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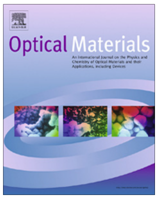

Structure and optical properties of glasses in binary liquid crystalline systems based on cobalt octanoate

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ABSTRACT

The effect of composition and aggregative state (melt, mesophase, glass) on the coordination state of Co (II) ions in an octanoate ligand field has been studied for binary liquid crystalline systems based on cobalt (II) octanoate by the analysis of electronic absorption spectra. It has been shown that several coordination forms of Co (II) ions: octahedral, tetrahedral and dodecahedral ones can coexist in cobalt octanoate based systems. It has been found by positron annihilation lifetime spectroscopy and small-angle X-ray scattering that glasses of cobalt octanoate based systems have a bilayer and nanoporous structure. The thickness of cation–anion bilayers in mesophases and glasses of binary systems depends on the polarizing power of cations: it is the smaller, the higher the polarizing power of cations.

1. Introduction

Metal alkanoates $(C_nH_{2n+1}COO)_mM^{+m}$ are representative of an unconventional class of liquid crystals, ionic metallomesogens, whose characteristic properties are a wide temperature range of mesophase, intrinsic ionic conductivity and a good ability to solvate both compounds with ionic structure and molecular compounds [1,2]. Moreover, they possess glass-forming properties, which makes it possible to create on their basis optically anisotropic glasses with smectic ionic ordering, which are of special interest in creating novel photorefractive materials for optoelectronics, nanophotonics, laser engineering and holography [3–5].

It is known that among metal octanoates, the most stable glasses are formed in systems based on 3d transition metals [6–8]; however, there are practically no data on the structure, thermo-physical, optical, nonlinear optical and other properties of these systems. Studies of the structure peculiarities and properties of these compounds in different aggregative states (melt, mesophase, glass) are of unquestionable interest both for the development of the sciences of glasses and liquid crystals and for materials science. The choice of cobalt octanoate based systems was due to the presence of an absorption band in the range 550–600 nm; thanks to this, they have promised in the creation of liquid crystal compositions for holographic grating recording using Nd (III) laser [3–5].

The materials containing Co (II) ions are interesting because predominance of one Co (II) coordination form or another depends on many factors: on the nature of the solvent used in the system [9], on temperature [9–12], on Co (II) ion concentration [13–15], on the nature of outer-sphere cation and its coordination [16], and on other factors. Unfortunately, comprehensive studies on the effect of various factors on the mode of coordination of Co (II) ions in liquid crystal systems were not practically carried out. Earlier, we presented some results on the study of optical properties in a binary system of cobalt octanoate with lanthanum octanoate [8] and in systems of cobalt octanoate with lithium and lead octanoates [7]. In this work, we have systematized earlier and new results on the study of the structure and optical properties of mesomorphic glasses based on binary systems of cobalt (II) octanoate with monovalent metal (lithium, sodium, potassium) octanoate and bivalent metal (zinc, cadmium, lead) octanoates.

2. Experimental

2.1. Materials

Lithium, sodium and potassium octanoates were prepared by the interaction of metal carbonates with octanoic acid in methanol; the salts obtained were recrystallized several times from hot methanol.

Cobalt, zinc, cadmium and lead octanoates were prepared using metathesis by addition of saturated aqueous solutions of bivalent metal nitrate to solutions of potassium octanoate in water. Zinc, cadmium and lead octanoates produced in this way were

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recrystallized several times from hot toluene. All metal octanoate salts were dried in a vacuum oven at 50 °C for one day.

Corresponding IR spectra of these salts showed that no water, carboxylic acid nor nitrate salts were present as significant impurities.

Phase equilibrium temperatures for pure metal octanoates and binary mixtures synthesized have been determined by differential thermal analysis (DTA) and polythermal polarization microscopy. A Paulik–Paulik–Erdey derivatograph (Q-1500 D) (with α-Al_2O_3 powder as reference substance) was used to obtain thermograms on heating at 2.5 °C min^{-1}. A polarizing microscope “Amplival” with hot stage “Boemius” was used to identify mesophases and isotropic liquid phases and to determine the temperatures of the crystal–mesophase or isotropic melt ($T_{melting}$), and mesophase–isotropic melt ($T_{clearing}$) transitions.

The phase transition temperatures of the pure salts synthesized in our laboratory (cobalt, alkali metal and thallium octanoates) were in good agreement (±2 °C) with the literature data [6,17–21].

Cobalt (II) octanoate $(C_7H_{15}COO)_2Co$ melts at 95 °C to form a smectic mesophase, which is a birefringent liquid with feebly marked microscopic texture apparently because of strong tendency to homeotropic orientation of liquid–crystalline domains, and then vitrifies on cooling. The mesophase clearing temperature of the cobalt octanoate has been determined at 164 °C.

Lithium octanoate $C_7H_{15}COOLi$ melts at 258 °C without mesophase formation. Sodium octanoate $C_7H_{15}COONa$ has solid–solid transition at 123 °C, melts to form a smectic mesophase at 220 °C and passes into isotropic liquid at 332 °C. Potassium octanoate $C_7H_{15}COOK$ has solid–solid transition at 54 °C and melts at 282 °C to form a smectic mesophase, which has a clearing temperature of 440 °C.

