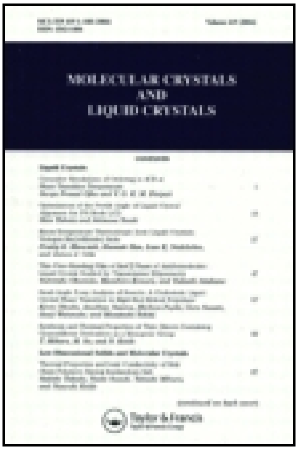

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Liquid Crystalline Materials for Electro-Optical Devices

L. M. Blinov [a] , E. I. Kovshev [a] & V. V. Titov [a]
[a] Organic Intermediates and Dyes Institute, 103787, Moscow, U.S.S.R.
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Liquid Crystalline Materials for Electro-Optical Devices†

L. M. BLINOV, E. I. KOVSHEV and V. V. TITOV
Organic Intermediates and Dyes Institute, 103787, Moscow, U.S.S.R.

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The most important physical and electro-optical parameters are reported for some liquid-crystal compositions which are produced industrially in the USSR. All the materials have positive dielectric anisotropy and are intended for use in field-effect devices.

1 INTRODUCTION

In the last few years, some novel liquid crystal materials with positive dielectric anisotropy ($\epsilon_a > 0$) were developed in our institute. They differ considerably from other materials, and the aim of this paper is to acquaint those who are interested in liquid crystal applications with their principal physical and performance characteristics.

The materials can be divided into three groups. In the first is included the only composition ZhK-614 which has a higher value of the dielectric anisotropy ($\epsilon_a \approx 18$) and a wider temperature range of the nematic phase ($-7 \div +71°C$) compared with the well-known mixtures of cyanobiphenyls. This composition can be used in traditional twist-displays.

In the second group, the compositions are included having small values of the optical anisotropy, $\Delta n \approx 0.04$–0.08, and variable (from +0.2 to + 9.5) values of ϵ_a (ZhK-805, 910, 911, 912). These substances are basically intended for color displays using light interference S- or B-effects.[1] The same materials (especially ZhK-805) can be used as transparent matrices for UV absorption spectroscopy.

The third group involves two materials (ZhK-999 and ZhK-1000) having

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TABLE I

Material	Chemical basis of a mixture	M.p.(°C)	C.p.(°C)	Dielectric permittivities[1] $\epsilon_{\parallel}$	$\epsilon_{\perp}$	ϵ_a	Sign for $\Delta\chi$[2]	Δn $\lambda = 589$ nm	η_2[3] (cP)
ZhK-614	cyanophenyl esters	−7	+71	25.9	7.6	18.3	+	0.22	25
ZhK-805	cyclohexane carboxylic acids	−27	+95	2.46	2.29	0.17	−	0.053	25
ZhK-910	cyclohexane carboxylic acids	−27	+58	5.0	3.2	1.8	−	0.044	14.3
ZhK-911	cyclohexane carboxylic acids	0	+79	8.5	3.5	5.0	?	0.067	27.6
ZhK-912	cyclohexane carboxylic acids	+5	+72	12.3	4.1	8.2	+	0.075	29.6
ZhK-999	azoxy-compounds and phenyl benzoates	−3	+76	9.3 5.4	7.3 7.3	2.0 −1.9	+	0.244	36.4
ZhK-1000	phenyl benzoates	−7	+62	9.7 5.1	7.4 7.4	2.3 −2.3	+	0.13	62.1
E7	cyanobiphenyls	−9	+60	19	5.4	13.6	+	0.224	32

Notes: (1) The values of $\epsilon_{\parallel}$, $\epsilon_{\perp}$ and ϵ_a are given at frequency $f = 1$ kHz for the first five materials. For ZhK-999 and ZhK-1000, the upper and lower figures correspond to $f_1 = 200$ Hz and $f_2 = 40$ kHz, respectively.
(2) $\Delta\chi$—diamagnetic anisotropy.
(3) η_2—the viscosity corresponding to the director orientation along the capillary flow.

low-frequency inversion of the sign of ϵ_a. They can be widely used in fast light intensity modulators or light polarization switches.

The most general characteristics (at 25° C) for all the materials are shown in Table I. For the sake of comparison, the same parameters of the well-known cyanobiphenyl mixture E7 are also included in the table.

