

Phase diagram and optical properties of liquid crystalline binary cobalt caprylate — lanthanum caprylate liquid crystal system

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Phase equilibria, the temperature and concentration ranges of liquid crystal and glass formation in the binary system $\text{La,Co||C}_7\text{H}_{15}\text{COO}$ have been investigated by differential thermal analysis and polarization microscopy. Electron absorption spectra and fluorescence spectra of Co(II) cation in mesophases and glasses of the binary system have been analyzed as a function of temperature and the concentration of the components. It has been shown that octahedrally coordinated Co(II) ions prevail in the binary system, though tetrahedral complexes are also present and influence the system optical properties.

Методами дифференциального термического анализа и поляризационной микроскопии исследованы фазовые равновесия и определен концентрационно-температурный интервал существования жидких кристаллов и стекол в бинарной системе $\text{La,Co||C}_7\text{H}_{15}\text{COO}$. Исследованы электронные спектры поглощения и спектры флуоресценции катиона Co(II) в мезофазах и стеклах бинарной системы в зависимости от температуры и концентрации компонентов. Показано, что в бинарной системе преобладают октаэдрически координированные ионы Co(II) , хотя присутствуют и тетраэдрические комплексы, которые влияют на оптические свойства системы.

1. Introduction

Metal caprylates belong to an unconventional class of ionic metal alkanooate liquid crystals — ionic metalmesogens, characterized by a wide temperature range of mesophase existence, intrinsic ionic conductivity, and good ability to solvate both compounds of molecular and ionic structure [1]. Moreover, they are of special interest in the development of novel photorefractive materials for optoelectronics, laser engineering and holography due to the possibility to form optically anisotropic glasses with smectic ionic ordering in metal alkanooate systems [2].

A low-melting vitrifiable mesomorphic metal-alkanoate composite can be obtained using multicomponent systems as well as synthesizing low-melting glass-forming mesogenic metal alkanooates. It is known that among metal alkanooates, the alkanooates

of some bivalent metals, such as lead, cadmium, and transition $3d$ metals, show the lowest melting points and the ability to overcooling and vitrification [3, 4]. Studies of the structure peculiarities and properties of these compounds in different aggregation states (melt, mesophase, glass) are no doubt of an interest in the development of both the sciences of glasses and liquid crystals and materials science.

Co^{2+} ion was used before by a number of authors as a probe-dopant for the determination of the structure of salt melts and/or glasses in various systems such as borates [5, 6], carboxylates [7–9], sulfates [8], nitrates [7], and chlorides [11]. In these works, data on the coordination state of cobalt ions in glasses and melts with different acid-base properties had been obtained from absorption spectra of Co^{2+} ion. It had been

shown that the predominance of the octahedral or tetrahedral coordination form of Co^{2+} depends both on temperature and on the nature of ligands surrounded by cobalt ions [5, 6].

In this work, the phase diagram of a binary cobalt (II) caprylate/lanthanum (II) caprylate system has been studied, and the concentration and temperature ranges of the liquid crystal and glass existence have been determined. Moreover, electron absorption spectra and fluorescence spectra of Co(II) cation in mesophases and glasses of the binary system as a function of temperature and the concentration of the components have been studied to obtain information on the mutual arrangement of ions in caprylate mesophases and glasses and on the coordination of Co(II) ions in the caprylate ligand field.

2. Experimental

Metal caprylates were prepared by metathesis by adding saturated aqueous solutions of Co(II) or La(III) nitrate to a solution of potassium caprylate in methanol (Fluka, puriss grade). The caprylates obtained were washed repeatedly with hot water and dried in a vacuum oven at 50°C for a day. The IR spectra data of the salts synthesized indicated the absence of water, carboxylic acid and nitrate salts. The constituents weighed in the required molar ratio were mixed thoroughly mechanically and melted together in argon atmosphere to prevent possible decomposition of samples. The samples were stored in dry argon atmosphere. The phase equilibrium temperatures in binary systems were studied by polythermal polarization microscopy and DTA. A Paulik-Paulik-Erdey Q-1500 D derivatograph (Hungary) with platinum/platinum-rhodium thermocouple (standard substance Al_2O_3) was used. The heating rate in all experiments was 2.5 deg/min . An Amplival hot-stage polarizing microscope was used to identify possible mesophase and to estimate the crystal/mesophase (T_m) and mesophase/isotropic liquid (T_{cl}) phase equilibrium temperatures. The electron absorption spectra of melts and glasses were recorded in the 400–800 nm range on a Perkin Elmer UV/VIS Lambda 35 spectrophotometer with heating unit (up to 200°C). Quartz cells of 10 μm thickness were used. The fluorescence spectra were recorded in the 400–900 nm range on a Perkin Elmer LS 55 spectrophotometer using a xenon arch lamp as the light source.

