Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Electrical conductivity of lyotropic and thermotropic ionic liquid crystals consisting of metal alkanoates

Yuriy Garbovskiy[a]; Alexander Koval'chuk[a]; Alexandra Grydyakina[a]; Svitlana Bugaychuk[a]; Tatyana Mirnaya[b]; Gertruda Klimusheva[a]

[a] Institute of Physics, Prospect Nauki 46, 03028 Kiev, Ukraine [b] Institute of General and Inorganic Chemistry, 03142 Kiev, Ukraine

To cite this Article Garbovskiy, Yuriy , Koval'chuk, Alexander , Grydyakina, Alexandra , Bugaychuk, Svitlana , Mirnaya, Tatyana and Klimusheva, Gertruda(2007) 'Electrical conductivity of lyotropic and thermotropic ionic liquid crystals consisting of metal alkanoates', Liquid Crystals, 34: 5, 599 — 603

To link to this Article: DOI: 10.1080/02678290701292439

URL: http://dx.doi.org/10.1080/02678290701292439

Liquid Crystals, Vol. 34, No. 5, May 2007, 599–603

Taylor & Francis
Taylor & Francis Group

Electrical conductivity of lyotropic and thermotropic ionic liquid crystals consisting of metal alkanoates

YURIY GARBOVSKIY†, ALEXANDER KOVAL'CHUK†, ALEXANDRA GRYDYAKINA†, SVITLANA BUGAYCHUK†, TATYANA MIRNAYA‡ and GERTRUDA KLIMUSHEVA*†

†Institute of Physics, Prospect Nauki 46, 03028 Kiev, Ukraine
‡Institute of General and Inorganic Chemistry, Palladina Ave. 32/34, 03142 Kiev, Ukraine

(*Received 2 May 2006; in final form 26 January 2007; accepted 3 February 2007*)

The electrical properties of ionic smectic liquid crystal (ISLCs), specifically, (i) oriented and non-oriented samples of lyotropic ISLC potassium caproate and (ii) oriented samples of thermotropic ISLC cobalt decanoate, are investigated in detail. The electrical conductivity of lyotropic smectic potassium caproate is higher than that of isotropic electrolytes. A giant anisotropy in the electrical conductivity of oriented samples of thermotropic ISLC cobalt decanoate is observed. The mobility of charge carriers in lyotropic ISLC is measured for the first time. The unusual electrical properties of ISLCs, which are governed by their layered structure, show that they have application potential in optoelectronic devices.

1. Introduction

A comprehensive review of the investigation of electrical conductivity in diverse lyotropic mesophases was given by Winsor [1]. It was noted that the electric conductivity was increased in the most regular lamellar phase in comparison with that in phases with higher water content. However, no measurements were reported of the electrical conductivity in oriented and non-oriented polydomain lyotropic ionic smectic phases of potassium caproate, which has now been investigated in detail in the present work. Thermotropic ionic smectic liquid crystals (ISLCs) of low homologues of alkanoate acids were reported for the first time by Ubbelohde *et al.*, and the intrinsic ionic conductivity of a thermotropic ISLC established [2, 3]. It was found that metal cations were mainly responsible for charge transport in an ISLC; results obtained by Duruz and Ubbelohde [4] indicated anisotropy of the electrical conductivity in the ISLC. Proof of anisotropic ionic transport was obtained by Meisel and Seybold [5], who measured the electrical conductivity in the homeotropic oriented ISLC of thallium laurate. In this work the authors determined that the electrical conductivity along the smectic cation–anion layers was three times that measured perpendicular to the cation–anion layer direction. From our data, the anisotropy of the newly reported thermotropic ISLC of cobalt decanoate greatly exceeds this value. A quasi-crystalline description of electrical conductivity was developed in for thermotropic ISLCs [6–8], but no detailed research on the transport properties in oriented ISLC samples have been reported.