2 DIELECTRIC PROPERTIES

The temperature dependencies of the dielectric permittivities $\epsilon_{\parallel}$ and $\epsilon_{\perp}$, which have been measured by the standard bridge technique,[2] are shown in Figure 1 for the materials from the first and second groups. It should be noted that the materials ZhK-805 and 910 have both a positive dielectric and a negative diamagnetic anisotropy. This widens the scope of application of these materials in UV spectroscopy (ZhK-805 is transparent[3] up to $\lambda = 250$ nm).

The frequency curves of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ (at 25° C) are depicted in Figure 2 for materials ZhK-999 and 1000. Varying the percentage of the components having different signs and values of ϵ_a we could manage to obtain mixtures with approximately equal values $|\epsilon_a| \approx 2$ on both sides of the inversion frequency (f_i) of the sign of ϵ_a. The temperature dependence of f_i for ZhK-999 and 1000 is shown in Figure 3.

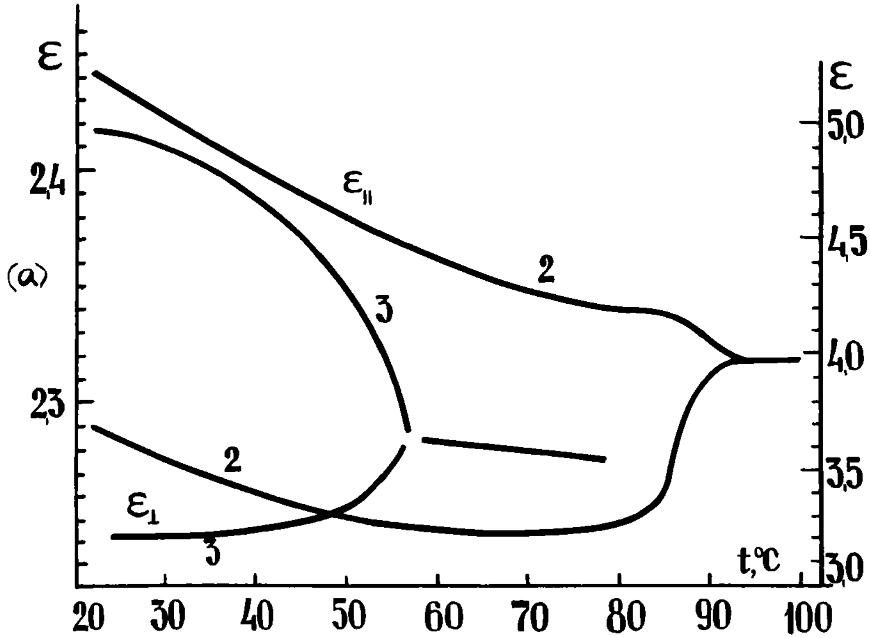

FIGURE 1 (a) (b) Temperature dependence of the dielectric permittivities for materials ZhK 614 (1), ZhK 805 (2), ZhK 910 (3), and ZhK 914 (4).

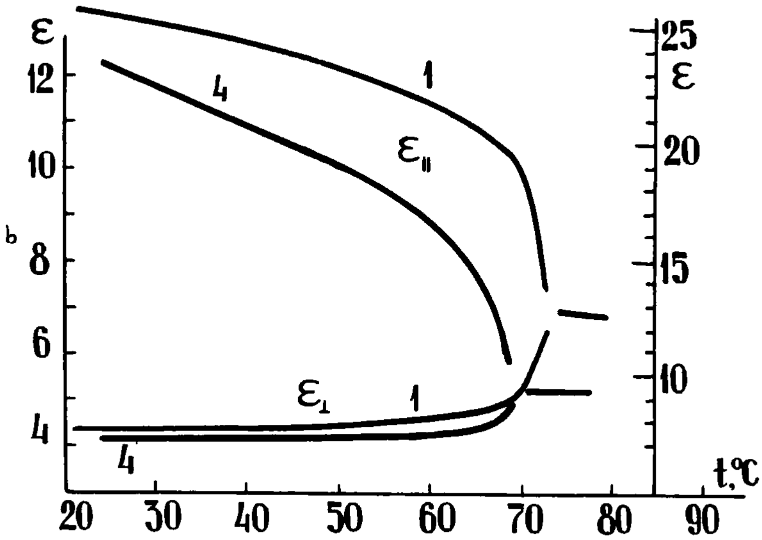

FIGURE 1b (cont'd.)

