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Tunable optical and nonlinear optical response of smectic glasses based on cobalt alkanoates

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The nonlinear optical response of anisotropic smectic glasses based on cobalt alkanoates has been studied using dynamic holography. Laser-dynamic gratings induced by the action of nanosecond laser pulses were observed and analysed for such materials. It was found that the cubic optical nonlinearity of all the anisotropic glasses studied had an electronic origin in the nanosecond range, caused by nonlinear polarisation of the cobalt alkanoate complexes. Fundamental optical (refractive index and absorption coefficient) and nonlinear optical (nonlinear susceptibility and polarisability) parameters of mesomorphic glasses based on cobalt alkanoates could be tuned by varying the length of the alkanoate anion chain, thereby determining the interlayer smectic distance.

Keywords: metal alkanoates; smectic glasses; third-order nonlinear optical response

1. Introduction

Metal alkanoates, $(C_nH_{2n+1}COO^-)_kMe^{+k}$, in which Me^{+k} is a metal cation, $C_nH_{2n+1}COO^-$ is an alkanoate anion, and $k = 1$–3 and $n \geq 3$, exhibit almost all states of condensed matter, including the solid crystalline state (including plastic crystals), the liquid state (molten salts, and even ionic liquids), the liquid crystalline state (for example, both thermotropic and lyotropic liquid crystals), isotropic and anisotropic glasses, and also low-dimensional systems such as Langmuir–Blodgett films [1–4]. Recently, a variety of metal alkanoates and their various phase states have been used to fabricate optical and nonlinear optical materials, for instance double-layer cells such as "photosensitive film – ionic lyotropic liquid crystal" [5], ionic lyotropic liquid crystals doped with electrochromic impurities [5, 6], and mesomorphic glasses containing dissolved dye molecules [7]. It may be noted that all the composite materials mentioned can also be considered to be homogeneous or inhomogeneous "guest–host" systems, the guest being photosensitive dopants or films with strong and rapid nonlinear optical response, and the host being soft or rigid mesomorphic ionic matrices which can be used as orienting, holding, viscoelastic, transport or heat-conducting anisotropic media [5–9]. Such novel guest–host composite materials exhibit rapid ($\sim$ ns–ps) and sufficiently strong ($\chi^{(3)}$ $\sim$10–8 esu) cubic nonlinear optical response, and are promising for a variety of applications.

An alternative method of developing such advanced materials is by studying the fundamental properties of the pure mesomorphic metal alkanoates which consist of *d*- and *f*-electron metal ions [1, 8, 9]. Such metal ions (including metal alkanoates) are widely used as active centres for laser emission, and in magnetic, optical and nonlinear optical materials [1, 9, 10]. With regard to these promising applications, a detailed study of the physical properties of the transition and rare earth metal alkanoates is of considerable fundamental and practical importance.

Our previous results have shown that pure cobalt decanoate mesomorphic glasses can be used as materials for pulsed dynamic holographic recording [8, 9]. In the present paper we present the results of a systematic study of the nonlinear optical properties of mesomorphic glasses based on pure cobalt alkanoates, with different alkanoate anion chain length.

2. Materials and cell preparation

2.1 Materials

Cobalt alkanoates (caprylate, decanoate or laurate) were prepared by metathesis by adding saturated aqueous solutions of Co(II) nitrate (Fluka, puriss grade) to a solution of a potassium alkanoate in water. The compounds obtained were washed repeatedly with hot water and dried in a vacuum oven at 50°C for 24 h. The IR spectra of the resulting salts confirmed the absence of water, carboxylic acid and nitrates.

The phase transition temperatures of the salts synthesised were in good agreement with the literature [11, 12]. For instance, cobalt caprylate, CoC_8, melts at 95°C to form a smectic mesophase, which

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is a birefringent liquid with feebly marked microscopic texture, apparently due to a strong tendency to homeotropic orientation of the liquid-crystalline domains; this clears at 164°C, which agrees with the literature [11]. On isotropic melting, signs of decomposition occur close to 200°C. The cobalt caprylate mesophase vitrifies on cooling. Cobalt decanoate, CoC_{10}, exhibits a solid–solid transition at 81°C and melts at 107°C to form a smectic mesophase [12]. It was not possible in this case to define the temperature at which the mesophase clears, due to decomposition above 200°C. The mesophase vitrifies on cooling.

