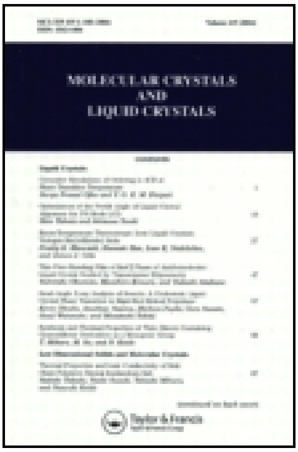

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Nonlinear Optics of Electrochromic and Photosensitive Cells of Ionic Liquid Crystals and Mesomorphic Glasses

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Nonlinear Optics of Electrochromic and Photosensitive Cells of Ionic Liquid Crystals and Mesomorphic Glasses

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We study structural and nonlinear optical properties of lyotropic ionic liquid crystals with electrochromic impurities and mesomorphic glasses of the homological series of Co alkanoates. Nontraditional nonlinear optical mechanisms of these materials are proposed. The investigated cells are characterized by high value of optical nonlinearity ($\chi^{(3)} \sim 10^{-7}$–10^{-8} esu), fast recording and relaxation of dynamical holographic gratings. They are perspective to applying in high-speed telecommunication systems.

Keywords Mesomorphic glasses; nonlinear optics; photosensitive cells

1. Introduction

Liquid crystals are widely used for creation of novel composite materials with new functional properties. In the present paper we consider nonlinear optical properties of novel materials based on metal alkanoate lyotropic liquid crystals and mesomorphic glasses. Metal alkanoate salts are able to form lyotropic and thermotropic ionic liquid crystals, as well as mesomorphic glasses at room temperature [1]. Metal alkanoates are self-organized in smectic A bi-layer structure that consist of hydrophobic alkanoate chains and electrostatic layers, which include metal cations and carboxyl anions. Cells based on metal alkanoates with electo-photosensitive centers exhibit fast nonlinear optical response under the action of pulsed laser radiation.

We investigate nanocomposite cells of potassium caprylate ($C_7H_{15}COOK$) lyotropic liquid crystals with electrochromic viologen molecules. Electrochromic impurities (viologens) were studied in solution [2,3], in polymeric matrixes [4], in liquid crystals [5] and in crystalline state [6]. They posses different physical-chemical

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Address correspondence to G. Klimusheva, Institute of Physics of NAS Ukraine, Prospect Nauki 46, Kiev, Ukraine. Tel.: (38 044) 524-7841; Fax: (38 044) 525-1589; E-mail: klimush@iop.kiev.ua properties such as electro-, thermo- and photochromism. We have investigated nonlinear optical response of electrochromic viologens in metal-alkanoate LILC matrix [7]. In the present paper we discuss fast nonlinear optical mechanism being original for the colored cells of LILC-viologen.

We study structure and nonlinear optical properties of homologous series of cobalt (II) alkanoates, namely caprylate, decanoate and laurate $(Co^{2+}(C_nH_{2n+1}COO)_2^-$, where n-7, 9, 11). These thermotropic ionic liquid crystals (ILC) and their mesomorphic glasses (MG) are coloured due to the presence of cobalt ions. We propose and discuss the fast nonlinear optical mechanism in these materials connected with nonlinear polarizability of Co-alkanoate coordination substances.

For investigation of nonlinear optical response of our materials we use both the dynamic holographic method and the nonlinear transmission measurements. The two-beam scheme is applied for the dynamic grating recording [8]. The second harmonic radiation of pulsed Q-switching Nd:YAP laser (Tem00-mode, laser wavelength $\lambda = 539{,}8$ nm, the pulse duration $\tau = 20$ ns, the pulse repetition rate $\nu = 3$ Hz) is used. We also apply a continuous He-Ne laser (power P = 2 mW, $\lambda = 633$ nm) to investigate the dynamic grating relaxation. By measuring the diffraction efficiency of the dynamic grating we study the nonlinear mechanisms that lead to the third-order optical susceptibility in the prepared cells.

Fast nonlinear optical response in thin films have been studied widely during last decades due to potential applications in optical telecommunications. Our materials with their nonlinear characteristics can compete with such materials as semiconductor quantum wires (InSb, HgCdTe,CdS) [9], metal nanoparticle composites in dielectric matrix (Au:SiO_2, Au:Al_2O_3, Au:$Ba_{0.6}Sr_{0.4}TiO_3$) [10], conjugative polimers with TiO_2 nanoparticles (PMMA – TiO_2) [11]. But they have advantages of their low cost and simplicity of preparation due to their chemical synthesis.