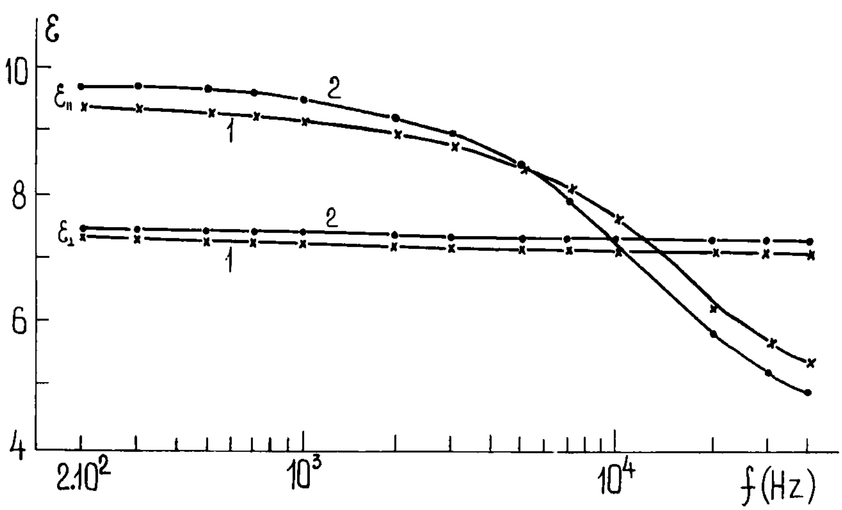

FIGURE 2 Dielectric permittivities of materials ZhK-999 (1) and ZhK-1000 (2) as functions of frequency at $t = 25°$ C.

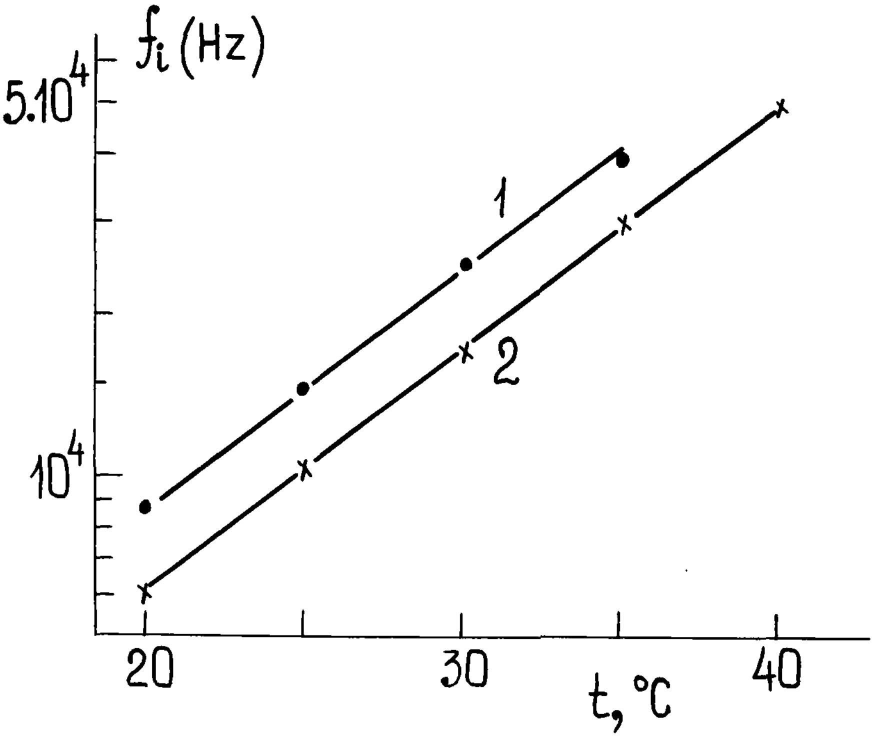

FIGURE 3 Temperature dependence of the inversion frequency of the sign of ϵ_a for ZhK-999 (1) and ZhK-1000 (2).