Cobaltlaurate, CoC_{12}, melts to form a smectic mesophase at 67°C. It was not possible to define the temperature of clearing since the mesophase texture was pseudo-isotropic when observed by polarised light, apparently due to a strong tendency towards homeotropic orientation of the liquid-crystalline domains. The mesophase again vitrified on cooling.

Such a vitrified state can be considered as a "frozen" liquid crystalline state and remains stable at room temperature over a prolonged period – indeed samples are still in the glassy state even a year after preparation. Owing to this, the glasses studied are anisotropic and can be described as "mesomorphic glasses", in contrast to the well-known isotropic glasses.

2.2 *Cell preparation*

Sandwich-like cells (cell thickness 30–100 μm) were filled with the liquid crystalline material under study at a hot-plate temperature $T > T_{C\text{–}LC}$, in which $T_{C\text{–}LC}$ is the temperature of the phase transition, crystal to liquid crystal, using both a capillary technique [13, 14] and the "pushing" method, in which the crystal powders are melted in the lower glass substrate and then covered with the upper substrate at the same temperature. Cell thickness was fixed using Teflon stripes. It was revealed by polarising microscopy that all the materials studied were homeotropically aligned on untreated glass substrates, and that the homeotropic alignment was of good quality, both in the liquid crystalline and vitrified states. The smectic layers of the materials studied were thus oriented parallel to the plane of the substrate.

It should be noted that the homeotropic alignment of the materials under study was also confirmed using crystal rotation [13] and X-ray small-angle scattering methods [14].

3. Experimental methods

Thermal polarising optical microscopy, together with crystal rotation and conoscopic techniques, was employed in order to provide basic optical characterisation of cobalt-containing metal alkanoates, both in the liquid crystalline and vitrified states. This allowed characteristics such as alignment, pretilt angle, optical quality and optical anisotropy to be studied. Such methods are widely used in liquid crystalline science and their detailed description is freely available [13, 14]. The phase transition temperatures were studied by polythermal polarisation microscopy and by differential thermal analysis. A Paulik–Paulik–Erdey Q–1500 D derivatograph (Hungary) with a platinum–platinum rhodium thermocouple was used, with Al_2O_3 as standard. The heating rate in all experiments was 2.5°C min^{-1}. An Amplival hot-stage polarising microscope was used to identify a possible mesophase and to estimate crystal–mesophase (T_{melting}) and mesophase–isotropic liquid (T_{clearing}) phase equilibrium temperatures.

The structure of cobalt-containing metal alkanoates was studied using X-ray small-angle scattering, as described for instance by Kumar [14].

The absorption spectra of the melts and glasses were recorded in the range 400–800 nm on a Perkin–Elmer UV–VIS Lambda 35 spectrophotometer, with heating unit up to 200°C.

The nonlinear optical properties of the mesomorphic glasses were studied using laser-induced dynamic gratings, a technique also known as two-wave degenerate mixing, or dynamic holography [15, 16]. Measurements were made using the second harmonic of a pulsed Q-switched Nd:YAP laser (TEM_{00} mode, wavelength, $\lambda = 539.8$ nm, pulse duration, $t_p = 20$ ns, and pulse frequency, $\nu = 3$ Hz) as the source of intense coherent radiation. Two coherent laser beams were intersected on the sample under study, allowing dynamic gratings to be recorded. The gratings recorded were investigated in a self-diffraction regime by measurement of the diffraction efficiency, η, defined as the ratio of the intensity of the first-order diffracted laser beam (I_{+1}) to that of the incident laser beam ($I_{0,1}$) : $\eta = \frac{I_{+1}}{I_{0,1}}$.

