

NONLINEAR OPTICAL RESPONSE OF SMECTIC GLASSES BASED ON COBALT ALKANOATES

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PACS 78.15.+e, 61.30.Gd
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The nonlinear-optical response of anisotropic smectic glasses based on cobalt-alkanoates is studied using the method of dynamic holography. Laser-induced dynamic gratings under the action of nanosecond laser pulses are observed and analyzed for such materials. It is found that a cubic optical nonlinearity of all studied anisotropic glasses is of electronic origin in the nanosecond diapason and caused by a nonlinear polarization of cobalt-alkanoates complexes.

1. Introduction

Metal alkanoates $((C_nH_{2n+1}COO^-)_kMe^{k+})$, where Me^{k+} – metal cation, $C_nH_{2n+1}COO^-$ – alkanoate-anion, $k = 1-3$, $n \geq 3$, can form various states of condensed matter: solid crystalline state, liquid state, liquid crystalline, isotropic and anisotropic glasses [1–4]. Recently, such a variety of metal alkanoates and their phase states was used in order to fabricate optical and nonlinear optical materials, for instance, double-layer cells “photosensitive film – ionic lyotropic liquid crystal” [5], ionic lyotropic liquid crystals doped with electrochromic impurities [5, 6], and mesomorphic glasses with dissolved dye molecules [7].

An alternative way of the development of advanced materials is a study of the fundamental properties of pure mesomorphic metal-alkanoates which consist of d - and f -electron metal ions [1, 8, 9]. Such metal ions are widely used as active centers of laser emission and magnetic, optical and nonlinear-optical materials [1, 9, 10]. Regarding these promising applications, the detailed studies of the physical properties of the transition and rare-earth metal-alkanoates are of the most fundamental and practical importance.

Our previous results show that pure cobalt-decanoate mesomorphic glasses can be used as materials for the pulsed dynamic holographic recording [8, 9]. In this pa-

per, we describe studies of the nonlinear-optical properties of the mesomorphic glasses based on cobalt-alkanoates: 1) homologous series of pure cobalt alkanoates; 2) binary and ternary systems based on cobalt|potassium|lithium octanoates.

2. Materials and Cell Preparation

2.1. Materials

The following types of chemical compounds were used in the studies of nonlinear-optical properties: 1) three representatives of homologous series of cobalt alkanoates $(C_nH_{2n+1}COO^-)_2Co^{2+}$ ($n = 7, 9, 11$); 2) binary systems – $(C_7H_{15}COO^-)_2Co^{2+}|C_7H_{15}COO^-Li^{1+}$, 0.5:0.5 molar ratio, and $(C_7H_{15}COO^-)_2Co^{2+}|C_7H_{15}COO^-K^{1+}$, 0.5:0.5 molar ratio; 3) ternary system – $(C_7H_{15}COO^-)_2Co^{2+}|C_7H_{15}COO^-Li^{1+}|C_7H_{15}COO^-K^{1+}$, 0.5:0.25:0.25 molar ratio.

As was shown in our previous works, all studied materials form the liquid crystal state (Smectic A) [11, 12] under melting. It should be noted that the above-mentioned liquid crystalline materials can be easily vitrified under cooling. Such a vitrified state can be considered as the “frozen” liquid crystal state and is stable for a long time at room temperature (in fact, samples are still in the glass state even after 1 year after their preparation) [12]. For this reason, the studied glasses are anisotropic and can be called “mesomorphic glasses” in contrast to the well-known isotropic glasses.

2.2. Cell preparation

Sandwich-like cells (cell thickness $d_{cell} = 30-100 \mu m$) were filled with the studied liquid crystalline materials at a hot plate at temperatures $T > T_{C-LC}$ (T_{C-LC} –

