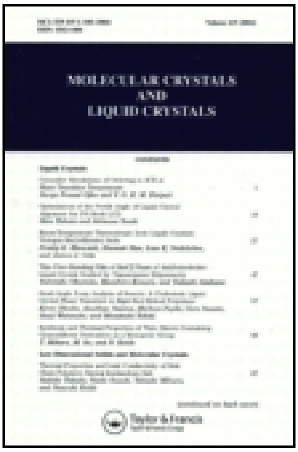

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Spectral Properties of Nematic Liquid Crystal Mixtures Composed with Long and Short Molecules in THz Frequency Range

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Properties of liquid crystal materials in THz frequency range can be interesting from application point of view.

In this paper the influence of short and long molecules added to liquid crystal 6CHBT were investigated. Change of refractive indices and absorption coefficients for 6CHBT mixtures were compared in the 0.3 - 3 THz frequency range. Influence of temperature on the mentioned parameters of liquid crystal were investigated. Our study show that even a slight change in shape and the composition of the molecules dopants affects the macroscopic properties of liquid crystal. These properties depend on the length of chains, the number of benzene or cyclohexane rings or the spatial distribution of molecules and the interactions between them in the liquid crystal mixture. Spectra measurements on the terahertz time-domain spectrometer were performed.

Keywords Liquid crystal; spectroscopy; terahertz

1. Introduction

For the past two decades, the terahertz technology stay a one of most important field of interest in many science centers. Many research teams have been investigated the physical properties of liquid crystals in the visible range. Liquid crystals due to the ease of retuning are widely used above and below the THz range. Over the last decade were built devices based on liquid crystals operating in the THz band, e.g. filters [1], phase shifters [2], phase gratings [3]. These devices can be used in medicine, pharmacy, industry, etc. The most studied liquid crystal is *4′-n-pentyl-4-cyanobiphenyl* (5CB) [4–8].

In this work we present the results of measurements of pure liquid crystal compound 6CHBT and ten mixtures based of 6CHBT. We investigate how changes in the length of molecules and number of aromatic rings affects the physical properties of liquid crystal mixtures using terahertz time-domain spectroscopy (THz-TDS).

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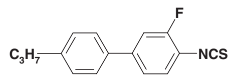
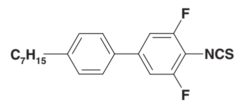
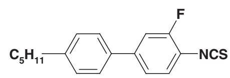
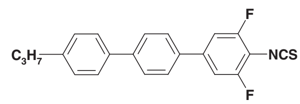
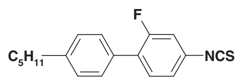
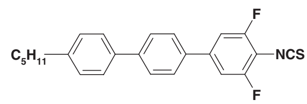
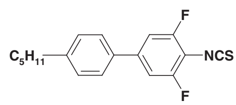
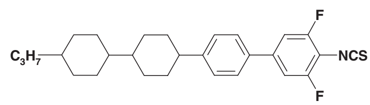
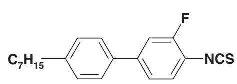
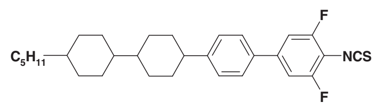
Table 1. Structure of molecules added to the compound of 6CHBT and phase transition temperatures (nematic-liquid) of measured LC mixtures.

	Molecules	T_{Iso}[°C]		Molecules	T_{Iso} [°C]
1.		35.5	6.		25.0
2.		35.5	7.		61.6
3.		22.5	8.		94.5
4.		22.5	9.		143.0
5.		35.9	10.		105.5

2. Liquid Crystal Materials

Liquid crystal mixtures were synthesized in the Military University of Technology. These are new two-component materials on the basis of 6CHBT compound. Chemical structure and temperature of phase transitions nematic-liquid of these materials in Table 1 is shown. All mixtures are mixed in a molar ratio of 2:1 (6CHBT + n), except mixture 7 where is 15% compound weight in 6CHBT. Molecules in a mixture differ in length of alkyl chain, number of aromatic rings and the number and placement of fluorine atoms. The optical properties of 6CHBT mixtures were investigated. Ordinary n_o (molecules are perpendicular to polarization incident wave) and extraordinary n_e (molecules are parallel to polarization incident wave) refractive index were investigated using an Abbe refractometer for wavelength *589* nm. The results are shown in later part of the paper in Table 2.