2. Structure of LILC with Electrochromic Impurity and Metal Alkanoate MG

The structure of both pure and doped LILC of potassium caprylate had been investigated earlier by small angle X-ray scattering technique. LILC of potassium caprylate forms smectic A phase. It was found that the viologen with used concentration 2–4 weight % does not disturb the LC ordering, so admixture molecules are naturally built up into the matrix.

Specific feature of thermotropic metal alkanoate ionic liquid crystals is that they have ability of subcooling to form ionic smectic mesomorphic glasses at room temperature. For example the small angle X-ray diffraction analysis of the $Co^{2+}(C_7H_{15}COO)_2^-$ structure by heating and cooling is shown on the Figure 1. Such MGs are characterized by ordering and good optical quality. The bilayer spacing d_l decreases sharply at the phase transition temperature $T_{C\text{-}LC}$ that takes place under heating of metal alkanoate salts. After that liquid crystals are cooled and d_l is still the same as at temperature $T > T_{C\text{-}LC}$. It means that under cooling procedure liquid crystalline smectic structure has "frozen" into vitrified state.

Conoscopic method was used to confirm anisotropic properties of the studied mesomorphic glasses and to determine their birefringence. Typical conoscopic picture of the uniaxial crystal was observed for studied glasses during experiment. Such result clearly indicates anisotropic optical properties (optical birefringence) of the metal alkanoate mesomorphic glasses. Also it was found (using crystal

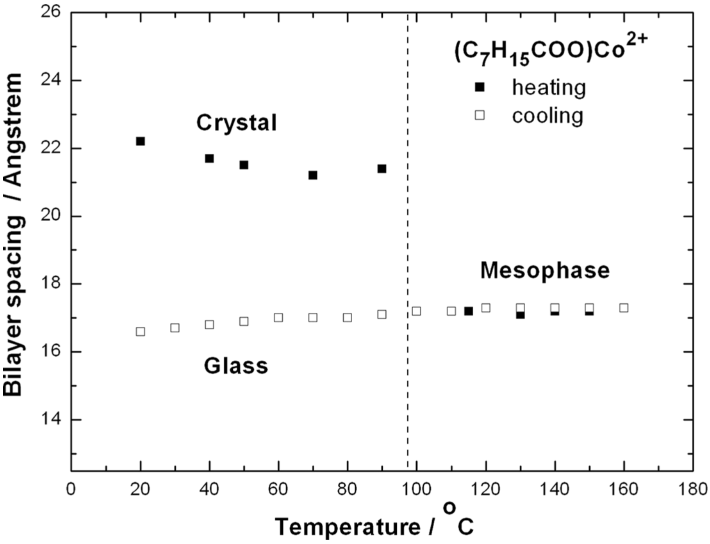

Figure 1. Temperature dependence of the bilayer spacing for cobalt caprylate.

rotation method) that pretilt angle of molecules of the mesomorphic glasses is in the range 89.9°–89.5° (homeotropic alignment).

3. Absorption Spectra

The potassium caprylate is mixed with water in the proportion of 1:1 to form a lyotropic ionic liquid crystal. Electrochromic impurities of viologens are dissolved in the LILC matrix (2–4 wt.%). Two different viologens are used, namely: (1) N, N′-diheptyl-4,4′-bipyridilium dibromide ($HB^{2+}2Br^-$) and (2) N,N′-di(2-carboxy-ethil)-4,4′-bipyridilium dichloride ($CEB^{2+}2Cl^-$). The common structural formula for both viologens is the following:

where **R** is a substitute, **A** is a counterion. In the case of $HB^{2+}2Br^-$ $\mathbf{R} = C_7H_{15}$, $\mathbf{A}^- = Br^-$ and $\mathbf{R} = (CH_2)_2COOH$, $\mathbf{A}^- = Cl^-$ for $CEB^{2+}2Cl^-$.