The common formula of metal alkanoates is $(C_nH_{2n+1}COO^{-1})_kM^{+k}$, where M is a metal and $k=1$–3. Small angle X-ray scattering data show that the molecules of the metal alkanoate matrix in the mesophase are packed in bilayers consisting of hydrophobic alkyl chains and conductive layers which contain (a) metal cations and anionic carboxyl groups in a thermotropic ISLC, or (*b*) metal cations, carboxyl groups and water in the case of a lyotropic ISLC [8, 9]. As a result, metal alkanoate ISLCs have a smectic A structure. A lyotropic ISLC was obtained by mixing a salt with water in the weight proportion 1:1. We investigated the electrical properties of the pure and doped lyotropic ISLC of potassium caproate ($C_9H_{19}COOK$). For the first time we investigated in detail the electrical properties of a uniform oriented thermotropic ISLC of cobalt decanote $(C_9H_{19}COO^{-1})_2Co^{2+}$. From our X-ray investigations the thickness of the bilayers is $d=3.153$ nm for the lyotropic ISLC of potassium caproate, figure 1 (a), and $d=2.08$ nm for the cobalt decanoate ISLC, figure 1 (b) [9, 10]. From to estimations based on X-ray studies the cation–anion layers in the lyotropic ISLC containing water are thin, with thickness of about 0.3 nm. We discuss the experimental data obtained on the electrical properties and their anisotropy in the metal alkanoate ISLCs.

---

*Corresponding author. Email: klimush@iop.kiev.ua

ISSN 0267-8292 print/ISSN 1366-5855 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290701292439

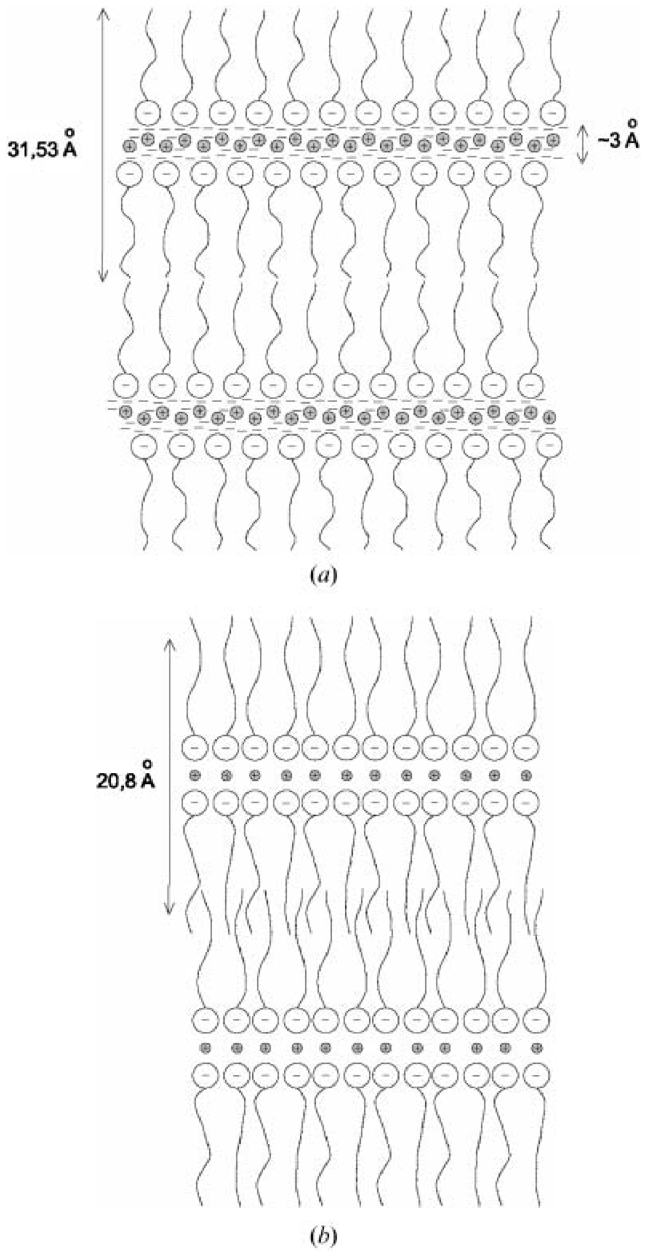

Figure 1. Schematic representation of the bilayer structure of the ISLC. (*a*) The arrangement of the alkanoate anions, univalent metal cations and water molecules in the lyotropic ISLC of potassium caproate. (*b*) The arrangement of the alkanoate anions and bivalent metal cations in the thermotropic ISLC of cobalt decanoate.

2. Sample preparation and experimental techniques

The lyotropic ISLC of potassium caproate in a flat glass cell forms smectic A domains with planar molecular packing. The mesophase of cobalt decanoate is known to be a thermotropic ISLC [10]; on heating this salt the phase transition crystal – smectic A takes place at a temperature of 95°C.