3. Calculating the Physical Parameters

The amplitude of the electric field *E(x)* after passing through the medium of length *x* can be described as [9]:

$$E(x) = E_0 \exp\left(-i\frac{\omega\tilde{n}x}{c}\right) = E_0 P(x), \tag{1}$$

where ω is angular frequency propagating wave, c is speed of light in the vacuum, E_0 is amplitude incident electric field, *P(x)* is the propagation coefficient through a medium wave frequency dependent, $\tilde{n}(\omega) = n(\omega) - i\kappa(\omega)$ is frequency dependent complex refractive index and $\kappa(\omega) = \frac{\alpha(\omega)\cdot c}{2\omega}$ is extinction coefficient.

Table 2. Refractive indices and birefringence for visible range and 1.5 THz measured at 25°C

	589 [nm]			1.5 [THz]		
LC mixtures	n_o	n_e	Δn	n_o	n_e	Δn
6CHBT	1.5212	1.6699	0.1487	1.497	1.668	0.171
1	1.5445	1.7050	0.1605	1.543	1.681	0.138
2	1.5327	1.6973	0.1646	1.520	1.677	0.157
3*	1.5394	1.6965	0.1571	1.493	1.659	0.166
4*	1.5392	1.6931	0.1539	1.483	1.596	0.113
5	1.5318	1.7007	0.1689	1.533	1.677	0.144
6*	1.5350	1.6926	0.1576	1.456	1.607	0.151
7	1.5225	1.7210	0.1985	1.533	1.698	0.165
8	1.5294	1.7776	0.2482	1.525	1.736	0.211
9	1.5139	1.7281	0.2142	1.521	1.726	0.205
10	1.5149	1.7064	0.1915	1.497	1.678	0.181

*measured at 17°C.

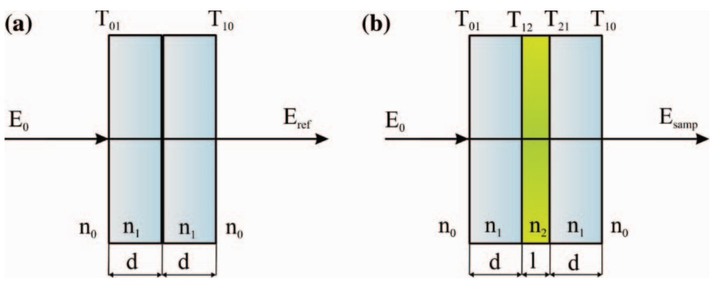


Figure 1. Schematic of the propagation THz wave through the a) reference and b) cell with liquid.

In Figure 1 is shown a schematic THz wave propagation through two directly adjacent plates, which were a reference in the measurements, and wave passing through the cell with liquid crystal. The amplitude of the electric field E_{ref} after passing through two plates of length *2d* can be described as:

$$E_{ref} = E_0 P_0(x - 2d) T_{01} P_1(2d) T_{10}, \tag{2}$$

where $T_{ij} = \frac{2n_i}{n_i + n_j}$ is the amplitude transmission coefficient through the interface (Fresnel coefficient). The amplitude of the electric field E_{samp} after passing through the cell with LC is given by:

$$E_{samp} = E_0 P_0(x - 2d - l) T_{01} P_1(d) T_{12} P_2(l) T_{21} P_1(d) T_{10}, \tag{3}$$

The complex transmission coefficient $T(\omega)$ is given by:

$$T(\omega) = \frac{E_{samp}}{E_{ref}} = P_0(-l) T_{12} P_2(l) T_{21}, \tag{4}$$

after simple transformations we obtain:

$$T(\omega) = \frac{4n_1n_2}{(n_1+n_2)^2}\exp\left(-\frac{\omega\kappa_2 l}{c}\right)\cdot\exp\left(-i\,(n_2-1)\,\frac{\omega l}{c}\right), \tag{5}$$

$$T(\omega) = \left|\frac{E_{samp}}{E_{ref}}\right|\cdot\exp\left(-i\,\Delta\varphi\right), \tag{6}$$

