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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 ($\chi^{(3)}$ ~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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