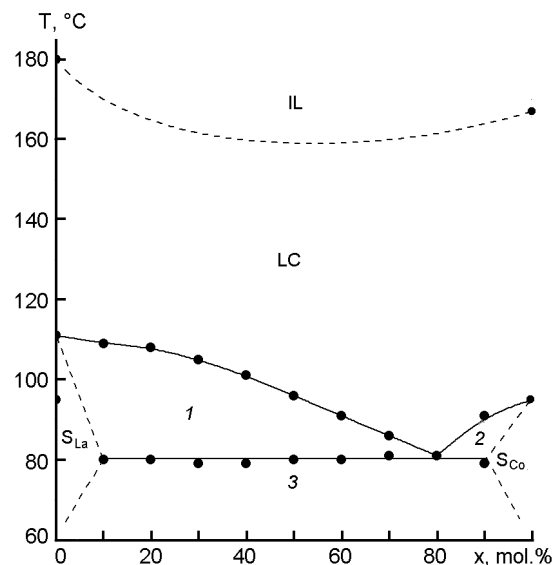


Fig. 1. Phase diagram of the $\{x(\text{C}_7\text{H}_{15}\text{COO})_2\text{Co} + (100-x)(\text{C}_7\text{H}_{15}\text{COO})_3\text{La}\}$ binary system: (1) $S_{\text{La}} + L_C$, (2) $L_C + S_{\text{Co}}$, (3) $S_{\text{La}} + S_{\text{Co}}$ are two-phase regions, where S_{La} , S_{Co} are lanthanum and cobalt caprylate solid phases.

3. Results and discussion

The phase transition temperatures of the individual salts synthesized agree well with literature data [12, 13]. For instance, cobalt caprylate $(\text{C}_7\text{H}_{15}\text{COO})_2\text{Co}$ melts at 95°C to form a smectic mesophase as a birefringent liquid with feebly marked microscale texture (perhaps because of strong trend to homeotropic orientation of liquid-crystalline domains), which clears at 164°C in agreement with literature data [12]. The isotropic melt shows decomposition signs near 200°C . Cobalt caprylate mesophase vitrifies on cooling. Lanthanum caprylate $(\text{C}_7\text{H}_{15}\text{COO})_3\text{La}$ exhibits a crystal/unidentified mesophase M transition at 95°C ; then a smectic mesophase A is formed at 111°C , which clears at 180°C [13]. The mesophase vitrifies on cooling.

The phase diagram of the $\{x(\text{C}_7\text{H}_{15}\text{COO})_2\text{Co} + (100-x)(\text{C}_7\text{H}_{15}\text{COO})_3\text{La}\}$ binary system is presented in Fig. 1. It is seen that continuous smectic liquid-crystalline solutions are formed in the system due to an eutectic reaction between the pure components at 80°C , $x = 80 \text{ mol.}\%$. Addition of cobalt caprylate in even small amounts ($<1 \text{ mol.}\%$) to lanthanum caprylate results in the degeneracy of the unidentified mesophase M . We failed to construct wholly the curve of mesophase clearing temperatures in the system because the mesophase texture of binary composites was pseudoisotropic when observed in polarized light, per-