4. Experimental results and discussion

4.1 *X-ray small-angle scattering*

The smectic structure of the materials studied was confirmed using X-ray small-angle scattering. Using this powerful technique the smectic bilayer spacing, *dl* (in other words, the interlayer smectic distance), and its temperature dependence were measured for all the materials under study. The typical temperature dependence of the bilayer spacing is shown in Figure 1. On heating, *dl* decreased slightly up to the phase transition temperature, T_C–L_C, after which it

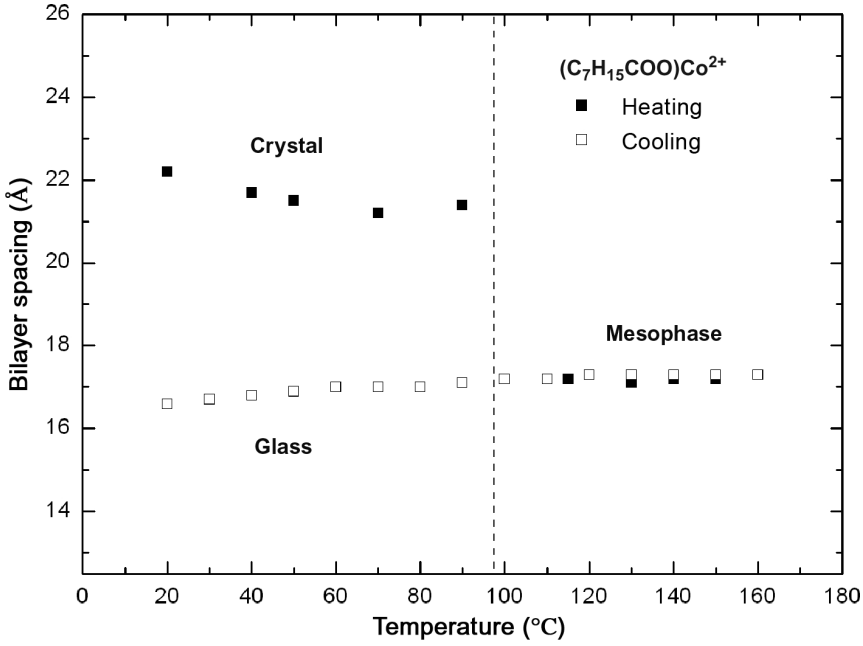

Figure 1. Temperature dependence of the bilayer spacing in cobalt caprylate.

decreased sharply. After this point the liquid crystals were cooled, and *dl* remained constant at temperatures $T \geq T_C$–L_C. This meant that on cooling, the liquid crystalline smectic structure was frozen in a vitrified condition. Such interdependence of *dl* and *T* confirmed both the smectic structure of the materials studied and the mesomorphic glass formation taking place during cooling from the liquid crystalline state to room temperature.

4.2 Conoscopic characterisation

An improved conoscopic method was employed to confirm the anisotropic properties of the mesomorphic glasses under study and to determine their birefringence. A typical conoscopic picture of the uniaxial crystal was observed for the glasses during experimentation. Such a result clearly indicates anisotropic optical properties (optical birefringence) of the mesomorphic glasses. Using crystal rotation, it was also found that the pretilt angle of the molecules of the mesomorphic glass cell lay in the range 89.90–89.50°, indicating homeotropic alignment.

4.3 Absorption spectra

All the mesomorphic glasses studied absorbed light in the visible optical region, 500–600 nm. The electronic absorption spectrum of mesomorphic cobalt caprylate glass (Figure 2) occupied a broad band in the range 480–630 nm, with a maximum at 563 nm and characterised by a pronounced shoulder at 536 nm.