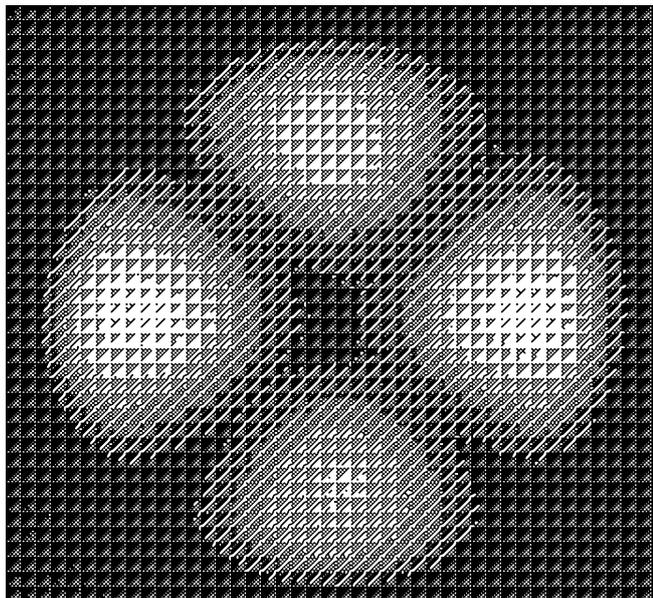


Fig. 1. Typical conoscopic picture of a uniaxial crystal observed for the studied glasses during the experiment which indicates a homeotropic alignment

temperature of the phase transition “crystal–liquid crystal”) using both the capillary technique [11, 12] and the crushing method. After the melting to the liquid crystal state, all samples were cooled to achieve the glass state. It was found (using the method of polarizing microscopy) that all studied materials are homeotropically aligned at non-treated glass substrates.

3. Experimental Methods

Thermal polarizing optical microscopy complemented with the improved conoscopic method were used in order to provide the basic optical characterization of cobalt-alkanoate mesomorphic glasses [13, 14]. In this way, such characteristics as alignment, pretilt angle, and optical quality were measured.

Electronic spectroscopy was used to measure the absorption spectra of mesomorphic glasses in the visible optical diapason (400–700 nm).

Nonlinear-optical properties of the mesomorphic glasses were studied, by using the method of laser-induced dynamic gratings [15, 16]. Measurements were made using the second harmonic of a pulsed Q-switched Nd:YAP laser (TEM₀₀-mode, wavelength $\lambda = 539.8$ nm, pulse duration $t_p = 20$ ns, and the pulse frequency $\nu = 3$ Hz) as a source of the intense coherent radiation. Recorded gratings were investigated in the self-diffraction regime via measuring the diffrac-

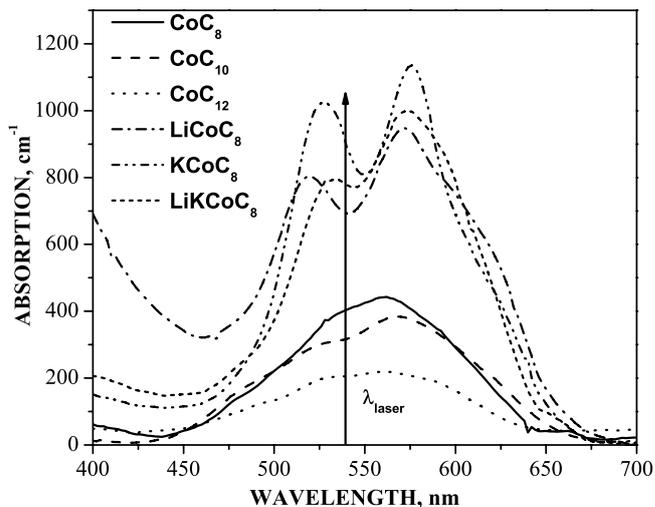


Fig. 2. Absorption spectra of the mesomorphic glasses measured at room temperature. Arrow indicates the wavelength (539.8 nm) of a pulsed laser used in experiments

tion efficiency η (η can be defined as the ratio of the intensity of the first-order diffracted laser beam I_{+1} to the intensity of the incident laser beam $I_{0.1}$: $\eta = (I_{+1})/(I_{0.1})$).

4. Experimental Results and Discussions

4.1. Conoscopic characterization

The improved conoscopic method was used to confirm anisotropic properties of the studied mesomorphic glasses and to determine their birefringence. A typical conoscopic picture of the uniaxial crystal observed for the studied glasses is shown in Fig. 1. Such a result clearly indicates the anisotropic optical properties (optical birefringence) of the mesomorphic glasses and their homeotropic alignment. It was also found (using the crystal rotation method) that the pretilt angle of molecules of a mesomorphic glass cell is in the range 89.9° – 9.5° (homeotropic alignment).