It is known that two-charged bipyridyl dication of viologen reduces in two steps under the action of electric field capturing one electron on each stage. At the first stage the one-electron reduction of a bipyridyl dication into radical cations takes place. At the second stage a radical cation catches one more electron and transforms into a biradical, which instantly turns into a neutral molecule with plane quinoid structure. Biradicals could interact with initial ones, thus forming dimers and even bigger associates. LILC matrix practically doesn't influence the oxidation-reduction reactions of viologens, which take place near electrodes. We observe the adsorption of viologen molecules on the cathode to form thin film of viologen redox products under the external electric field. The adsorption of viologen layer on the cathod is more pronounced for $HB^{2+}2Br^-$ than for $CEB^{2+}2Cl^-$. Our estimations show that a layer formed on the cathode under the action of direct electric field has thickness not bigger than 400 nm.

Without applying the electric field LILC-viologen samples do not absorb light in the visible region. The one-electron reduction of the viologen molecule takes place on applying the voltage of 2,5 V. The sample obtains typical for radical cations blue colour that is approved by the appearance of a characteristic band in the electron absorption spectra with the maximum of 605 nm (Fig. 2, curve 1).

With the subsequent increasing of the voltage up to 3 V we observe the drastic fall down of the absorption band, and the sample again becomes almost transparent in visible region. These changes correspond to the second reduction stage with forming of biradicals and neutral molecules with plane quinoid structure. After increasing the voltage value up to 4 V the sample gets red color and the band with the maximum on 520 nm appears in the spectrum that indicates the appearance of the dimers (Fig. 2, curve 2). This process is due to moving of the initial molecules from deeper layers of a sample to the cathode under the action of the electric field and bond with reduced biradicals to form the dimers.

All studied mesomorphic glasses absorb light in the visible optical diapason (500–600 nm, Fig. 3). The observed absorption can be considered in terms of ligand field theory [12], as the excitation of cobalt octahedral complexes.

Let us consider absorption properties of the homologous series of cobalt alkanoates CoC8 – CoC10 – CoC12. As can be seen from Figure 3, the absorption coefficient α is decreasing monotonously from 400 cm^{-1} to 200 cm^{-1} in the case of homologous series of cobalt alkanoates: α (CoC8) > α (CoC10) > α (CoC12). Such decreasing in optical absorbance is caused mainly by two factors: (1) the decreasing of cobalt complexes concentration for the series CoC8 – CoC10 – CoC12, (2) the decreasing of *d-d* transition dipole moments $\mu_{d\text{-}d}$ for such series [12]: $\mu_{d\text{-}d}$(CoC8) > $\mu_{d\text{-}d}$(CoC10) > $\mu_{d\text{-}d}$(CoC12).

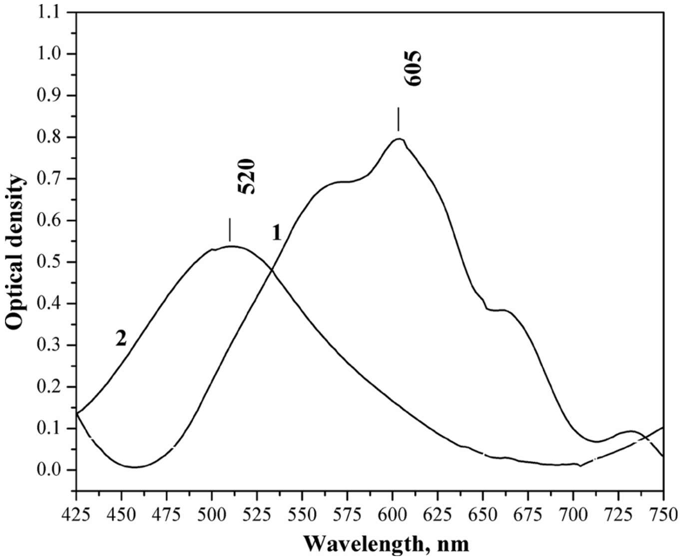

Figure 2. Absorption spectrum of LILC doped with HB^{2+} 2Br^{-} under the action of the electric field. Curve 1 corresponds to the voltage value of U = 2.5 V, curve 2 – to U = 4 V.