Zinc octanoate $(C_7H_{15}COO)_2Zn$ forms no liquid crystal phase. It melts at 140 °C with change into a viscous isotropic liquid, which agrees with literature data. Cadmium octanoate $(C_7H_{15}COO)_2Cd$ is not described in literature; according to our data, it melts at 98 °C to form a smectic mesophase, which clears at 168 °C. The mesophase vitrifies on cooling. Lead octanoate $(C_7H_{15}COO)_2Pb$ exhibits a solid–solid transition at 79 °C and melts to form a smectic mesophase at 81 °C, which has a clearing temperature of 107 °C, which agrees with the data obtained earlier.

The binary mixtures were prepared by melting the reweighed components under argon and then recrystallizing them at 80 °C during several hours or days, if it was needed. Samples were stored in argon before the measurements.

2.2. Characterization

Optical absorption spectra in the visible wavelength range were recorded on a Perkin Elmer UV/VIS Lambda 35 spectrophotometer fitted with an attachment allowing measurements up to 200 °C. Quartz sample cells 10–30 μm in thickness were used for investigations here. Spectra were taken under cooling conditions at a rate of −2 °C min^{-1}.

For small-angle X-ray scattering (SAXS) measurements at different temperatures, samples in the form of powder were placed in thin-walled capillaries for X-ray analysis 0.7 mm in diameter with a wall thickness of 0.01 mm, which were then mounted in a furnace with lavsan windows. The temperature was measured with a copper-constantan thermocouple with an accuracy of 0.1 °C. The SAXS spectra have been obtained on an AMUR device (Cu Kα radiation, Ni filter, $U = 40$ kW, scan angle range $2\theta = 2$–6°, step 0.05°, measurement time $t = 5$ s). An ATSAS 2.3 program system was used in the processing of results and calculation of structure parameters [22].

In our PAL experiments with ORTEC spectrometer the full width at half maximum was 0.270 ns, and a ^{22}Na isotope with 0.4 MBq activity was used as a positron source (with input of 9%), placed between two identical samples. The measured PAL spectra were fitted by LT computer program of Kansy [23], using a sum of a few weighted exponential functions, convoluted with the measured resolution function of the spectrometer. We used three measured PAL spectra for the investigated pair of samples, they differing in the total number of counts or, in other words, ordinary annihilation events in the range of 800,000–1,200,000. Each of these spectra was multiply treated owing to slight changes in the number of final channels, background of annihilation and time shift of the spectrum. The best results were selected on the basis of FIT (short abbreviation originated from “fitting”), determined as statistically weighted least-squares deviation between experimental points and theoretical curve. We formed a few groups which contained different number of experimental points N within each kind of the chosen mathematical treatment procedure.

Only results with FIT values close to 1.0 (the optimal FIT deviation range from 0.95 up to 1.1–1.2) were considered as optimal ones. At the next stage, these FIT values and determined PAL characteristics were controlled depending on the back-ground of annihilation and time shift of PAL spectrum, the results showing that only slight changes were chosen by us. It should be noted that source correction and spectrometer resolution function were kept unchangeable in the above algorithm.

3. Results

3.1. Investigation by the SAXS method

The structure of alkanoate anion is such that on the one hand, it must ensure ready vitrification of salt melt owing to its low symmetry and large size. On the other hand, it is an amphiphilic ion with anisotropic distribution of Coulomb charge, which causes its tendency to form ordered two-dimensional phases of the type of smectic ionic liquid crystals. These two trends in the behavior of alkanoate anion are in constant struggle. Thus, increase in anion anisometry, e.g. through the growth of alkanoate anion aliphatic chain, reduces the tendency of melts to vitrification since in this case, the tendency to the formation of orientation-ordered phases increases. Therefore, it is very interesting to investigate the vitrification of metal octanoates since an intermediate situation exists in these salts, when the tendency to glass formation is as strong as that to ordering.

In binary systems of cobalt octanoate with mono- and bivalent metal octanoates glass formation was observed in wide concentration ranges (Table 1).

A SAXS investigation of cobalt octanoate and systems based on it showed that crystalline and liquid crystalline phases have a layer structure. In all systems, the diffraction maximum of compounds in the crystalline state is in the range of small angles, $2\theta = 3.5$–4.5 (Fig. 1) and shifts to larger values with increasing temperature, its intensity decreasing. In the mesophase of all systems, one diffraction peak with maximum in the range 4.8–5.2 (depending

Table 1
Glass-forming regions in binary systems based on cobalt octanoate.

Binary system	Glass-forming region, [x, mol%]
$x\ Co(C_7H_{15}COO)_2 + (100-x)\ C_7H_{15}COOLi$	$10 < x \leqslant 100$
$x\ Co(C_7H_{15}COO)_2 + (100-x)\ C_7H_{15}COONa$	$30 < x \leqslant 100$
$x\ Co(C_7H_{15}COO)_2 + (100-x)\ C_7H_{15}COOK$	$30 < x \leqslant 100$
$x\ Co(C_7H_{15}COO)_2 + (100-x)\ Pb(C_7H_{15}COO)_2$	$10 < x \leqslant 100$
$x\ Co(C_7H_{15}COO)_2 + (100-x)\ Cd(C_7H_{15}COO)_2$	$0 \leqslant x \leqslant 100$
$x\ Co(C_7H_{15}COO)_2 + (100-x)\ Zn(C_7H_{15}COO)_2$	$20 < x \leqslant 100$