4.2. Absorption spectra

All studied mesomorphic glasses absorb light in the visible optical diapason (500–600 nm, see Fig. 2). The observed spectrum can be considered in terms of ligand field theory [17, 18], as the excitation of cobalt octahedral and tetrahedral complexes. The presence of a broad absorption band with unresolved structure in the cobalt alkanoate mesomorphic glass indicates the coexistence of several coordination forms of Co^{2+} ions:

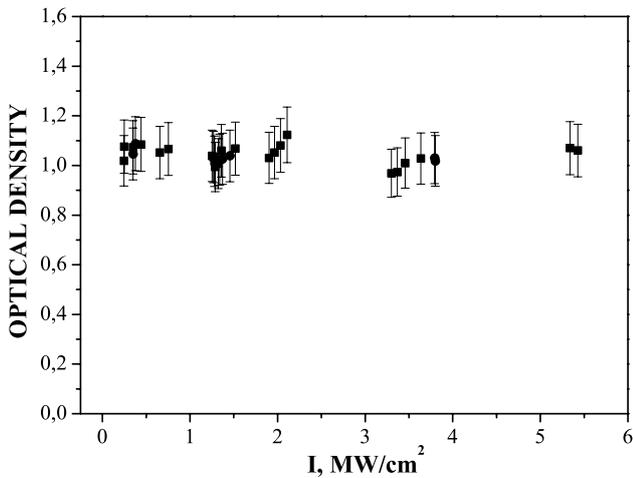


Fig. 3. Typical dependence of the optical density of the mesomorphic glasses on the laser beam intensity for the studied mesomorphic glasses

– the bands with maxima at 530 nm (${}^4T_{1g}({}^4F) \rightarrow {}^4T_{1g}({}^4P)$ transition) and 565 nm (${}^4T_{1g}({}^4F) \rightarrow {}^4A_{2g}({}^4F)$ transition) are typical of octahedrally coordinated Co^{2+} ions;

– in the case of binary systems, the band with a maximum at 620 nm (${}^4A_2({}^4F) \rightarrow {}^4T_1({}^4P)$ transition) is observed, which is typical of tetrahedral complexes.

4.3. Nonlinear transmission and third-order nonlinear-optical response of the mesomorphic glasses

It is found that the optical density D of all studied mesomorphic glasses does not depend on the intensity I of a laser beam (Fig. 3). So, only the linear absorbance of a laser beam should be taken into consideration, by analyzing the experimental results described below.

It is found that all studied materials demonstrate the quadratic dependence of the self-diffraction efficiency versus the intensity: $\eta \sim I^2$ (Fig. 4). Such a dependence indicates the cubic nonlinear-optical response of all studied materials at the nanosecond time diapason.

Studying the erasure kinetics of residual thermal gratings in the microsecond diapason shows the exponential time dependence of the diffraction efficiency in the first diffraction order (Fig. 5). Such a dependence is characteristic of thermal gratings. But, comparing the thermal grating diffraction efficiency η_T with the diffraction efficiency of a grating recorded in the mode of self-diffraction η shows that $\eta_T \ll \eta$ ($\eta/\eta_T \approx 100$).

Laser-induced changes in the refractive index Δn are proportional to the incidence laser beam intensity I :

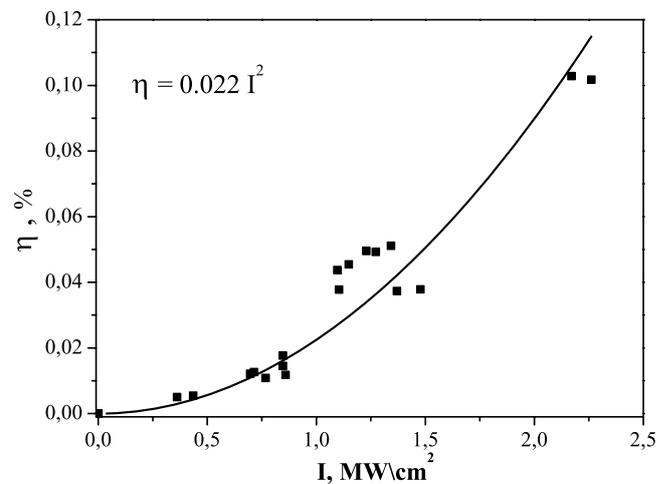


Fig. 4. Typical dependence of the self-diffraction efficiency versus the intensity of incident laser beams for studied mesomorphic glasses