3 REFRACTIVE INDICES

The temperature dependencies of $n_\parallel$ and $n_\perp$ measured by refractometry are shown in Figure 4. In Table II are given the data on the dispersion of the optical anisotropy for all the materials (at 25° C). The latter were obtained using spectrophotometric measurements of the phase delay for polarized light transmitted through a liquid crystal layer.[2]

4 VISCOSITY CURVES

The temperature dependence of the Miecsowicz viscosity coefficient $\eta_2 = \frac{1}{2}(\alpha_3 + \alpha_4 + \alpha_6)$, which corresponds to the director orientation along the direction of material flow in a capillary, is depicted in Figure 5. The experimental technique has been discussed.[4]

The most interesting peculiarity of Figure 5 is the extremely low viscosity for materials ZhK-805 and ZhK-910 (the value $\eta_2 = 14.3$ cP at $t = 25°$C

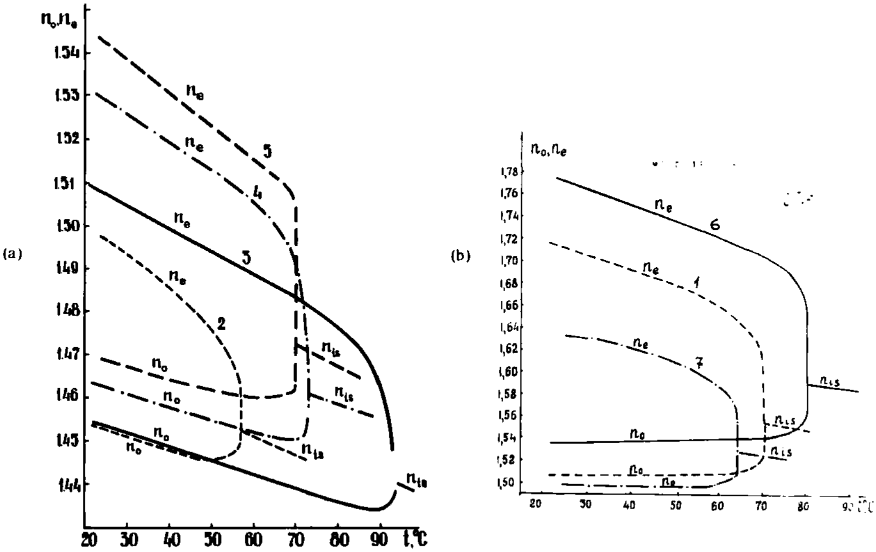

FIGURE 4 (a) (b) Temperature dependence of the refractive indices n_e and n_o at wavelength λ = 589 nm for ZhK-614 (1), ZhK-805 (2), ZhK-910 (3), ZhK-911 (4), ZhK-912 (5), ZhK-999 (6), and ZhK-1000 (7).

should be compared, for instance, with the value $\eta_2 \approx$ 32 cP for the cyanobiphenyl mixture E7).

5 ELECTRO-OPTICAL BEHAVIOR

Though the materials are intended for various applications, for the sake of uniformity, we demonstrate their contrast-voltage characteristics only in the twist-effect transmittance mode. The measurements were made using a He–Ne laser with a light vector perpendicular to the director on the front surface of a layer of thickness $d \approx 12\ \mu$m. An analyser was perpendicular to the incident light vector. The optical contrast $K = I_0/I$ as a function of voltage (at frequency 500 Hz) is given in Figure 6 (I_0 and I are the light intensities entering and leaving a cell, respectively). The voltages corresponding to values of the optical transmission of 10 and 90% (V_{10} and V_{90}) are given in Table III, together with the ratio $(V_{10}-V_{90})/V_{90}$ determining the multiplexing capability of a material.

One can see in Table III that a maximum slope of the contrast-voltage curve is characteristic of materials ZhK-911 and 912, combining a low optical anisotropy with a fairly high value of ϵ_a.

