depends on their nature. Doping with metal oxide nanoparticles ($BaTiO_3$, Fe_2O_3 and t. e.) [16–22] leads to a 10–25% decrease in refractive index anisotropy, a 5–9% increase of Fredericks threshold voltage, and a reduction of the temperature range of the nematic mesophase. In contrast, the addition of gold nanoparticles [1,23–25] and quantum dots (CdSe, CdS:Mn, etc.) [2,26–28] has been shown to improve the performance characteristics of the LC system. Nanoparticles slightly reduce the temperature range of nematic mesophase (by 1–2 K), increase the refractive index anisotropy by 2−7% for gold nanoparticles and by 5−10% for quantum dots, and also decrease the Fredericks threshold voltage by 5−20%. Gold nanoparticles are of greater interest due to the more environmentally friendly synthesis process. Despite the positive effect, most studies are conducted in limited spectral and temperature ranges, which requires further study to better understand the interaction of nanoparticles with the LC matrix [1,2,16–28]. The impact of nanoparticles on the electro-optical characteristics of LC systems has been actively studied in recent years, and such effects have been described in a number of papers. For example, the addition of gold nanoparticles to the LC matrix leads to an increase of conductivity and a change of dielectric properties, which significantly affects the threshold characteristics and transients in such systems [29].

A key research field in the development of new liquid crystal-based devices involves investigating the influence of nanoparticles on optical parameters across a broad spectral range, as well as determining the electro-optical characteristics throughout the entire temperature range of the nematic mesophase existence. A hardware-software complex for the study of electro-optical parameters of liquid crystals was developed to solve this problem, LC composites with gold nanoparticles were synthesized, and their influence on electro-optical parameters of nematic liquid crystal in a wide range of temperatures and wavelengths was studied.

Materials and methods

The well-studied nematic liquid crystal ZhK-1289 consisting of 8CB (39 wt%), nOCB (30 wt%), Demus's ether (28 wt%), Gray's ether (3 wt%) [1,2,28] was chosen as the LC matrix to study the effect of gold nanoparticles. This LC mixture is characterized by a wide temperature range of

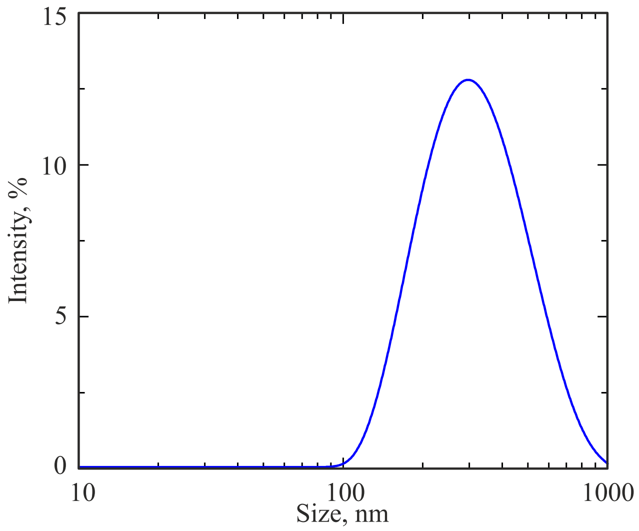

Figure 1. Gold nanoparticle size determination.

nematic mesophase existence (237–337 K) and a refractive index anisotropy value (Δn) of 0.156 at room temperature and a wavelength of 632.8 nm. Gold nanoparticles with a size of 350 nm were added to the mixture. The size of gold nanoparticles was determined by dynamic light scattering method, Fig. 1 shows the size distribution of gold nanoparticles.

Gold nanoparticles were added by mixing a solution of gold nanoparticles in chloroform and nematic liquid crystal followed by evaporation of the solvent. Then, individual cells made of glass with ITO thin film coating were filled with the obtained LC mixtures with the following concentrations: 0.03 and 0.003 wt%. The cells were filled under capillary forces in the isotropic phase of ZhK-1289 ($T = 353$ K). The thickness of the liquid crystal layer in the cells was 6 μm.

Electro-optical parameters were determined using the developed hardware-software complex [29,30]. The complex includes a broadband radiation source Ocean Insight DH-2000, a spectrophotometer S3000, two crossed polarizers, an LC cell arranged in such a way that the angle between the director and the resolved direction of each polarizer is $\pm 45^\circ$, and an STM32F4 generator supplying a sinusoidal signal with a frequency of 1 kHz and an amplitude from 0 to 20 V. The temperature of the LC cell was controlled using a TCM-X107 PID controller with a temperature set point error of 0.01 K and stabilization of 0.02 K.

The well-known expression for light intensity was used to determine the phase difference between the ordinary and extraordinary rays [1,28,31–33]:

$$I = I_0 \sin^2 \frac{\Delta\Phi}{2},$$

where I is the intensity of the passed beam, I_0 is the maximum intensity, $\Delta\Phi$ is the phase delay between the ordinary and extraordinary beams.