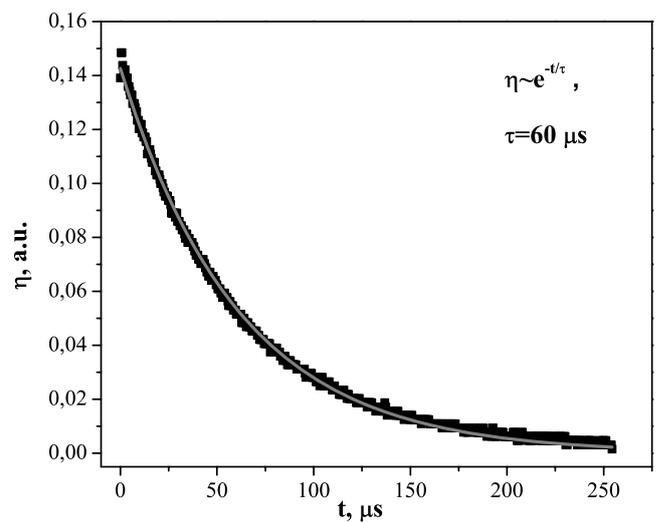


Fig. 5. Typical time dependence of the residual thermal gratings diffraction efficiency for studied mesomorphic glasses

$\Delta n = n_2 I$, where n_2 – nonlinear refractive index which is a macroscopic characteristic of the nonlinear-optical properties of the materials. The nonlinear refractive index can be extracted from the measured values of the self-diffraction efficiency, as it is described in works [12, 16]:

$$n_2 = \frac{\lambda}{\pi d_{\text{eff}} I_0} \sqrt{\frac{\eta}{T}}. \quad (1)$$

Here, λ – wavelength of a laser beam, d_{eff} – effective cell thickness, and T – transmission. In the case of dynamic gratings, $I_0 = m(I_1 + I_2)$, where $m = \frac{2\sqrt{I_1 I_2}}{I_1 + I_2}$, I_1 and

I_2 are the intensities of beams which interfere on the investigated sample, and m – modulation depth. The nonlinear refractive indices of the all studied mesomorphic glasses are collected in Table 1.

The third-order nonlinear-optical response can be caused by various physical mechanisms (e.g., nonlinear electronic polarization, thermal heating, electrostriction, molecular reorientation, *etc.*) [15, 16]. Therefore, the measured value of nonlinear refractive index can be considered as a sum of actual nonlinear refractive indices (each additive in this sum corresponds to a definite physical mechanism).

Cobalt-alkanoate complexes (tetrahedral and octahedral coordinations [17]) can be considered as anharmonic oscillators under applying the external electromagnetic field (mechanism of electronic hyperpolarizability). Such changes in the electronic polarizability of the cobalt-alkanoate complexes can give rise to the third-order nonlinear-optical response.

In addition to the mechanisms of third-order optical nonlinearity described above (changes in the electronic polarizability of cobalt ions under the action of an external electro-magnetic field), the thermal optical nonlinearity also should be taken into consideration, since all studied materials consisting of cobalt complexes absorb light at the laser wavelength (see Fig. 2). So, the measured value of nonlinear refractive index n_2 is the sum of two main additives: the first of them n_2 is of the electronic origin, and the second one $n_2^{\{\text{thermal}\}}$ is of the thermal origin. The next step is to separate the contributions of these considered mechanisms to the measured nonlinear-optical response of smectic glasses.