The cells are prepared using nickel electrodes and glass supports to provide electrical conductivity measurements. Two geometric configurations of electrodes were used to investigate the anisotropy of electrical properties [11]. In the first, the electrodes are placed in one plane between glass supports and the electrodes assign the thickness of the cell. The second is a sandwich-like configuration, in which the cell thickness is given by teflon strips.

The electrical conductivity of samples was measured by the oscilloscopic technique, using a triangular signal with peak voltage 0.1–0.25 V [12]. Such a small voltage was applied to avoid electrolysis processes in the lyotropic ISLC samples. The electrical conductivity was measured in the frequency range 10^4–10^6 Hz, where no dispersion of the resistance was observed. We determined the geometric parameter of the cells from the formula $k=\ell/(d\cdot z)$, where d is the sample thickness, z is the length of the metallic electrodes and ℓ is the distance between them. The electrical conductivity σ_{ac} was found from the measured values of the volume resistance R and the cell geometric parameter k using the relationship $\sigma_{\mathrm{ac}}=k/R$. To provide temperature measurements a specially developed thermostat was used that stabilized the temperature with an accuracy of ± 0.5 K.

The mobility of the charge carriers in the ISLC was measured by the reverse field technique [13]. In this method a direct voltage (~2 V) was applied to a cell until the current stationary state was reached. After the polarization voltage was cut off, a direct voltage with reversed polarity (~1.8 V) was applied to the cell. A transient current was monitored by a self-recorder, and the carrier mobility μ calculated from the time in which the maximum value of this current was reached. The value μ was found from the relation $\mu=d^2/(U\cdot t)$, where d is the sample thickness, U is the reverse voltage and t is the drift time of the charge carriers between the electrodes.

3. Electrical properties of the potassium caproate lyotropic ISLC

The first series of experiments were made with the electrodes located in one plane. The ISLC has polydomain structure between glass supports with planar molecular orientation. In this configuration the electric field was applied mainly perpendicular to cation–anion layers; the thickness of the cells was 50 μm. At room temperature we obtained a conductivity value $\sigma_{\mathrm{ac}}=10\,\Omega^{-1}\,\mathrm{m}^{-1}$ for lyotropic ISLC potassium caproate. The temperature dependence of the volume resistance R was measured in the temperature range T=20–60°C. It can be described by the exponential dependence:

$$\frac{R}{T} = R_0 \exp\left(E_a/kT\right). \tag{1}$$

We obtained the same results both with increasing and decreasing temperature. The logarithm of the volume resistance versus inverse temperature value lies on a straight line, see figure 2 (*a*). The activation energy of the electric conductivity E_a is determined from the line inclination angle: $E_a=0.21$ eV.

In the sandwich-like electrode configuration the thickness of the cells is larger (1–1.5 mm) and the samples have a non-ordered multi- domain structure. The measured electrical conductivity in sandwich-like cells is higher at room temperature than for the first configuration ($\sigma_{ac}=32$–$36\,\Omega^{-1}\,\text{m}^{-1}$). At the same time the activation energy, defined from temperature dependences of the volume resistance, is smaller: $E_a=0.16$–0.17 eV. A typical temperature dependence of the volume resistance of lyotropic ISLC potassium caproate in this case is shown in figure 2 (*b*).