The response (τ_r) and relaxation (τ_R) times of the twist-effect, correspond-

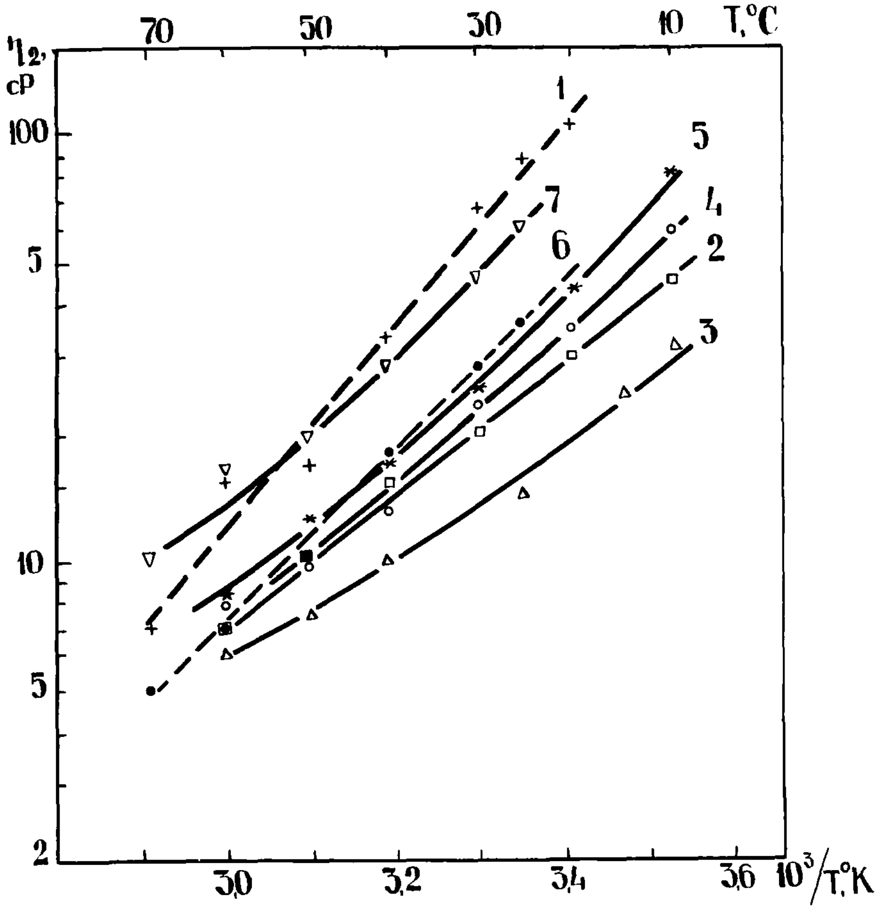

FIGURE 5 The viscosity coefficient η_2 as a function of temperature for ZhK 614(1), ZhK-805 (2), ZhK 910 (3), ZhK-911 (4), ZhK-912 (5), ZhK-999 (6), and ZhK-1000 (7).

ing to an on and off voltage V_0 across cells of thickness $d \approx 13\,\mu m$ ($t = 23°C$), are given in Table IV (the characteristics of ZhK-999 and 1000 working by the two-frequency addressing mode will be given below).

One can see in Table IV that, at room temperature, the switching rate for all our materials is markedly worse than that for the cyanobiphenyl mixture *E*7. However, the situation changes in favor of some of our materials with decreasing temperature, since the temperature slopes of the curves $\tau_R(T)$ are quite different for various compounds (Figure 7). Indeed, ZhK-910 works in the twist-effect mode down to −45° C, having $\tau_R \approx 50$s at this temperature. At −20° C, the relaxation time for ZhK-910 ($T_R \approx 2.5$ s) is one order of magnitude lower than the corresponding time for the cyanobiphenyl mixture. It

TABLE II

ZhK-614		ZhK-805		ZhK-910		ZhK-911		ZhK-912		ZhK-999		ZhK-1000	
λ(nm)	Δn	λ(nm)	Δn	λ(nm)	Δn	λ(nm)	Δn	λ(nm)	Δn	λ(nm)	Δn	λ(nm)	Δn
423	0.26	423	0.0554	438	0.0447	416	0.072	420	0.081	428	0.383	407	0.131
457	0.24	465	0.0546	500	0.0437	476	0.069	444	0.079	448	0.328	435	0.151
508	0.22	517	0.0536	590	0.043	518	0.067	472	0.077	488	0.277	474	0.144
592	0.205	589	0.0531	652	0.0427	571	0.066	508	0.076	521	0.254	528	0.148
656	0.20	677	0.0528			645	0.065	552	0.074	572	0.232	611	0.133
								590	0.073	660	0.214	668	0.131
								685	0.071				