assuming that $n_0 = 1$ (refractive index of air). From the real part of complex transmission coefficient in a simple way to determine the absorption coefficient, while the imaginary part of refractive index of LC, which are given by:

$$n_2 = 1 + \frac{c}{\omega l}\Delta\varphi, \tag{7}$$

$$\alpha_2 = -\frac{2}{l}\ln\left(\frac{(n_1+n_2)^2}{4n_1n_2}\cdot\left|\frac{E_{samp}}{E_{ref}}\right|\right), \tag{8}$$

where $\Delta\phi = \phi_{samp} - \phi_{ref}$ is phase difference and ϕ_{samp} and ϕ_{ref} are the phases of the THz field passing through the sample and the reference cell, respectively.

Formulas do not included reflections inside the cell (effect Fabry-Perot). For simplicity the Fresnel coefficients were calculated only from the real part of the refractive index.

4. Experiment

Cells that were used for measurements consisted of quartz plates with a thickness of 1.50 ± 0.05 mm and spacers in the form of copper wires with a diameter of 0.50 ± 0.01 mm. Liquid crystal was placed between the plates. In order to align the LC molecules a mean electric field of 30 kV/m with the modulation frequency of 1 kHz was applied. Reference were two directly adjacent quartz plates (Fig. 1). Measurements for the ordinary ray were obtained when the polarization of the incident THz radiation was perpendicular to the long axis of LC molecules, for the extraordinary ray - if the polarization was parallel to the LC molecules long axis.

Teraview TPS 3000 unit with accessories in transmission configuration for Time Domain Spectroscopy measurement was used. Schematic diagram of the spectrometer is shown in Fig. 2. Time Domain Spectroscopy is a widely used technique in THz range and is described in detailed in many books and articles [5, 10, 11]. TDS spectrometer consists of a femtosecond sapphire laser which generates terahertz pulses. Pulses are split on the Polarization Beam Splitter (PBS). The first part of the beam impinges on the emitter where under the influence of the radiation is generated THz wave. This wave is collimated by an off-axis paraboloidal mirror propagated through the sample and is collimated and focused again by a second of off-axis paraboloidal mirror onto a detector, where on the other side falls the second part of the laser beam. The beam size of the Terahertz wave is about 1 cm. The sample were placed perpendicularly to the incident radiation, in the middle of the distance between the emitter and detector. To eliminate water vapor, chamber of the spectrometer was purged with dry air.

The measurement result is the THz signal dependence on time (Fig. 3). Using Fast Fourier Transform (FFT) the amplitude spectra versus frequency is obtained (Fig. 4). The first pulse shown in Fig. 3 is a reference measurement of the wave passing through the

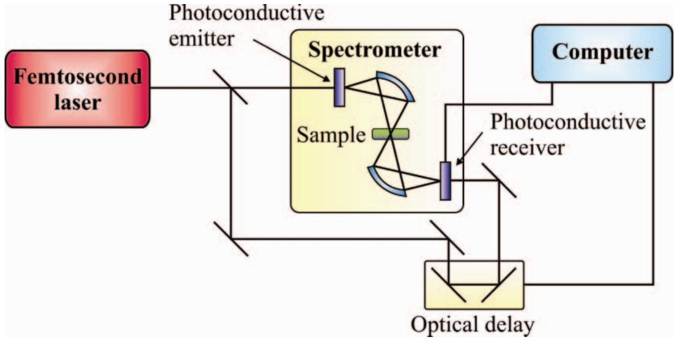


Figure 2. Schematic diagram of the spectrometer [10].

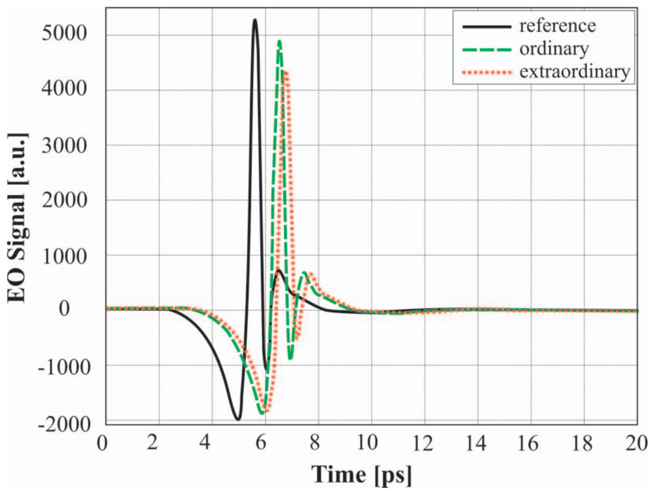


Figure 3. Reference and sample THz-pulses of 6CHBT.