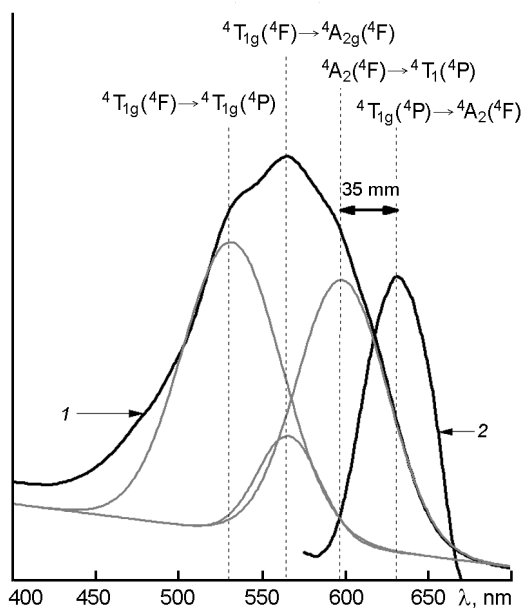


Fig. 2. Optical absorption spectrum of Co^{2+} ions in mesomorphic $\text{Co}(\text{C}_7\text{H}_{15}\text{COO})_2$ glass (1) (expanded into Gaussians) and fluorescence spectrum (2).

haps because of strong trend to homeotropic orientation of liquid-crystalline domains. For the binary system of cobalt and lanthanum caprylates, the formation of mesomorphic glasses takes place in the whole concentration range.

To establish the coordination state of $\text{Co}(\text{II})$ ions surrounded by caprylate ligands in liquid-crystalline melts and glasses of the binary cobalt caprylate/lanthanum caprylate system, electron absorption and fluorescence spectra have been considered. The glasses formed in the binary system are of pink color, the coloration becoming more intense with increasing cobalt caprylate concentration. For all samples, a thermochromic effect was observed, i.e. color change with temperature change. At temperatures above 110°C , the color of the mesophase obtained was always blue, and on cooling to room temperature, the samples turned pink. In all cases, the temperature-induced color changes were reversible.

The $\text{Co}(\text{II})$ ion has the electron configuration d^7 . All coordination numbers from 8 to 2 are known for it, but the numbers 6 (octahedral complexes) and 4 (tetrahedral complexes) are predominant. According to the Tanabe-Sugano diagram [14], three transitions can manifest themselves in octahedral cobalt (II) complexes: ${}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{T}_{1g}({}^4\text{P})$ (ν_1), ${}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{A}_{2g}({}^4\text{F})$ (ν_2), and ${}^4\text{T}_{1g}({}^4\text{F}) \rightarrow$

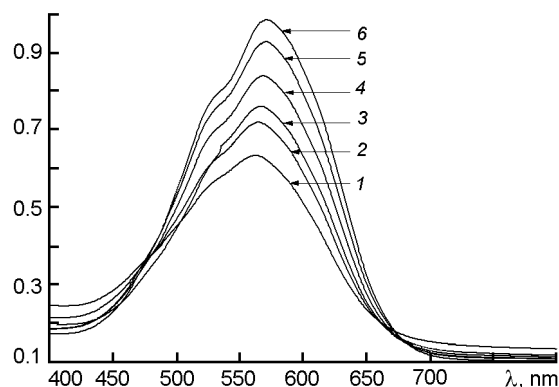


Fig. 3. Optical absorption spectra of $\text{Co}(\text{II})$ ions in the molten $\{x(\text{C}_7\text{H}_{15}\text{COO})_2\text{Co} + (100-x)(\text{C}_7\text{H}_{15}\text{COO})_3\text{La}\}$ system of equimolar composition at different temperatures; T, $^\circ\text{C}$: 1-70, 2-90, 3-110, 4-130, 5-150, 6-170.

${}^4\text{T}_{2g}({}^4\text{F})$ (ν_3). The absorption band ν_3 is in the near IR region while ν_1 and ν_2 in the visible region, ν_2 being less intense than ν_1 .

According to the Tanabe-Sugano diagram, three transitions, too, manifest themselves in tetrahedral cobalt (II) complexes: ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{P})$ (ν_1), ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{F})$ (ν_2), and ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_2({}^4\text{F})$ (ν_3). For tetrahedral complexes, only one absorption band ν_1 is in the visible region; two other lying in the near IR region [14, 15].