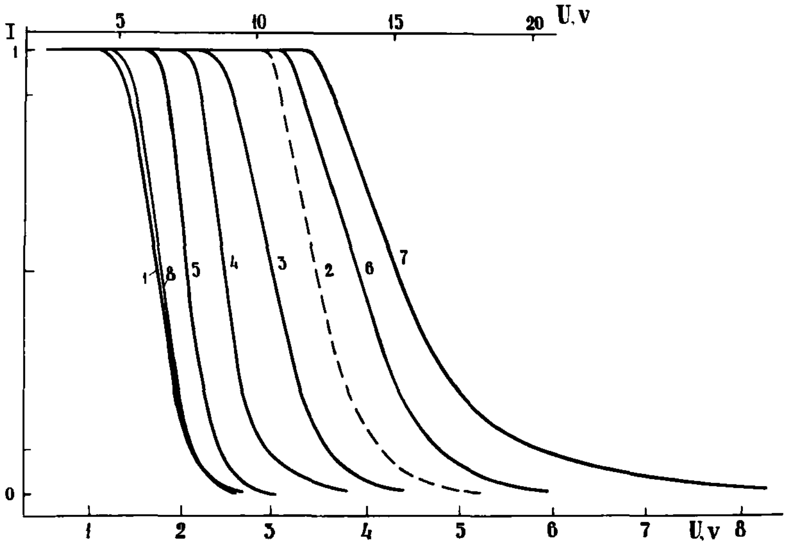

FIGURE 6 Optical transmission of twist-calls as a function of voltage. The upper scale is only for curve 2. Materials: ZhK-614 (1), ZhK-805 (2), ZhK-910 (3), ZhK-911 (4), ZhK-912 (5), ZhK-999 (6), ZhK-1000 (7), E7 (8).

TABLE III

Material	V_{90}	V_{10}	$\frac{V_{10}-V_{90}}{V_{90}}$
ZhK-614	1.5	2.1	0.4
ZhK-805	10.7	15	0.4
ZhK-910	2.55	3.6	0.41
ZhK-911	2.3	3.0	0.3
ZhK-912	1.95	2.5	0.28
ZhK-999	3.3	4.8	0.49
ZhK-1000	3.6	5.8	0.62
E7	1.65	2.24	0.36

TABLE IV ($t = 22°C$)

Material	V_0 (volts)	τ_r (ms)	τ_R (ms)
ZhK-614	3	700	500
ZhK-805	25	350	300
ZhK-910	5	220	220
ZhK-911	5	250	300
ZhK-912	4	350	340
E7	3	220	110

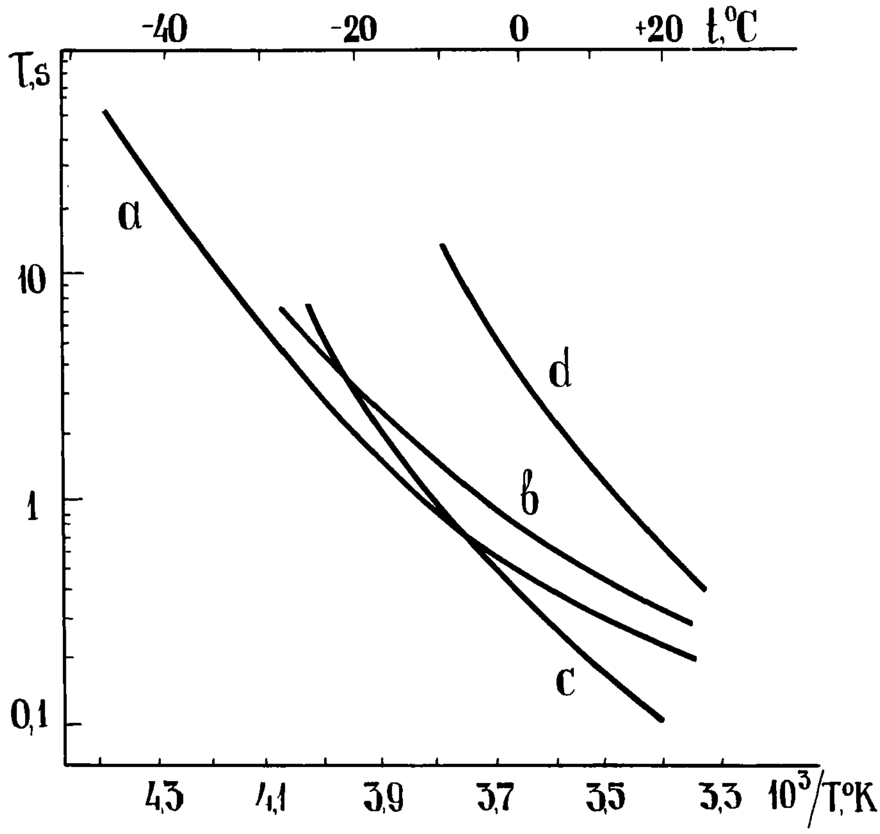

FIGURE 7 Temperature dependence of relaxation time in the twist-effect mode (cell thickness $d \approx 13$ μm). Materials: ZhK-910 (a), ZhK-805 (b), E7 (c), ZhK-614 (d).