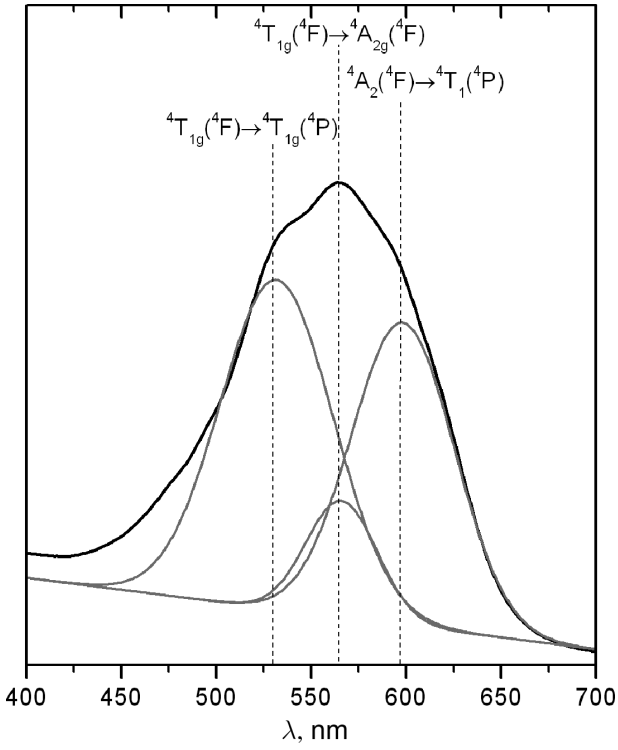

Figure 2. Optical absorption spectrum of Co^{2+} ions in mesomorphic cobalt caprylate glass (resolved into Gaussian components).

The observed spectra could be considered, under terms of ligand field theory [17, 18], as excitation of the cobalt octahedral and tetrahedral complexes. The presence of a broad absorption band of unresolved structure in cobalt alkanoate mesomorphic glasses indicated the coexistence of a number of coordination forms of Co(II) ions. The resolution of the electronic absorption spectrum into Gaussian components provides evidence of the presence of two coordination forms of Co(II) ions; the bands with maxima at 531 nm ($^4T_{1g}(^4F) \rightarrow {}^4T_{1g}(^4P)$ transition) and 565 nm ($^4T_{1g}(^4F) \rightarrow {}^4A_{2g}(^4F)$ transition) are typical for octahedrally coordinated Co(II) ions, and the band with a maximum at 595 nm ($^4A_2(^4F) \rightarrow {}^4T_1(^4P)$ transition) is typical of tetrahedral complexes. Taking into account the fact that the molar absorption coefficient for tetrahedral Co(II) complexes is much larger than that for octahedral complexes [17], it may be assumed from Figure 2 that the predominant coordination form of Co(II) ions in pure cobalt caprylate glass is octahedral, although the tetrahedral coordination form is also present.

It can be seen in Figure 3 that in the case of a homologous series of cobalt alkanoates the absorption coefficient, α, decreases uniformly from 400 cm^{-1} to 200 cm^{-1}, and α (CoC_8) > α (CoC_{10}) > α (CoC_{12}). Such a decrease in optical absorbance arises principally from two factors, firstly a decrease in the cobalt complex concentration over the series CoC_8 – CoC_{10} – CoC_{12}, and secondly, a decrease in the d–d transition dipole moment, μ_{d-d}, over this series.

It should be noted that the changes observed in the absorbance properties of the materials studied can be used for developing tunable advanced optical materials. The main reason for this is the experimental fact that the fundamental linear optical properties of cobalt alkanoate glasses can be tuned by varying the length of the alkanoate anion.

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

It was found that the optical density, D, of all the mesomorphic glasses studied was independent of the intensity, I, of the laser beam (Figure 4). Only the linear absorbance of the laser beam need therefore be taken into account when analysing the experimental results described in the following.

It was found that all the materials studied demonstrated quadratic dependence of self-diffraction efficiency *versus* intensity: $\eta \sim I^2$ (Figure 5).