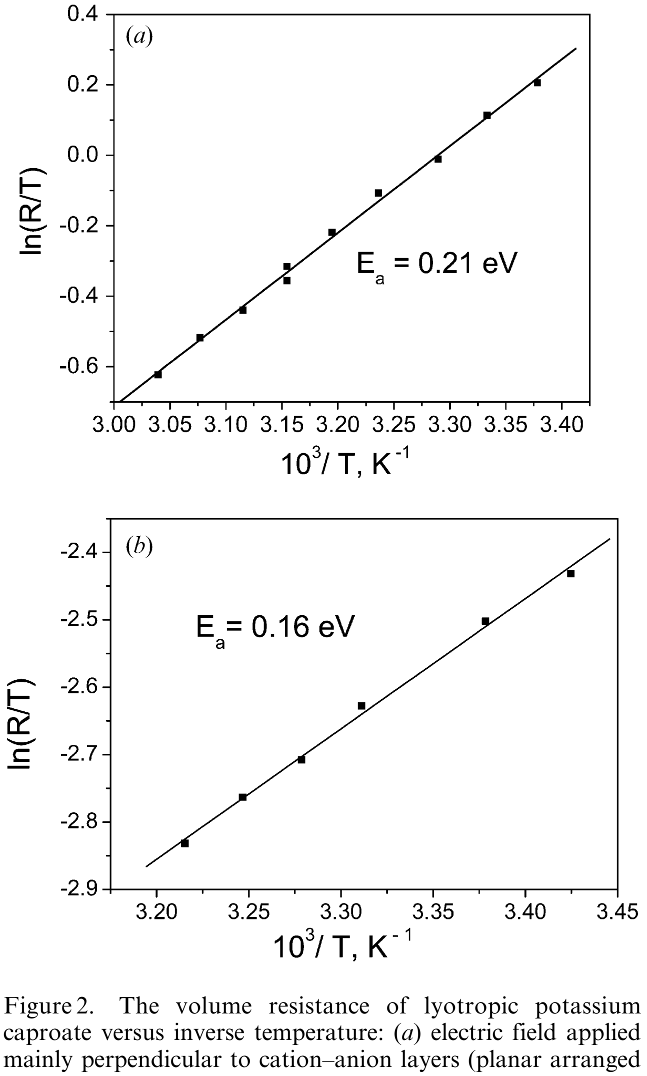

Figure 2. The volume resistance of lyotropic potassium caproate versus inverse temperature: (*a*) electric field applied mainly perpendicular to cation–anion layers (planar arranged electrodes); (b) thick non-ordered polydomain samples (sandwich-like configuration of electrodes).

For the first time the charge carrier mobility μ was determined in sandwich-like cells by the reverse field method. The thickness of the cells was 0.4 mm; the obtained mobility was $\mu=2\times10^{-7}\,\text{m}^2\,\text{V}^{-1}\,\text{s}^{-1}$.

Our experimental data show that the lyotropic ISLC of potassium caproate has a large electrical conductivity, which is higher than the conductivity of isotropic solutions [1, 14]. We also obtain different values of electrical conductivity and ISLC activation energy for ISLC samples that have different thickness and ordering of liquid crystal domains. The number of ISLC domains with oriented cation–anion layers along an applied field is higher; the electrical conductivity of the ISLC samples is also higher. Our experimental results indicate the anisotropic character of the electrical properties of the ISLC. Note that polymethine dye impurities (of both cation and anion types at 0.01 %wt. [15]) in the lyotropic ISLC have little effect on the high intrinsic conductivity of the pure matrix.

4. Electrical properties of the cobalt decanoate thermotropic ISLC

To measure the electrical conductivity, cells with both geometric electrode configurations were used. The cells thickness was 85 μm in both cases, and nickel electrodes were used. The thermotropic ISLC had uniform homeotropic orientation in the cells, and in the planar electrode configuration the applied field was oriented mainly along cation–anion layers of the ISLC. The measured electric conductivity was $\sigma=6{,}3\times10^{-5}\,\Omega^{-1}\text{m}^{-1}$ at 95°C, increasing exponentially with temperature. The temperature dependence of the volume resistance of the thermotropic ISLC was investigated in the range of the mesophase, $T=90$–120°C, see figure 3 (*a*). The activation energy of the conductivity was $E_a=0.17$ eV.

In the cells with the sandwich-like configuration of electrodes the electric field is directed perpendicular to the cation–anion layers and is parallel to carbon–hydrogen chains in the ISLC. The measured value of electrical conductivity was $\sigma_{\perp}=8\times10^{-9}\,\Omega^{-1}\,\text{m}^{-1}$ at t=95°C; that is, four orders of magnitude smaller than the conductivity along the cation–anion layers. The corresponding temperature dependence of the volume resistance is shown in figure 3 (b). At the same time, the activation energy of electrical conductivity was greatly increased, $E_{a\perp}=0.89$ eV. We observed a distinct anisotropy both of the conductivity and of the