Temperatures of phase transitions in the modes of heating and cooling of the studied samples

Sample	$N \to Iso$	Mode
ZhK-1289	333	$T_{heating}$, K
ZhK-1289 + GNP (0.003 wt%)	332	$T_{heating}$, K
ZhK-1289 + GNP (0.03 wt%)	326	$T_{heating}$, K
Sample	$N \to Iso$	
ZhK-1289	332	$T_{cooling}$, K
ZhK-1289 + GNP (0.003 wt%)	331	$T_{cooling}$, K
ZhK-1289 + GNP (0.03 wt%)	325	$T_{cooling}$, K

According to the expression, the volt-contrast response is a dependence with alternating minima and maxima at $\Delta\Phi = 2\pi k$ and $\Delta\Phi = 2\pi k + \pi$, respectively.

Results and discussion

The thermogram provided in Fig. 2, *a* shows that the clearing temperature for the pristine nematic mixture of ZhK-1289 is consistent with literature data. The addition of nanoparticles leads to a shift of the clearing temperature toward a decreasing range of nematic mesophase existence as shown in Fig. 2, *b*.

Analysis of the obtained data shows that at low concentration (0.003 wt%) the phase transition temperature shifts by 1 K. With the increase of the concentration to 0.03 wt%, the effect on the clearing temperature becomes more pronounced, resulting in a shift of the phase transition temperature by 7 K. The obtained values of the temperature of phase transition from nematic mesophase to isotropic phase and back are given in the table. The change of phase transition temperature is attributable to the fact that the size of gold nanoparticles (GNP) is much larger than the size of liquid crystal molecules, which affects the dipole-dipole interactions and reduces the ordering in the composites. This results in a reduction of the energy required to destroy the LC system.

Analysis of the light transmission spectra through the studied sample allows the construction of volt-contrast characteristics (VCC) for arbitrary wavelengths in the visible range. Fig. 3 shows the obtained VCC at 303 K for a wide range of wavelengths. The figure shows that the number of extrema decreases as we move to the long wavelength region, indicating the dispersion of refractive index anisotropy. Analysis of the obtained VCC indicates the variation of light transmission of the LC mixture at different wavelengths.

The maximum delay $\Delta\Phi$, which can be determined using volt-contrast curves, is related to the refractive index

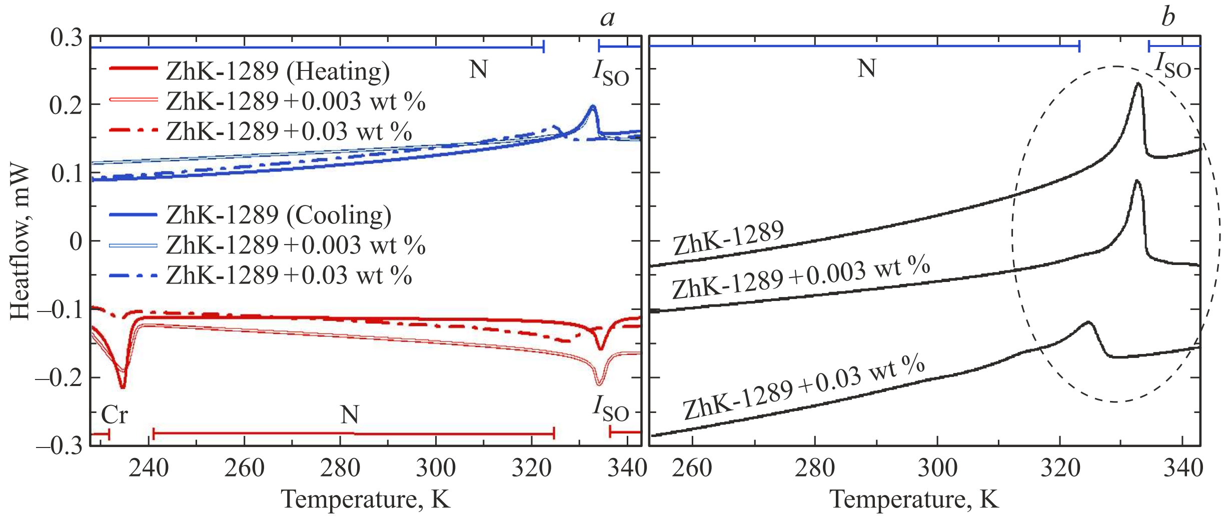

Figure 2. Thermograms of LC composites with gold nanoparticles.