Such dependence indicates a cubic nonlinear optical response of all the materials studied in the ns time range. Laser-induced changes in refractive index, Δn, are proportional to the incident laser beam intensity, I: $\Delta n = n_2 I$, where n_2 is the nonlinear refractive index, which is a macroscopic characteristic of the nonlinear optical properties of the material under study. The nonlinear refractive index can be extracted from the measured values of the self-diffraction efficiency in a convenient manner [16]:

$$\eta = T \cdot J_1^2(\Phi_{NL}) \approx T \cdot \left(\frac{\Phi_{NL}}{2}\right)^2, \qquad (1)$$

where T is transmission, J_1 is the first-order Bessel function and Φ_{NL} is the laser-induced nonlinear phase

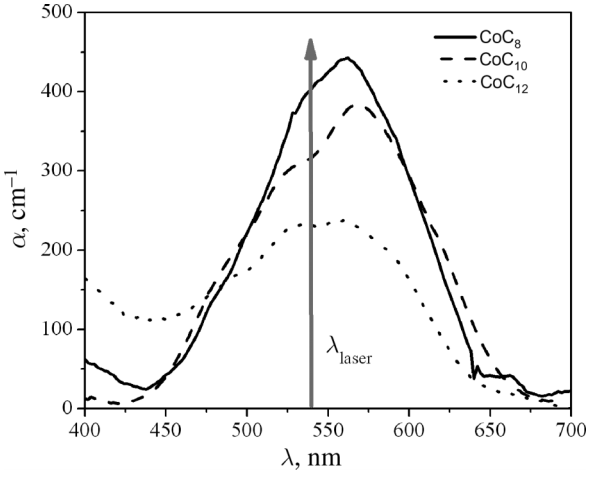

Figure 3. Absorption spectra of cobalt alkanoates (cobalt caprylate, CoC_8; cobalt decanoate, CoC_{10}; and cobalt laurate, CoC_{12}) mesomorphic glasses measured at room temperature. The arrow indicates the wavelength (539.8 nm) of the pulsed laser used in nonlinear optical experiments.

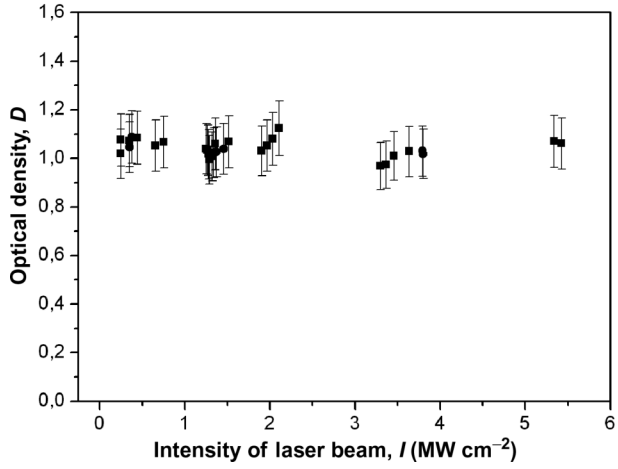

Figure 4. Typical dependence of the optical density of the mesomorphic glasses of cobalt laurate on laser beam intensity.

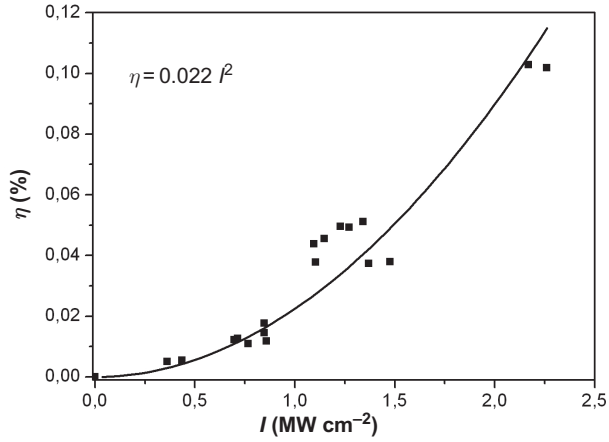

Figure 5. Typical dependence of the self-diffraction efficiency *versus* intensity of the incident laser beams for cobalt laurate.