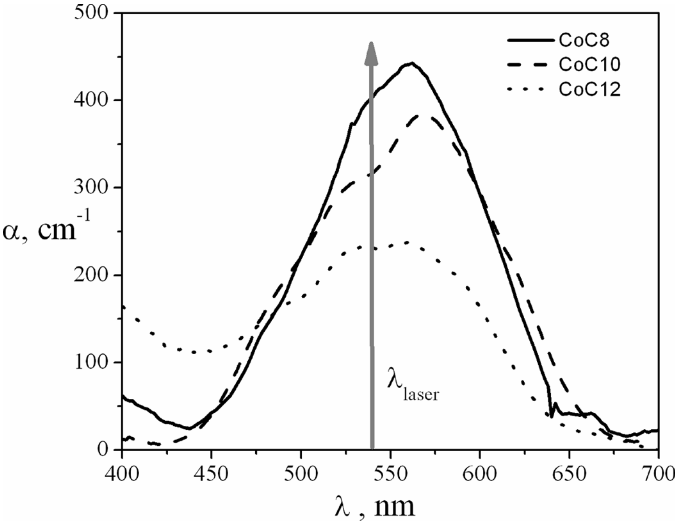

Figure 3. Absorption spectra of the metal alkanoates mesomorphic glasses measured at room temperature. Arrow indicates wavelength (539.8 nm) of the pulsed laser used in nonlinear-optical experiments.

4. Third-Order Nonlinear-Optical Response of the Electrochromic LILC Cells and Mesomorphic Glasses

All investigated samples demonstrate recording of holographic dynamical gratings under the action of a laser pulse. Although the laser wavelength lies on the absorption band of the materials, the heating nonlinear mechanism is negligibly small there because smectic ionic metal alkanoate matrix provides fast heat relaxation.

Based on the analysis of the absorption spectra of viologen's coloured systems we proposed the model of reversible photoconversion of dimers into radical cations under the action of an intense laser radiation. According to the model of the photoconversion a holographic grating is recorded as a result of spatial modulation and different linear polarization between the dimers and the radical cations taking into account that the number of both the dimers and the radical cations is changing under the excitation of strong laser radiation. The scheme of energy levels of the dimers and the cation radicals and possible transitions between them under the laser pulse action is shown on Figure 4. Calculated dependences of the grating diffraction efficiency on the intensity are described the experimental results [7].

It is worth emphasizing that ionic lyotropic liquid crystal plays a significant role in the investigated systems LILC-viologen: 1) as the consequence of a planar orientation of LILC molecules, admixture molecules are also planar oriented; this facilitates the electric field-stimulated adsorption of viologen molecules on the cathode, electron capture (reduction) and formation of photosensitive radical cations and dimers; 2) high viscosity and elastic properties of LILC promote maintenance of a morphology of a thin photosensitive layer during the holographic recording (that is no ablation of viologen molecules to a LILC volume); 3) a heat contact between viologen layer and LILC causes the recording of just a dynamical grating. LILC using is also convenient from a technological point of view: LILC does not flow as a liquid because of its great viscosity.

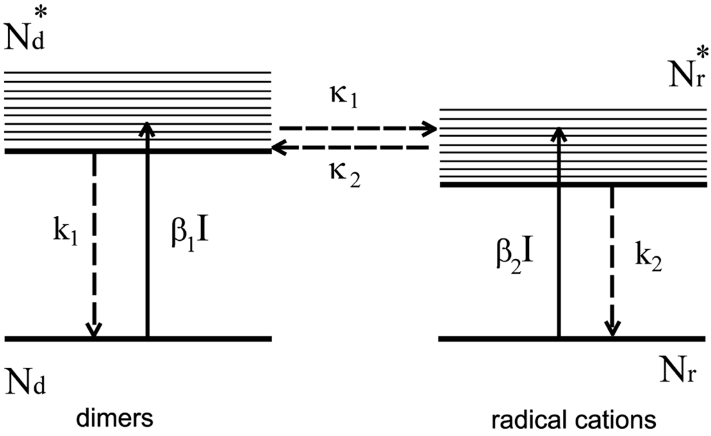

Figure 4. The scheme of ground and excited states of dimers and radical cations. k_1 and k_2 are the probabilities of nonradiactive transition from excited to ground states for the dimers and the radical cations correspondently, κ is the probability of the photoconversion between excited states, $\beta = A\sigma/h\nu$, A is the quantum yield, σ is the absorption cross-section, $h\nu$ is the energy of a photon, I is the radiation intensity.

Let's now consider the nonlinear mechanism in Co alkanoate mesomorphic glasses. It was found that optical density D of all studied mesomorphic glasses did not depend on the intensity I of the laser beam (Fig. 5). So, only linear absorbance of the laser beam should be taken into consideration for analyzing experimental results described below.

It was found that all studied MGs demonstrate quadratic dependence of the self-diffraction efficiency versus intensity: $\eta \sim I^2$ (Fig. 6).