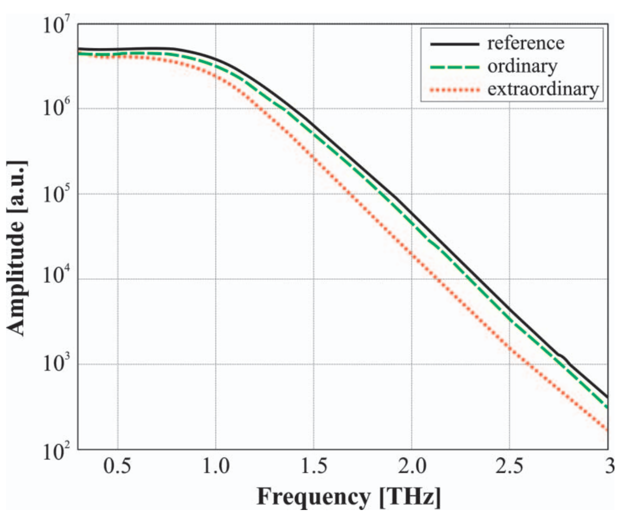


Figure 4. Amplitude spectra of reference and sample pulses of 6CHBT.

two quartz plates. Other two pulses correspond to the wave after the passing through the sample for ordinary and extraordinary polarization. From these data refractive indices, birefringence and absorption coefficients were calculated.

5. Results and Discussion

In Fig. 5 the refractive indices for ordinary n_o and extraordinary n_e rays of pure compound 6CHBT and two selected liquid crystal mixtures (1 and 8) are presented. The mixture 6CHBT+8 (mixture 8) has the highest values of the refractive indices. Doped molecules of these mixture consist of three benzene rings, five atoms of carbon in alkyl chain and two fluorine atoms. It is the longest molecule with benzene rings. The comparison of refractive indices and birefringence in visible light (yellow line of sodium) and 1.5 THz are shown in Tab. 2. Three mixtures (3, 4 and 6) were measured in 17°C because they temperatures of phase transition are below room temperature. The refractive indices n_o and n_e of these mixtures are smaller than in the case of mixtures measured at room temperature (Tab. 2).

Above 1 THz the highest values of birefringence correspond to mixtures 8, 9 and 10, which have the longest cores of doped molecules. From among these three mixtures the smallest values of birefringence has mixture 10. That behavior also corresponds to the visible range. In the nest step the mixtures 1, 2 and 5 were compared. They differ only in the length of the alkyl chain. Birefringence of the mixture 1, with three carbon atoms in the alkyl chain, does not depend on frequencies and below 1 THz takes the highest values. For mixtures 2 and 5 the values of birefringence initially rapidly increases. Then above 1.5 THz they maintain constant values. They are larger than for mixture 1 only over 1 THz. Mixtures 1, 7 and 9 differ in the number of aromatic rings in the core doped molecules.

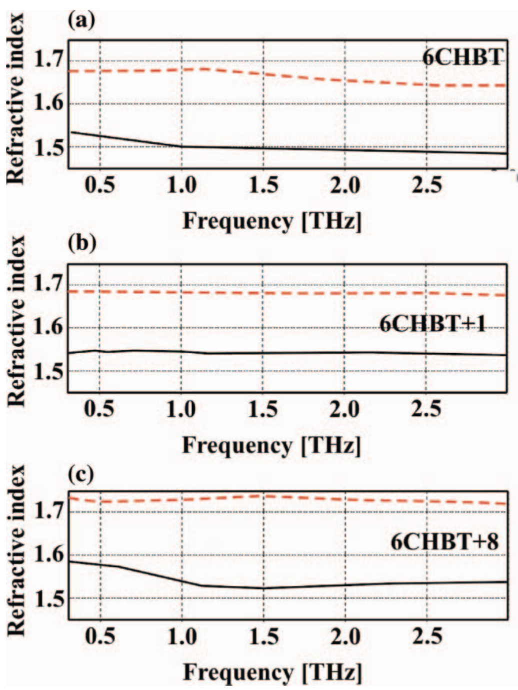


Figure 5. Refractive indices selected LC materials (solid line – ordinary, dotted line – extraordinary).