shift. In the case of absorbing material, Φ_{NL} can be found as follows. Firstly, let us take into account the exponential dependence of the intensity of the laser beam $I(z)$ which is propagated through the media with linear absorption coefficient, α, along direction z:

$$I(z) = e^{-\alpha \cdot z} \cdot I_0, \tag{2}$$

where I_0 is the input intensity of the laser beam. In this case we can write an expression for the laser-induced changes in the refractive index $\Delta n(z)$ of the samples under study at any distance, z:

$$\Delta n(z) = n_2 \cdot I(z) = n_2 \cdot e^{-\alpha \cdot z} \cdot I_0. \tag{3}$$

The total nonlinear phase shift can be found by integration over the cell thickness d_{cell}:

$$\Phi_{\mathrm{N}L} = \int_0^{d_{\mathrm{C}ell}} \frac{2 \cdot \pi}{\lambda} \cdot \Delta n(I(z)) \cdot dz = \frac{2 \cdot \pi}{\lambda} \cdot n_2 \cdot I_0 \cdot d_{\mathrm{e}ff}, \tag{4}$$

where d_{eff} is the effective cell thickness:

$$d_{\mathrm{e}ff} = \frac{1 - e^{-\alpha \cdot d_{\mathrm{C}ell}}}{\alpha}, \tag{5}$$

and α can be found by measurement of the optical density, D, of the cells studied:

$$\alpha = \frac{D}{d_{\mathrm{C}ell} \cdot \log e}. \tag{6}$$

Taking these expressions into account, the nonlinear refractive index can be extracted from the measured diffraction efficiency as follows:

$$|n_2| = \frac{\lambda}{\pi \cdot d_{\mathrm{eff}} \cdot I_0} \cdot \sqrt{\frac{\eta}{T}}, \tag{7}$$

where λ is the wavelength of the laser beam. In the case of dynamic gratings, $I_0 = m\,(I_1 + I_2)$, where I_1 and I_2 are the beam intensities which interfere on the sample investigated, and m is the modulation depth:

$$m = \frac{2 \cdot \sqrt{I_1 \cdot I_2}}{I_1 + I_2}.$$

Nonlinear refractive indexes for all the mesomorphic glasses studied are summarised in Table 1.

Third-order nonlinear optical response can be caused by a variety of physical mechanisms, for instance by nonlinear electronic polarisation, thermal heating, electrostriction or molecular reorientation [15, 16], and therefore the measured value of the nonlinear refractive index can be considered to be the sum of the actual nonlinear refractive indexes, each additive corresponding to a definite physical mechanism.

Under an external electro-magnetic field, cobalt alkanoate complexes of tetrahedral and octahedral coordination [17] can be regarded as non-harmonic oscillators, a mechanism of electronic hyperpolarisability. Such changes in the electronic polarisability of cobalt alkanoate complexes can give rise to a third-order nonlinear optical response.

In addition to the mechanisms of third-order optical nonlinearity described above, the result of changes in electronic polarisability of the cobalt ions under the action of the external electro-magnetic field, thermal optical nonlinearity must also be taken into consideration since all the cobalt complexes studied absorbed light at laser wavelength (see Figure 3, above). The measured value of the nonlinear refractive index, n_2, is the sum of two components, the first being of electronic origin, $n_2^{\mathrm{electronic}}$, and the second, n_2^{thermal}, of

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

	CoC_8	CoC_{10}	CoC_{12}
n_2, cm^2 W^{-1} (measured)	11.2×10^{-10}	8.3×10^{-10}	4.5×10^{-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} (λ = 539.8 nm)	404.2	317.6	230.9

Note: a.u. = arbitrary units

thermal origin. The next step is to separate the contribution of these mechanisms in order to measure the nonlinear optical response of smectic glasses.