The obtained dependence indicates cubic nonlinear-optical response of all studied MGs in nanosecond time diapason: laser-induced changes of refractive index Δn

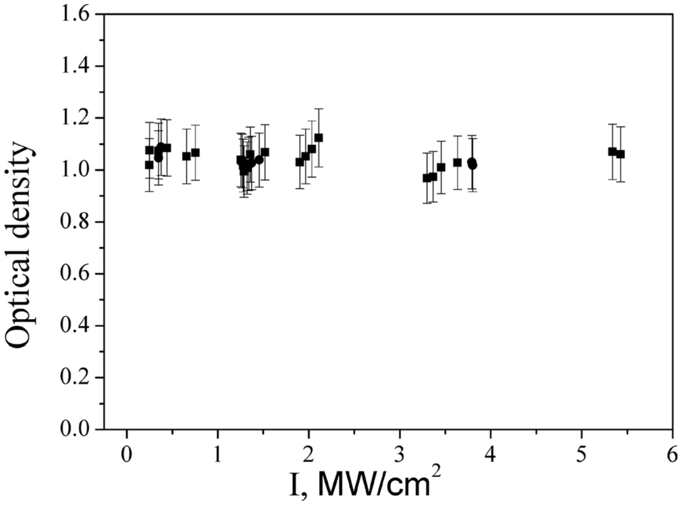

Figure 5. Typical dependence of the optical density of the mesomorphic glasses of cobalt laurate on laser beam intensity.

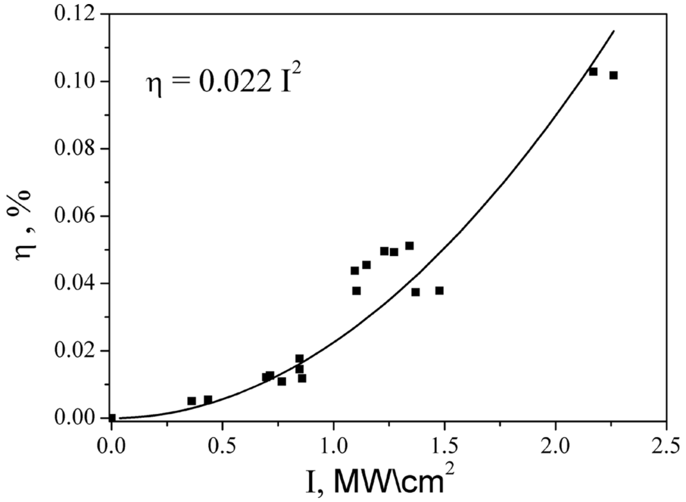

Figure 6. Typical dependence of the self-diffraction efficiency versus intensity of the incident laser beams for cobalt laurate.

are proportional to the incidence laser beam intensity I: $\Delta n = n_2 \cdot I$, 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 diffraction efficiency η as follows:

$$|n_2| = \frac{\lambda}{\pi \cdot d_{eff} \cdot I_0} \cdot \sqrt{\frac{\eta}{T}} \tag{1}$$

where λ is the wavelength of the laser beam, I_o is the laser beam input intensity, $d_{eff} = (1 - e^{-\alpha d})/\alpha$ is the effective cell thickness, T is the transmission.

Nonlinear refractive indexes of the studied mesomorphic glasses are collected in Table 1. It should be noted that for all studied materials observed optical nonlinearity is caused by the presence of the cobalt-alkanoate complexes. Cobalt-alkanoate complexes (dodekahedral or octahedral coordination [12]) can be considered as anharmonic oscillators under applying of the external electro-magnetic field (the mechanism of the electronic hyperpolarizability). Such changes in the electronic polarizability of the cobalt-alkanoate complexes can give rise to the third-order nonlinear-optical response.

Table 1. Measured nonlinear refractive indexes of the studied mesomorphic glasses, their absorption coefficients, and calculated thermal nonlinear refractive indexes

	CoC_8	CoC_{10}	CoC_{12}
n_2, cm^2/W (measured)	$11.2 \cdot 10^{-10}$	$8.3 \cdot 10^{-10}$	$4.5 \cdot 10^{-10}$
n_2, a.u. (measured)	2.49	1.84	1
$n_2^{\{thermal\}}$, a.u. (calculated)	1.75	1.38	1
α, cm^{-1} ($\lambda = 539.8$ nm)	404.2	317.6	230.9