The electron absorption spectrum of mesomorphic cobalt caprylate glass (Fig. 2) is a broad band in the 480–630 nm range with maximum at 562.7 nm and is characterized by a pronounced shoulder at 535.7 nm. The broad absorption band of unresolved structure in liquid-crystalline melt or glass with high cobalt ion concentration indicates the coexistence of several $\text{Co}(\text{II})$ ion coordination forms. The electron absorption spectrum expansion into Gaussian components indicates the presence of two $\text{Co}(\text{II})$ ion coordination forms; the bands with maxima at 531 nm (${}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{T}_{1g}({}^4\text{P})$ transition) and 565 nm (${}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{A}_{2g}({}^4\text{F})$ transition) are typical of octahedrally coordinated $\text{Co}(\text{II})$ ions, and the band with maximum at 595 nm (${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{P})$ transition) is typical of tetrahedral complexes. Taking into account the fact that the molar absorption coefficient for tetrahedral $\text{Co}(\text{II})$ complexes is much higher than for octahedral complexes, it can be assumed basing on Fig. 2 that the predominant coordination form of $\text{Co}(\text{II})$ ions in pure cobalt caprylate glass or mesomorphic melt is octahedral one,

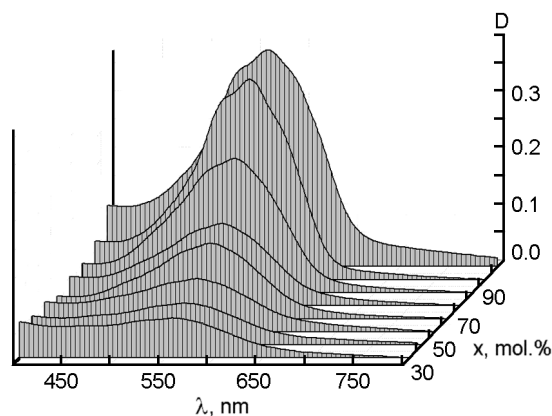


Fig. 4. Optical absorption spectra of Co(II) ions in mesomorphic glasses of the binary system $\{x(\text{C}_7\text{H}_{15}\text{COO})_2\text{Co} + (100-x)(\text{C}_7\text{H}_{15}\text{COO})_3\text{La}\}$ at different cobalt caprylate concentrations for a 10 μm thick sample.

though tetrahedral coordination form is also present.

The presence of tetrahedral coordination forms in cobalt caprylate glass is also indicated by fluorescence spectrum (Fig. 2). In the range studied (400–900 nm), only one fluorescence band peaked at 632 nm was observed, which corresponds to the $^4\text{T}_1(^4\text{P}) \rightarrow ^4\text{A}_2(^4\text{F})$ transition, which characterizes the presence of tetrahedrally coordinated Co(II) ions [15, 16]. The Stokes shift, for which fast relaxation to the lower vibrational level is responsible, is 35 nm for cobalt caprylate glass.

The electron absorption spectrum of Co(II) ions for pure cobalt caprylate melt does not exhibit any changes when the temperature increases from 70°C to 170°C. When lanthanum caprylate is added to a liquid-crystalline cobalt caprylate melt, a noticeable temperature dependence is observed, namely shifts of the Co(II) ion absorption band maxima towards longer wavelengths (≈ 10 nm) and an increase in their intensity at temperature elevation (Fig. 3).

For all samples of this system, an increase in absorption band intensity ($\Delta D/\Delta T > 0$) [14] at increasing temperature is observed, indicating the predominance of center-symmetrical octahedral complexes of Co(II) ions in the whole composition range. The change in melt color from pink to blue and a small shift of the absorption bands of Co(II) ions towards longer wavelengths on heating indicates an increase of tetrahedral Co(II) complexes concentration in the melt.

As is seen from Fig. 4, a natural decrease in the optical density of glass at decreasing Co(II) ion concentration is ob-

Table. Absorption and fluorescence band maxima of Co(II) ion in mesomorphic glasses of the $\{x(\text{C}_7\text{H}_{15}\text{COO})_2\text{Co} + (100-x)(\text{C}_7\text{H}_{15}\text{COO})_3\text{La}\}$ binary system

x , mol.% ($\text{C}_7\text{H}_{15}\text{COO}$) ₂ Co	Maximum, λ (nm)	
	Optical absorption spectrum	Fluorescence spectrum
100	562.7	632
90	559.7	635
80	557.4	637
70	557.1	640
60	557.0	642
50	556.8	641
40	556.4	640
30	556.1	641
20	–	643
10	–	645
5	–	646
1	–	648

served, which is associated with decrease in chromophore concentration. The absorption band maxima wavelengths in the spectra of the cobalt and lanthanum caprylates binary system mesomorphic glasses are given in the Table. It is seen that with decrease in the cobalt caprylate concentration due to its dilution with lanthanum caprylate the absorption band maximum shifts towards shorter wavelengths. This indicates an increase in the field force of caprylate ligands in octahedral complexes of Co(II) ions in the binary system in comparison with pure cobalt caprylate.