4.5 Thermal optical nonlinearity

As mentioned above, in the case of absorbing materials thermal optical nonlinearity can contribute to the measured value of n_2, or $\Delta n = n_2\, I$, Equations (8) and (9):

$$\Delta n = \Delta n_{\text{electronic}} + \Delta n_{\text{thermal}} \tag{8}$$

$$\Delta n_{\text{thermal}} = \frac{dn}{dT} \cdot \Delta T. \tag{9}$$

Let us estimate the contribution of the thermal optical nonlinearity, ${n_2}^{\text{thermal}}$, to the measured value, n_2. As has been shown previously [19–21], the nonlinear phase shift, $\Phi_{\text{NL,T}}$, caused by thermal optical nonlinearity and thermal nonlinear refractive index ${n_2}^{\text{thermal}}$ can be found as follows, Equation (10):

$$\Phi_{\text{NL},T} = \int_0^{d_{\text{cell}}} \frac{2\cdot\pi}{\lambda} \cdot \frac{dn}{dT} \cdot \frac{\alpha \cdot I_0 \cdot e^{-\alpha\cdot z} \cdot t_{\text{p}}}{c_{\text{p}} \cdot \rho}\cdot$$

$$dz = \frac{2\cdot\pi}{\lambda} \cdot \frac{dn}{dT} \cdot \frac{1 - e^{-\alpha\cdot d_{\text{cell}}}}{c_{\text{p}} \cdot \rho} \cdot t_{\text{p}}\cdot$$

$$I_0 = \frac{2\cdot\pi}{\lambda} \cdot \frac{dn}{dT} \cdot \frac{\alpha \cdot d_{\text{eff}}}{c_p \cdot \rho} \cdot t_{\text{p}} \cdot I_0$$

$$n_2^{t_{thermal}} = \cdot\frac{dn}{dT} \cdot \frac{\alpha}{c_{\text{p}} \cdot \rho} \cdot t_{\text{p}}, \tag{10}$$

where $\mathrm{d}n/\mathrm{d}T$ is a thermo-optical constant, ρ is the density, c_{p} is the specific heat capacity, t_{p} the time duration of the laser pulse, and α the linear absorption coefficient.

As can be seen, ${n_2}^{\text{thermal}}$ is proportional to the absorption coefficient, α, of the material. Using this expression one can estimate nonlinear refractive indexes caused only by thermal optical nonlinearity (thermal nonlinear refractive indexes) for the materials studied. Estimated in such a manner, the value ${n_2}^{\text{thermal}}$ of mesomorphic glasses is of the order of 10–12 $\text{cm}^2\ \text{W}^{-1}$. The experimental value of n_2 ($\sim$10–10 $\text{cm}^2\ \text{W}^{-1}$) is two orders larger than estimated. Such a disagreement between estimation and experiment allows us to ignore thermal optical nonlinearity at the ns time scale and take into account only electronic nonlinearity.

For interest both the experimental data and the estimations (in arbitrary units) are shown in Table 1.

4.6 Electronic optical nonlinearity

Macroscopic (third-order electronic susceptibility, $\chi^{(3)}$) and microscopic (hyperpolarisability, γ_{NL}) nonlinear optical parameters of the mesomorphic glasses studied can be found using the following expression [15, 16], Equation (11):

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

$$= \gamma_{\text{NL}} \cdot N \cdot \left(\frac{n^2+2}{3}\right)^4, \tag{11}$$

where ε_0 is an electric constant, n is the refractive index, c is the velocity of light, and L is a local field factor, but for simplicity we will use the Lorenz local field factor:

$$L = \frac{n^2+2}{3}$$

and N is the concentration of the nonlinear optical active complexes:

$$N = \frac{m \cdot N_{\text{A}}}{V \cdot \mu} = N_{\text{A}} \cdot \frac{\rho}{\mu},$$

where m is the mass of the sample, N_{A} is the Avogadro constant, V the sample volume, μ the molar mass and ρ the density.

Using the above expressions, basic nonlinear optical parameters can be extracted from the experimental data (Table 2).