In addition to the mechanisms of the electronic hyperpolarizability, thermal optical nonlinearity also should be taken into consideration as all studied materials consisting of cobalt complexes absorb light at laser wavelength (Fig. 2). Effective cell thickness d_{eff} and thus $n_2^{\{thermal\}}$ is proportional to the absorption coefficient α of the material. Using this expression, one can estimate nonlinear refractive indexes caused by only thermal optical nonlinearity (thermal nonlinear refractive indexes) for studied materials. The results of such calculations and their comparison with the experimental data are shown in Table 1. As can be seen from Table 1, calculated data do not fit experimental results. Such disagreement between calculations and experiments allows us to neglect thermal optical nonlinearities at nanoseconds time scale and take into account only electronic nonlinearity.

Macroscopic (third order electronic susceptibility $\chi^{(3)}$) and microscopic (hyperpolarizability γ_{NL}) nonlinear-optical parameters of the studied mesomorphic glasses can be found using expressions described below [13,14]:

$$\chi^{(3)} = \varepsilon_0 \cdot c \cdot n^2 \cdot n_2 = \gamma_{NL} \cdot N \cdot L^4 = \gamma_{NL} \cdot N \cdot \left(\frac{n^2+2}{3}\right)^4 \qquad (2)$$

where ε_0 – electric constant, n – refractive index, c – light velocity, L – local field factor (for simplicity we will use Lorenz local field factor $L = (n^2+2)/3$), N – concentration of the nonlinear-optical active complexes ($N = m \cdot N_A / V \cdot \mu = N_A \cdot \rho/\mu$, where m – sample mass, N_A – Avogadro constant, V – sample volume, μ – compound molar mass, ρ – density). Using the expressions mentioned above basic nonlinear-optical parameters were received from the experimental data (Table 2).

As can be seen from Table 2, the susceptibilities $\chi^{(3)}$ of the homologous series of cobalt alkanoate CoC8 – CoC12 are decreasing with the increasing of anion length (or smectic bilayer spacing) from $6.65 \cdot 10^{-16}$ to $2.64 \cdot 10^{-16}\,\mathrm{m^2 \cdot V^{-2}}$. Such decrease is mainly caused by three factors: 1) the decreasing of the concentration N of the nonlinear-optical centers (cobalt complexes), 2) the decreasing of the local field factor L, 3) the decreasing of the hyperpolarizability γ_{NL}, which is a microscopic characteristic of the nonlinear-optical centers. For such homologous series local factor does not contribute sufficiently to the observed decreasing of the $\chi^{(3)}$. So, decreasing of the concentration N and γ_{NL} are the main factors which affect the observed decreasing of $\chi^{(3)}$ (Table 2). It means that cobalt-alkanoate complexes are photosensitive centers which determine also the nonlinear-optical response of the mesomorphic glasses at nanosecond time scale. As was mentioned above, the decreasing of $\chi^{(3)}$ correlates with cobalt complexes concentration decreasing.

Table 2. Nonlinear optical parameters of the studied mesomorphic glasses

	CoC8	CoC10	CoC12
$\chi^{(3)}$, $\mathrm{m^2 \cdot V^{-2}}$	$6.65 \cdot 10^{-16}$	$4.92 \cdot 10^{-16}$	$2.64 \cdot 10^{-16}$
$\chi^{(3)}$, esu	$4.8 \cdot 10^{-8}$	$3.5 \cdot 10^{-8}$	$1.9 \cdot 10^{-8}$
γ_{NL}, $\mathrm{m^5 \cdot V^{-2}}$*	$8.4 \cdot 10^{-44}$	$7.4 \cdot 10^{-44}$	$4.9 \cdot 10^{-44}$
γ_{NL}, esu*	$6.0 \cdot 10^{-30}$	$5.3 \cdot 10^{-30}$	$3.5 \cdot 10^{-30}$

*Hyperpolarizabilities γ_{NL} is calculated per one complex containing cobalt ion.
$\chi^{(3)}(esu) = \frac{9}{4\cdot\pi} \cdot 10^8 \chi^{(3)}(SI), \gamma_{NL}(esu) = \frac{9}{4\cdot\pi} \cdot 10^{14} \gamma_{NL}(SI)$.

Summarizing, nonlinear-optical response of the mesomorphic glasses based on cobalt-alkanoate can be tuned via changing of alkanoate-anion length (or smectic bilayer spacing) so that fundamental nonlinear-optical parameters ($\chi^{(3)}$, γ_{NL}) are increasing when alkanoate-anion length (or smectic bilayer spacing) is decreasing.