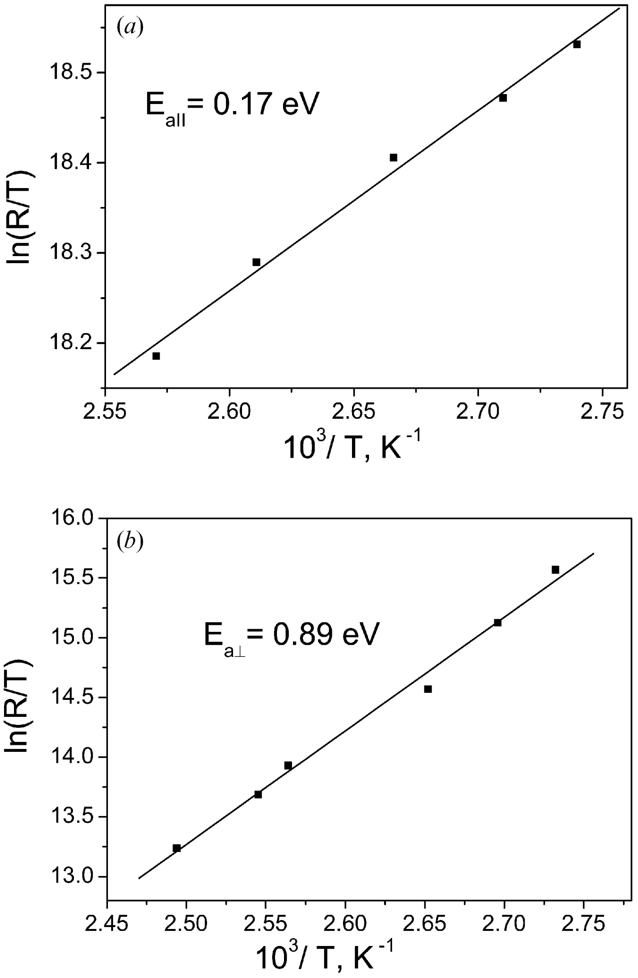

Figure 3. The volume resistance of the ordered thermotropic ISLC of cobalt decanoate versus inverse temperature: (*a*) electric field applied parallel to cation–anion layers (planar arranged electrodes); (*b*) electric field applied perpendicular to cation–anion layers (sandwich-like configuration of electrodes).

activation energy in the thermotropic ISLC. The movement of the cobalt cations is significantly hampered in the direction perpendicular to the cation–anion layers, evidently due to configurational changes and partial recovering of the carbon–hydrogen chains in the bilayered ISLC [16].

The observed values of electrical conductivity show that the thermotropic ISLC is a dielectrics with electrical conductivity higher to some degree than that of molecular liquid crystals. They are also distinguished from other liquid crystals by the high anisotropy of the electrical conductivity. Our measurements of charge carrier mobility show that μ has the same order of the magnitude as in lyotropic ISLC potassium caproate.

5. Discussion and conclusion

The experimental data for the lyotropic ISLC of potassium caproate are collected in table 1.

Further, we can also estimate the contribution to electric conductivity of OH^- ions in lyotropic ISLC, due to partial hydrolysis of the potassium caproate salt in the presence of water. From pH measurements the concentration c of OH^- ions is $c(OH^-)=10^{-6}\,mol \times l^{-1} = 6 \times 10^{20}\,m^{-3}$, and the electric conductivity contribution from OH^- ions is $\sigma(OH^-)=2 \times 10^{-5}\,\Omega^{-1}\,m^{-1}$. This value is six orders smaller in comparison with the experimental data. In our considerations we also neglect the contribution to electric conductivity of the long alkanoate anions ($C_9H_{19}COO^{-1}$) which have low mobility and form rigid bilayers in a smectic mesophase. Thus the K^+ ions are the main mobile charges responsible for electrical conductivity in lyotropic ISLC.

The observed high electrical conductivity in the lyotropic ISLC, which is higher than that in isotropic solutions [14], arises from the peculiarity of the structure of lyotropic smectic metal alkanoates. The mobility of potassium cations in a layer-structured ISLC exceeds that in dilute solutions [17]. On applying an electric field the potassium cations can easily migrate along the cation–anion layers of the ISLC. We consider a description of charge carrier transport in conductive lyotropic potassium caproate in terms of the electrolyte theory, but with taking into account the structural peculiarities of the ISLC with two-dimensional cation–anion layers of nanosized thickness. The solvation of potassium cations moving along the two-dimentional nanosized layers, is reduced in comparison with that in isotropic electrolytes. On the one hand, the counter-ions (the alkanoate anions) form rather rigorous bilayers in the smectic phase. On the other hand, hydration is low in the nanosized smectic layers in comparison with isotropic solutions. These factors lead to an increase in conductivity in the lyotropic ISLC. The activation energy indicates the energy needed for the cations (i) to break cation–anion bonds in the water layers, and (ii) to overcome the energetic barriers to movement between different domains.

The electrical characteristics of thermotropic ISLC cobalt decanoate permit the application of the quasicrystal model [2, 6, 7]. The value of electrical conductivity in the thermotropic ISLC corresponds to that for dielectrics.

Table 1. Electrical properties of the lyotropic ISLC of potassium caproate: n is the concentration of K^+ ions calculated from the relationship $n(K^+)=\sigma_{ac}/(q \times \mu)$, where q is the charge of the K^+ ion.