4.7 Tuning of the nonlinear optical properties of the cobalt alkanoate mesomorphic glasses

The data shown in Table 2 allow us to draw some conclusions about the effect of alkanoate anion length (or smectic bilayer spacing) on the nonlinear optical properties of the mesomorphic glasses.

Table 2. Nonlinear optical parameters of the mesomorphic glasses studied.

	CoC_8	CoC_{10}	CoC_{12}
$\chi^{(3)}$, $\text{m}^2\ \text{V}^{-2}$	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}, $\text{m}^5\ \text{V}^{-2*}$	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}

Notes : $\chi^{(3)}(esu) = \frac{9}{4\cdot\pi}\cdot 10^8\chi^{(3)}(SI)$, $\gamma_{\text{N}L}(esu) = \frac{9}{4\cdot\pi}\cdot 10^{14}\gamma_{\text{N}L}(SI)$.

*Hyperpolarisability, γ_{NL}, calculated for one complex containing cobalt ion.

As can be seen from Table 2, the susceptibilities, $\chi^{(3)}$, decrease with increasing anion length (or smectic bilayer spacing) from 6.65×10^{-16} to 2.64×10^{-16} m^2 V^{-2}). Such a decrease is caused by three principal factors:

- a decrease in concentration, N, of the nonlinear optical centres (cobalt complexes);
- a decrease in the local field factor, L; and
- a decrease in the hyperpolarisability, γ_{NL}.

In such a homologous series the local field factor does not contribute sufficiently to account for the decrease observed in $\chi^{(3)}$. The linear refractive indexes of these mesomorphic glasses actually changes only marginally, from 1.495 to 1.486, and the local field factor, $L = (n^2 + 2)/3$, does not affect $\chi^{(3)}$. Decreases in the concentration of N and γ_{NL} are therefore the main factors affecting the observed decrease in $\chi^{(3)}$ (Table 2).

As mentioned above, the decrease in $\chi^{(3)}$ correlates with decreasing concentration of cobalt complex. Additionally, it should be noted that the third-order nonlinear optical response of the mesomorphic glasses studied was also affected by interactions between the cobalt ions and the surrounding counter-ions, namely alkanoate anions.

In summary, the nonlinear optical response of the mesomorphic glasses based on cobalt alkanoates can be tuned by changing the alkanoate anion chain length (or smectic bilayer spacing). The fundamental nonlinear optical parameters ($\chi^{(3)}$, γ_{NL}) increase with decreasing alkanoate anion length (or smectic bilayer spacing).

5. Conclusions

A systematic study of the nonlinear optical properties of mesomorphic glasses based on cobalt alkanoates has been conducted. It has been found that such rigid glasses with an intrinsic layered structure exhibit an enhanced third-order nonlinear optical response ($\chi^{(3)} \sim 10^{-8}$ esu) of electronic origin (laser-induced electronic nonlinear polarisation) on a ns time scale. In addition, it has also been shown that at this time scale thermal optical nonlinearity can be neglected for these materials. Based on this conclusion, the main nonlinear optical parameters ($\chi^{(3)}$, γ_{NL}) have been recalculated.

It is found that the nonlinear optical response of cobalt-containing mesomorphic layered glasses is caused by cobalt alkanoate complexes at the main nonlinear optical centres, which are arranged in spatially ordered two-dimensional layers. The basic third-order nonlinear optical parameters, ($\chi^{(3)}$, γ_{NL}), are dependent on cobalt alkanoate concentration (this factor is dominant) and are also affected by interaction between cobalt cations and alkanoate anions.

Finally, anisotropic mesomorphic glasses based on cobalt alkanoates represent a novel type of tunable optical and nonlinear optical materials. Their fundamental physical properties, including linear absorption coefficient α, linear (n) and nonlinear (n_2) refractive indexes, third-order susceptibility, $\chi^{(3)}$, and molecular hyperpolarisability, γ_{NL}, can all be tuned by changing the alkanoate anion length (or smectic bilayer spacing). Such simple methods provide a novel approach in the design of optical and nonlinear optical materials.

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