5. Conclusions

Obtained experimental results prove that LILC-electrochromic viologen systems and mesomorphic glasses based on cobalt-alkanoates are new promising nonlinear-optical materials. The proposed mechanism of reversible photoconversion of viologens dimer into radical cations explains well the dynamic holographic experiments in the systems LILC-viologen. It was found that rigid Co-alcanoate MGs demonstrate high third-order nonlinear-optical response ($\chi^{(3)} \sim 10^{-8}$ esu) of an electronic origin (mechanism of the laser-induced electronic nonlinear polarization) at nanosecond time scale. Also it was shown that thermal optical nonlinearity could be neglected at nanosecond time scale for these materials. Based on this, the main nonlinear-optical parameters ($\chi^{(3)}$, γ_{NL}) were calculated.

It was found that cobalt-alkanoate complexes are main nonlinear-optical centers responsible for the nonlinear-optical response of cobalt-containing MG. Basic third-order nonlinear-optical parameters ($\chi^{(3)}$, γ_{NL}) depend on cobalt alkanoate concentration (this factor is dominant) as well as on surround interactions between cobalt ions and alkanoate-anions. This way, anisotropic mesomorphic glasses based on cobalt-alkanoates represent a novel type of tunable optical and nonlinear-optical materials: their fundamental physical properties (linear absorption coefficient α, linear (n) and nonlinear (n_2) refractive indexes, third-order susceptibility $\chi^{(3)}$, and molecular hyperpolarizability γ_{NL}) can be tuned via changing of the alkanoate-anion length (or smectic bilayer spacing). Such simple ways open a new field in the optical and nonlinear-optical material design.

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References

[1] Mirnaya, A., & Volkov, S. V. (2003). In: *Green Industrial Applications of Ionic Liquids, NATO Science Series II (Mathematics, Physics, and Chemistry)*, Rogers, R. D., *et al.* (Ed.), Kluwer: Dordrecht, 439.

[2] Shelepin, I. V., & Ushakov, O. A. (1975). *J. Phys. Chem.*, *XLIX*, 1736.

[3] Gratchev, V. N., Zhdanov, S. I., & Supin, G. S. (1978). *Electrochem.*, *XIV*, 1353.

[4] Monk, P. M. S., Fairweather, R. D., Ingram, M. D., & Duffy, J. A. (1993). *J. Electroanal. Chem.*, *359*, 301.

[5] Bordyug, A. B., Polishchuk, A. P., Klimusheva, G. V., Tolochko, A. S., Mirnaya, T. A., & Yaremchuk, G. G. (2005). *Rus. J. Phys. Chem.*, *79*, 866.

[6] Bokman, T. M., & Kochi, J. K. (1990). *J. Org. Chem.*, *55*, 4127.

[7] Bordyuh, A. B., Garbovskiy, Yu. A., Bugaychuk, S. A., Klimusheva, G. V., Mirnaya, T. A., Yaremchuk, G. G., & Polishchuk, A. P. (2009). *Opt. mat.*, *31*, 1109–1114.

[8] Klimusheva, G., Bugaychuk, S., Garbovskiy, Yu., & Kolesnyk, O. (2006). *Opt. Lett.*, *31*, 235–237.

[9] ■ (1985). *J. Opt. Soc. America B, Excitonic Optical nonlinearities, special issue*, Vol. 2, N 7.

[10] Cong Chen, Tingyin Ning, Yueliang Zhou, Dongxiang Zhang, Pei Wang, Hai Ming, & Guozhen Yang (2008). *J. Phys. D: Appl. Phys.*, *41*, 225301.

[11] Elim, H. I., Ji, W., Yawono, A. H., Xue, J. M., & Wang, J. (2003). *Appl. Phys. Lett.*, *82*, 2691.

[12] Volkov, S. V., & Yatsimirskii, K. B. (1977). *Spectroscopy of Molten Salts [in Russian]*, Naukova Dumka: Kiev.

[13] Eichler, H. J., Gunter, P., & Pohl, D. W. (1986). *Laser-Induced Dynamic Gratings*, Springer-Verlag: Berlin, Heidelberg, 256.

[14] ■ (1998). In: *Characterization Techniques and Tabulations for Organic Nonlinear Optical Materials*, Kusyk, M. G. & Dirk, C. W. (Eds.), Marcel Dekker: 894.