Sample	$\sigma_{ac}/\Omega^{-1}\,m^{-1}$	E_a/eV	$\mu/m^2\,V^{-1}\,s^{-1}$	n/m^{-3}
Oriented	10	0.21		10^{27}
Non-oriented	32	0.16	2×10^{-7}	10^{27}

Due to formation of a thermotropic smectic of homeotropic structure we have for the first time established that the electrical conductivity along the cation–anion layers is larger by four orders of magnitude than that in the perpendicular direction. The barriers preventing the motion of cobalt cations in the cation–anion layers are not large (0.16 eV). The activation energy of electrical conductivity along the cation–anion layers is four times smaller than the activation energy across the layers. In the latter case the long alkyl chains prevent the transport of cobalt cations, because in the temperature interval of the liquid crystal phase the alkyl chains are configurationally changed and are partly overlapped, in contrast to the crystalline state at room temperature.

The temperature dependences of charge mobility in the oriented thermotropic ISLC, as well as in thin uniformly oriented samples of lyotropic ISLC, are of interest for further development of the electrical conductivity model in ISLCs. It has been shown recently that composites based on the ISLC of metal alkanoates can be considered as new optical materials for the recording of dynamic diffraction gratings [15]. The experimental data obtained may be useful for the analysis of different nonlinear processes in such composites. It is significant also that electrically conductive lyotropic ISLC films may be used as soft electrodes. The electrical anisotropic properties of oriented ISLC samples may find applications in optoelectronic and photonic devices.

References

[1] P.A. Winsor. In *Liquid Crystals and Plastic Crystals*, N.H. Hartshorne (Ed.), pp. 122–143, Ellis Horwood, Chichester (1974).

[2] A.R. Ubbelohde, H.I. Michels, I.J. Duruz. *Nature*, **228**, 50 (1970).

[3] I.J. Duruz, H.I. Michels, A.R. Ubbelohde. *Proc. r. Soc. London*, **322 A**, 281 (1971).

[4] I.J. Duruz, A.R. Ubbelohde. *Proc. r. Soc. London*, **347**, 301 (1976).

[5] T. Meisel, K. Seybold, J. Roth. *J. therm. Anal*, **12**, 361 (1977).

[6] A.R. Ubbelohde. *The Molten State of Matter*. John Wiley (1978).

[7] Yu.K. Delimarskiy. *The Chemistry of Ionic Melts*. Naukova Dumka, Kiev (in Russian) (1980).

[8] T.A. Mirnaya, V.D. Prisyajnyuk, V.A. Shcherbakov. *Russ chem. Rev.*, **58**, 1429 (1989).

[9] S. Bugayhcuk, Yu.A. Garbovskiy, G.V. Klimusheva, A.B. Bordyuh, A.V. Gridyakina, O.G. Kolesnik, A.S. Tolochko, T.A. Mirnaya, A.P. Polishchuk, A.A. Ishchenko. *Nanosyst. Nanomater. Nanotechnol.* (Ukr), **2**, 1045 (2004).

[10] A.V. Gridyakina, A.P. Polishchuk, A.V. Koval'chuk, G.V. Klimusheva, A.S. Tolochko, T.A. Mirnaya, L.S. Sudovtseva. *Russ J. Phys. Chem.*, **79**, Suppl. 1, S71 (2005).

[11] L.M. Blinov. *Electro-magnetic Optics of Liquid Crystals*. Nauka, Moscow (1978).

[12] A.J. Twarowski, A.C. Albrecht. *J. chem. Phys.*, **70**, 2255 (1979).

[13] N.I. Gritsenko, V. Moshel'. *Ukr. phys J.*, **25**, 1830 (in Russian) (1980).

[14] A.A. Agaev, A.N. Nesrullaev, F.A. Rustamov. *Crystallography*, **32**, 519 (in Russian) (1987).

[15] G.V. Klimusheva, S.A. Bugaychuk, Yu.A. Garbovskiy, O.G. Kolesnic, T.A. Mirnaya, A.A. Ishchenko. *Opt. Lett.*, **31**, 235 (2006).

[16] T.A. Mirnaya, L.S. Sudovtsova, G.G. Yaremchuk, A.S. Tolochko, L.N. Lisetskii. *J. inorg Chem*, **49**, 1225 (in Russian) (2004).

[17] D.R. Lide (Eds), *Handbook of Chemistry and Physics* 84th Edn, CRC Press (2003–4).