TABLE V

$V_{LF} = V_{HF}$ (volts)	ZhK-999 T_{HF} (ms)	ZhK-999 τ_r (ms)	ZhK-999 τ_R (ms)	ZhK-1000 T_{HF} (ms)	ZhK-1000 τ_r (ms)	ZhK-1000 τ_R (ms)
40	2.0	0.7	1.2	2.2	1.0	1.6
50	1.5	0.5	0.8	1.5	0.75	1.0
60	0.8	0.4	0.6	1.0	0.5	0.7
70	0.7	0.2	0.4	0.8	0.3	0.5
80	0.7	0.15	0.25	0.5	0.25	0.35

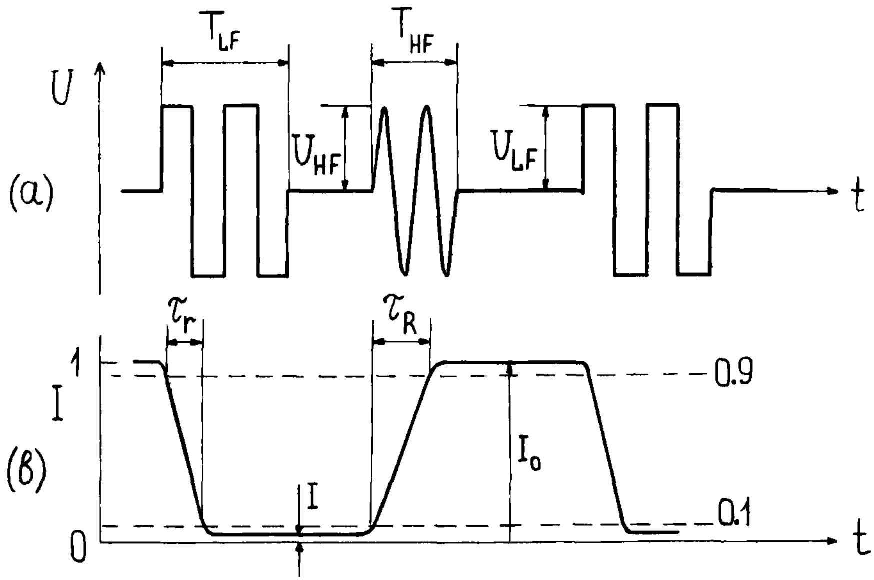

FIGURE 8 The form of oscillograms for driving voltage (a) and photoresponse of a twist-cell (b) for the two-frequency addressing mode.

should be mentioned, however, that the utilization of materials ZhK-910, 911, and 912 in the twist-effect regime with the usual white light source involves some difficulties due to the small value of Δn which gives rise to inteference colors. On the other hand, these compounds appear to be of great importance for various color displays.

For ZhK-999 and 1000, the most interesting regime is the two-frequency addressing mode. In Figure 8, oscillograms of driving voltages and twist-cell optical response are shown schematically. The low (*LF*) and high (*HF*) frequencies are 1 and 50 kHz. Using crossed polarizers, and having chosen the optical contrast $K \geq 100:1$, one can obtain the response and relaxation times in ms shown in Table V for a cell of thickness 10 μm (the perameters varied were the voltages V_{LF} and V_{HF} and the pulse duration T_{HF}; T_{LF} was constant and equal to 7.5 *ms*—see Figure 8).

It follows from the Table that one can obtain the whole on-off cycle within 500 and 600 μs, respectively for ZhK-999 and 1000. For cells of thickness 20 μm, the corresponding times are 1.2 and 1.7 ms. Thus, the materials ZhK-999 and 1000 in twist-cells of thickness 10 μm allow 100%-depth light modulation for frequencies up to 2 kHz, the contrast being more than 100 : 1. Such a high switching rate opens up the possibility of application of these materials in stereo-TV equipment, fast holographic page composers, etc.

Acknowledgments

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