The concentration dependence of fluorescence intensity at room temperature in glasses obtained by overcooling melts in the system $\{x(\text{C}_7\text{H}_{15}\text{COO})_2\text{Co} + (100-x)(\text{C}_7\text{H}_{15}\text{COO})_3\text{La}\}$ is presented in Fig. 5. As is seen from the Figure, when Co(II) ion concentration in the system increases (from 1 mol % to 10 mol %), the fluorescence intensity of the $^4\text{T}_1(^4\text{P}) \rightarrow ^4\text{A}_2(^4\text{F})$ transition is increased, which is due to an increasing amount of tetrahedrally coordinated Co(II) ions. In the concentration range $10 \leq x \leq 50$ mol. %, the fluorescence intensity remains practically unchanged, hence it can be concluded that in this concentration range, the amount of tetrahedrally coordinated cobalt ions changes only slightly. When the cobalt caprylate concentration is increased from 50 mol. % to 100 mol. %, the fluorescence

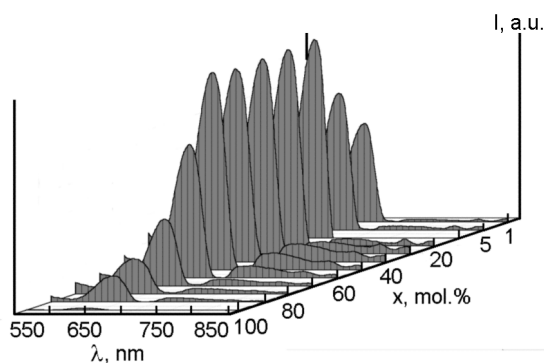


Fig. 5. Fluorescence spectra of Co(II) ions in mesomorphic glasses of the binary system $\{x(\text{C}_7\text{H}_{15}\text{COO})_2\text{Co} + (100-x)(\text{C}_7\text{H}_{15}\text{COO})_3\text{La}\}$ at different cobalt caprylate concentration.

intensity decreases due to concentration quenching of fluorescence.

The fluorescence band wavelengths for glasses formed of cobalt caprylate-lanthanum caprylate mixtures are given in the Table. In all samples, the fluorescence band maximum shifts towards longer wavelength with decreasing cobalt caprylate concentration due to its dilution with lanthanum caprylate. Since in this case the absorption maximum shifts towards shorter wavelength, the Stokes shift increases when the cobalt caprylate concentration is decreased.

4. Conclusions

Thus, the continuous smectic liquid-crystalline solutions are found to exist in the system of cobalt and lanthanum caprylates; when the solutions are cooled, the optically anisotropic mesomorphic glasses are formed. It has been shown that octahedrally coordinated Co(II) ions prevail in liquid-crystalline melts and glasses of the binary

system, though tetrahedrally coordinated Co(II) ions are also present and influence the system optical properties. It has been found that when the lanthanum caprylate concentration is increased, the amount of tetrahedral Co(II) complexes decreases with respect to that of octahedral complexes.

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Фазова діаграма та оптичні властивості рідкокристалічної бінарної системи каприлату кобальту з каприлатом лантану

I.I.Tokmenko, T.A.Mirna, G.G.Yaremchuk

Методами диференційного термічного аналізу та поляризаційної мікроскопії досліджено фазові рівноваги і визначено концентраційно-температурний інтервал існування рідких кристалів і стеклоу в бінарній системі $\text{La,Co}\|\text{C}_7\text{H}_{15}\text{COO}$. Розглянуто електронні спектри поглинання та спектри флуоресценції катіону Co(II) мезофазах і стеклах бінарної системи в залежності від температури і концентрації компонентів. Показано, що у бінарній системі переважають октаедрично координовані іони Co(II) , хоча присутні також тетраедричні комплекси, які впливають на оптичні властивості системи.