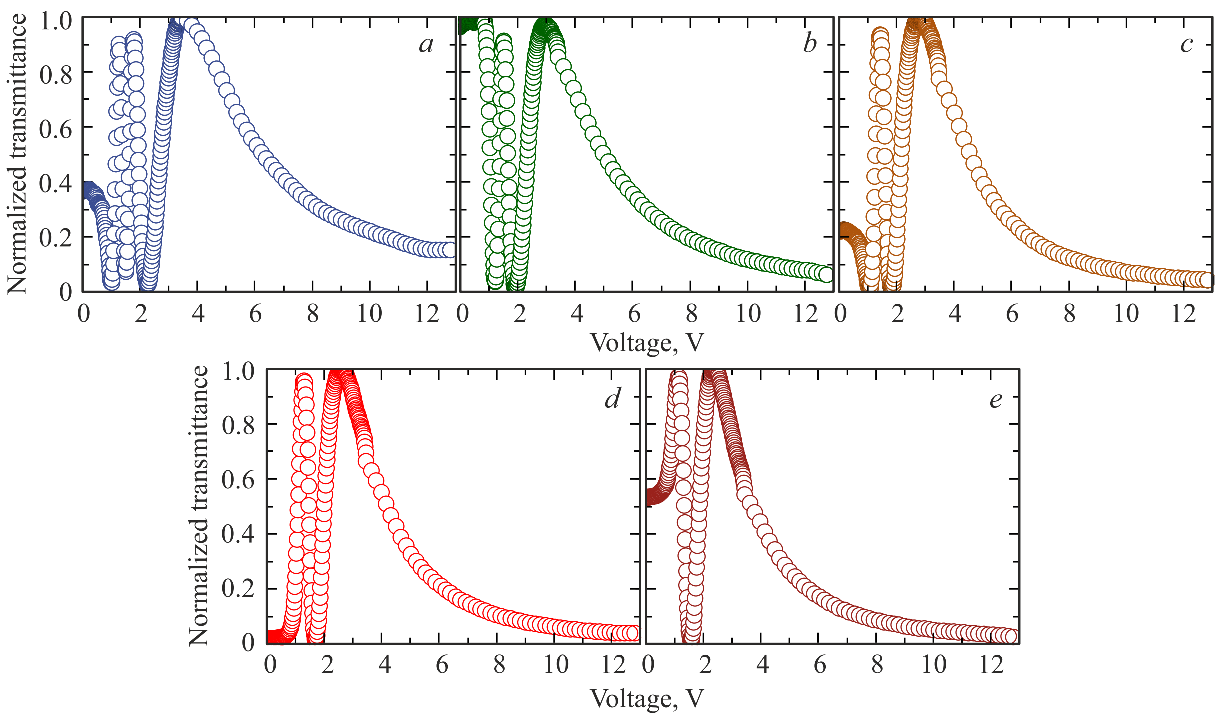

Figure 3. Volt-contrast characteristics of LC mixture of ZhK-1289 with gold nanoparticles (0.003 wt%) at different wavelengths: 480 (*a*, 530 (*b*), 590 (*c*), 632.9 (*d*), 700 nm (*e*).

anisotropy of the liquid crystal Δn according to the well-known expression [28]:

$$\Delta\Phi = \frac{2\pi d \Delta n}{\lambda}.$$

where d is the thickness of the liquid crystal layer, λ is the wavelength.

The determined values of refractive index anisotropy dispersion are shown in Fig. 4. The addition of gold nanoparticles reduces the refractive index anisotropy for both concentrations. The nanoparticles have the greatest effect in the wavelength range 590–700 nm, where the maximum decrease of the refractive index anisotropy of LC composites compared to pristine nematic mixture is observed. In numerical terms, the reduction of the refractive index anisotropy for the LC composite with a concentration of 0.003 wt% gold nanoparticles is 1.3% over the entire spectral range compared to the pristine nematic mixture. Increasing the concentration to 0.03 wt% leads to the formation of aggregates and a decrease of molecular order