4.4. Thermal optical nonlinearity

As was mentioned above, in the case of absorbing materials, the thermal optical nonlinearity can contribute to the measured value of n_2 or $\Delta n = n_2 I$:

$$\Delta n = \Delta n_{\text{electronic}} + \Delta n_{\text{thermal}}, \quad (2)$$

$$\Delta n_{\text{thermal}} = \frac{dn}{dT} \Delta T. \quad (3)$$

Let us estimate the contribution of the thermal optical nonlinearity $n_2^{\{\text{thermal}\}}$ to the measured value of n_2 . As can be shown [12, 19–21], the nonlinear refractive index $n_2^{\{\text{thermal}\}}$ caused by the thermal optical nonlinearity can be found as follows:

$$n_2^{\{\text{thermal}\}} = \frac{dn}{dT} \frac{\alpha}{c_p \rho} t_p. \quad (4)$$

Here, $\frac{dn}{dT}$ – thermo-optical constant, ρ – density, c_p – specific heat capacity, t_p – time duration of a laser pulse, and α – linear absorption coefficient.

Using this expression, one can estimate the nonlinear refractive indices caused by only the thermal optical nonlinearity (thermal nonlinear refractive indices) for studied materials (Table 1). In such a way, we estimated the value of $n_2^{\{\text{thermal}\}}$ for mesomorphic glasses to be of the order of 10^{-13} cm²/W. The experimental value ($\sim 10^{-10}$ cm²/W) is by two orders larger than the estimated one. Such a disagreement between the estimation and the experiment allows us to neglect thermal optical nonlinearities on the nanosecond time scale and to consider only the electronic nonlinearity.

4.5. Electronic optical nonlinearity

The macroscopic (third-order electronic susceptibility $\chi^{(3)}$) and microscopic (hyperpolarizability γ_{NL}) nonlinear-optical parameters of the studied mesomorphic glasses can be found, by using the expressions presented below [15, 16]:

$$\chi^{(3)} = \varepsilon_0 c n^2 n_2 = \gamma_{\text{NL}} N L^4. \quad (5)$$

Here, ε_0 – electric constant, n – refractive index, c – light velocity, L – local field factor (for simplicity, we will use the Lorentz local field factor $L = \frac{n^2+2}{3}$), and N – concentration of the nonlinear-optical active cobalt complexes. Using the above-mentioned expressions, the basic nonlinear-optical parameters were extracted from experimental data (Table 2).

4.6. Tuning of the nonlinear-optical properties of the cobalt-alkanoates mesomorphic glasses

As can be seen from Table 2, the susceptibilities $\chi^{(3)}$ of the cobalt-alkanoates mesomorphic glasses are decreasing with increasing the anion length (or smectic bilayer spacing) from 6.65×10^{-16} to 2.64×10^{-16} m² V⁻². Such a decrease is caused mainly by three factors: 1) decrease

Table 1. Nonlinear refractive indices of mesomorphic glasses

	CoC ₈	CoC ₁₀	CoC ₁₂
n_2 , cm ² /W	11.2×10^{-10}	8.3×10^{-10}	4.5×10^{-10}
$n_2^{\{\text{thermal}\}}$, cm ² /W	1.38×10^{-12}	1.14×10^{-12}	0.86×10^{-12}
	CoC ₈ :LiC ₈	CoC ₈ :KC ₈	CoC ₈ :LiC ₈ :KC ₈
n_2 , cm ² /W	4.6×10^{-10}	5.3×10^{-10}	4.6×10^{-10}
$n_2^{\{\text{thermal}\}}$, cm ² /W	2.43×10^{-12}	3.04×10^{-12}	2.68×10^{-12}

of the concentration N of the nonlinear-optical centers (cobalt complexes), 2) decrease of the local field factor L , 3) decrease of the hyperpolarizability γ_{NL} – microscopic characteristics of the nonlinear-optical centers. For such homologous series, the local factor does not contribute sufficiently to the observed decrease of $\chi^{(3)}$ (linear refractive indices of these mesomorphic glasses change very slightly, and, therefore, the local field factor L cannot affect $\chi^{(3)}$). So, a decrease of the concentration N and γ_{NL} are the main factors, which affect the observed decrease of $\chi^{(3)}$ (Table 2).

As was mentioned above, the decrease of $\chi^{(3)}$ correlates with decreasing the concentrations of cobalt complexes. Additionally, it should be noted that the third-order nonlinear optical response of the studied mesomorphic glasses is also affected via interactions of a cobalt ion (coordination center of complex) with the counterion surrounding (carboxyl groups of alkanooate-anions).