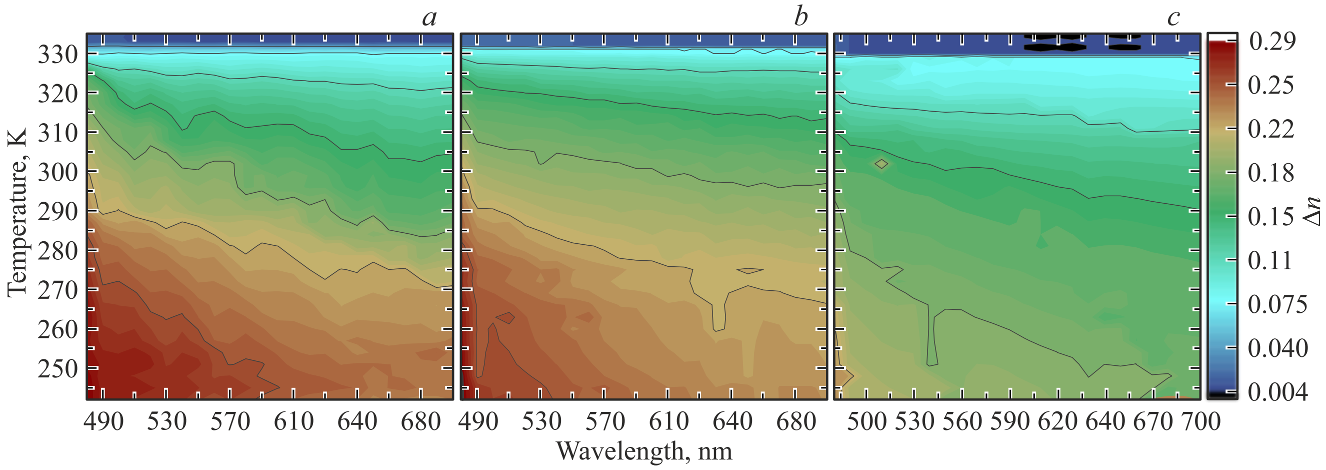

Figure 4. Dispersion dependence of refractive index anisotropy on temperature: (*a*) ZhK-1289, (*b*) ZhK-1289 + 0.003 wt%, (*c*) ZhK-1289 + 0.03 wt%.

in the mixture and, as a consequence, to a 20% decrease of the anisotropy of the refractive index.

One of the most important operating parameters of LC materials along with refractive index anisotropy is the operating voltage, which determines the energy efficiency of the final device. The Fredericks threshold stress was determined at the point of intersection of the horizontal plateau at $\Delta\Phi(U \to 0)$ and the linear section of the dependence $\Delta\Phi/\pi(U)$. Fig. 5 shows a plot of the dependence of the Fredericks threshold voltage of liquid crystal composites on temperature. The analysis of experimental data on the Fredericks threshold stress for the studied LC composites revealed a tendency for decrease of this parameter with the increase of concentration of gold nanoparticles. Specifically, 10% decrease of Fredericks threshold voltage is observed with a concentration of 0.003 wt%, whereas at a concentration of 0.03 wt%, this effect becomes more pronounced and the decrease is 15%.

This phenomenon is attributable to the influence of gold nanoparticles on the electrical properties of the LC matrix. Gold nanoparticles can adsorb free ions, which leads to a change of the electric field distribution in the composites. This results in a decrease of the number of free ions, which leads to a change of the dielectric properties of liquid crystals and a decrease of the Fredericks threshold voltage.

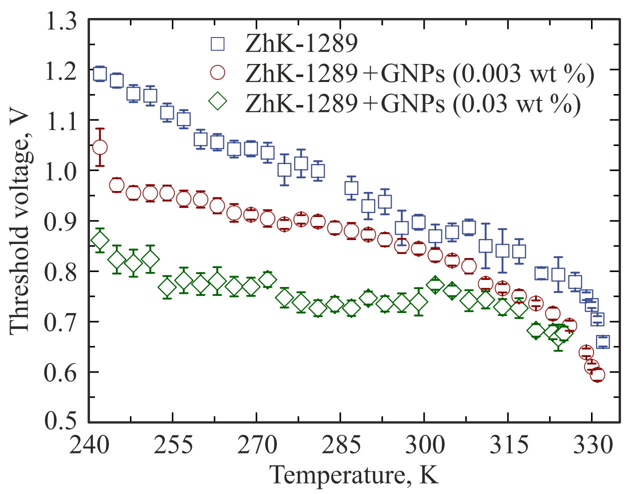

Figure 5. Temperature dependence of the Fredericks threshold voltage of pristine nematic ZhK-1289 mixture and LC composites obtained on its basis with nanoparticle concentrations of 0.003 and 0.03 wt%.

Conclusion

The influence of gold nanoparticles on the electro-optical parameters of ZhK-1289 in the broad spectral (480–700 nm) and temperature (242–335 K) ranges was determined. The results showed that the addition of nanoparticles leads to changes in phase transition temperature, refractive index anisotropy and Fredericks threshold voltage.

The phase transition temperature decreased by 1 K in case of a nanoparticle concentration of 0.003 wt%, and it decreased by 7 K at a nanoparticle concentration of 0.03 wt% which is attributable to the change of dipole-dipole interactions and a decrease of the ordering of the system. A decrease of the refractive index anisotropy was also recorded, especially in the wavelength region of 590–700 nm, with the largest effect at a concentration of 0.03 wt%.

In addition, a decrease of the Fredericks threshold voltage was observed, especially at a concentration of 0.03 wt%, which is attributed to the adsorption of free ions on the gold nanoparticles affecting the electric field and dielectric properties of the matrix. This opens the door to more efficient liquid crystal-based devices with improved performance for display technologies, antennas, and detection systems.

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Translated by A.Akhtyamov