5. Conclusions

We have presented the results of systematic studies of the nonlinear-optical properties of the mesomorphic glasses based on cobalt-alkanoate. It is found that such rigid glasses with intrinsic layered structure demonstrate the enhanced third-order nonlinear-optical response ($\chi^{(3)} \sim 10^{-8}$ esu) of the electronic origin (mechanism of laser-induced electronic nonlinear polarization) on the nanosecond time scale. It is shown that the thermal optical nonlinearity can be neglected on the nanosecond time scale for these materials. Based on this, the main nonlinear-optical parameters ($\chi^{(3)}$, γ_{NL}) are recalculated.

It is found that the nonlinear-optical response of the cobalt-containing mesomorphic layered glasses is caused by cobalt-alkanoate complexes as main nonlinear-optical centers, which are arranged into spatial ordered two-dimensional layers. The basic third-order nonlinear-

optical parameters ($\chi^{(3)}$ and γ_{NL}) depend on the cobalt alkanooate concentration (this factor is dominant) and are affected by interactions between cobalt ions and alkanooate-anions (in the case of pure cobalt-alkanoate glasses) or between metal cations and alkanooate-ions (for binary and ternary systems).

Finally, the anisotropic mesomorphic glasses based on cobalt-alkanoates represent a novel type of tunable optical and nonlinear-optical materials: their fundamental physical properties (nonlinear n_2 refractive index, third-order susceptibility $\chi^{(3)}$, and molecular hyperpolarizability γ_{NL}) can be tuned via changing the alkanooate-anion length and by varying the cation composition. Such simple ways open a new avenue in the field of the optical and nonlinear-optical material design.

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Table 2. Basic nonlinear-optical parameters of the mesomorphic glasses

	CoC ₈	CoC ₁₀	CoC ₁₂
$\chi^{(3)}$, m ² · V ⁻²	6.65×10^{-16}	4.92×10^{-16}	2.64×10^{-16}
$\chi^{(3)}$, esu	4.8×10^{-8}	3.5×10^{-8}	1.9×10^{-8}
γ_{NL} , m ² · V ⁻²	8.4×10^{-44}	7.4×10^{-44}	4.9×10^{-44}
γ_{NL} , esu	6.0×10^{-30}	5.3×10^{-30}	3.5×10^{-30}
	CoC ₈ :LiC ₈	CoC ₈ :KC ₈	CoC ₈ :LiC ₈ :KC ₈
$\chi^{(3)}$, m ² · V ⁻²	2.76×10^{-16}	3.1×10^{-16}	2.74×10^{-16}
$\chi^{(3)}$, esu	1.98×10^{-8}	2.25×10^{-8}	1.96×10^{-8}
γ_{NL} , m ² · V ⁻²	4.9×10^{-44}	5.9×10^{-44}	5.0×10^{-44}
γ_{NL} , esu	3.5×10^{-30}	4.2×10^{-30}	3.6×10^{-30}

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Received 22.09.11

НЕЛІНІЙНИЙ ОПТИЧНИЙ ВІДГУК СМЕКТИЧНИХ СТЕКОЛ НА ОСНОВІ АЛКАНОАТІВ КОБАЛЬТУ

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Резюме

У даній роботі наведено результати експериментальних досліджень оптичних та нелінійно-оптичних властивостей мезоморфних стекел алканоатів кобальту. Показано, що досліджені мезоморфні стекла мають чітку гомеотропну орієнтацію молекул та структуру смектичного кристала. При вивченні спектрів поглинання, виявлено, що у мезоморфному склі присутні октаедрична та тетраедрична координації іонів Co^{2+} . Реалізовано та досліджено голографічний запис тонких динамічних ґраток у мезоморфних стеклах алканоатів кобальту. Записані ґратки характеризуються високими значеннями кубічної діелектричної сприйнятливості $\chi^{(3)}$, гіперполяризованості γ_{NL} , коефіцієнта нелінійної рефракції n_2 та мають мікросекундні часи релаксації. Запропоновано фізичний механізм запису, що зумовлений нелінійною електронною поляризованістю, викликану дією інтенсивного лазерного випромінювання на комплекси катіонів кобальту.