In this case the greater number of rings increases the value of birefringence. Mixture 1 and 7 are composed of molecules with two and three benzene rings, respectively. Mixture 9 consist of two benzene rings and two cyclohexane rings. Furthermore a mixture 1 has molecules with only one fluorine atom, and mixtures 7 and 9 have molecules with two fluorine atoms. Mixtures 4, 8 and 10 also differ only by the number of aromatic rings in the doped molecules. They have only two carbon atoms more in the alkyl chain than mixtures 1, 7 and 9. The lowest birefringence has a mixture 4 with the shortest molecules length. The mixture 10 consist of molecules with two benzene rings and two cyclohexane rings has a lower birefringence than the mixture 8 compound of molecules with three benzene rings. Molecules of mixtures 7 and 8 differ only in the alkyl chain length. Larger values of birefringence have a mixture consisting of molecules with the longer alkyl chain. In the case of mixtures 9 and 10, where the molecules also differ only in the alkyl chain length, the situation is reversed. A mixture consisting of molecules with a shorter chain exhibits higher birefringence. This phenomenon may be associated with different types of molecules aromatic rings in mixtures 7, 8 and 9, 10. Furthermore mixture 7 has other proportion of ingredients than the rest mixtures. Additionally, it has temperature of phase transition nematic – crystal near room temperature.

Fig. 6 shows the absorption coefficients for ordinary α_o and extraordinary α_e rays of pure compound 6CHBT and two selected LC mixtures (1, 8). In the literature [8, 12, 13], all the pure LC compounds and LC mixtures have a lower absorption for the extraordinary ray than for ordinary ray. In the case of the pure compound of 6CHBT and mixtures 1, 3, 4 and 9, the absorption coefficients for the extraordinary ray have larger values than for ordinary one. For other mixtures, the dependence between the two coefficients look like in Fig. 6c).

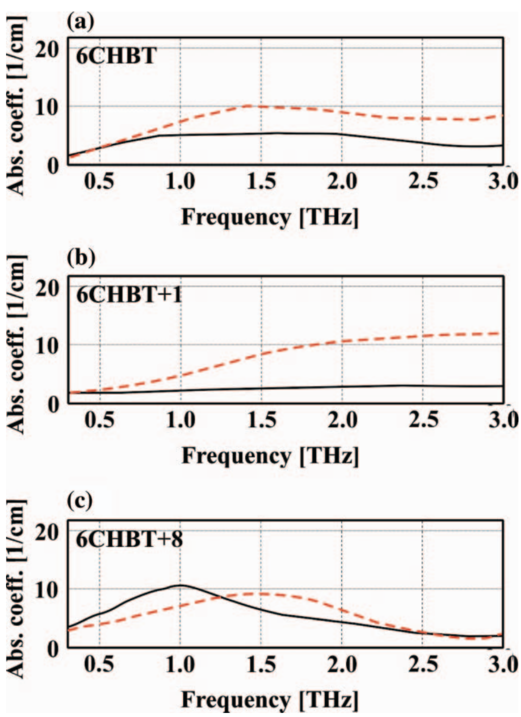


Figure 6. Frequency dependence of the absorption coefficient (solid line – ordinary, dotted line – extraordinary).

In addition, most studied mixtures except mixture 1 and 7, have absorption maxima near 1 THz for ordinary ray and near 1.5 THz for extraordinary ray (Fig. 8).

6. Summary

Spectral measurements in range 0.3 to 3 THz of liquid crystal mixtures synthesized based on 6CHBT were done. Physical properties such as birefringence, refractive indices and absorption coefficients for ordinary and extraordinary beam were obtained. The values of refractive indices measured in 17°C are lower than values of refractive indices measured in 25°C. All measured mixtures, except pure compound 6CHBT and mixture 3, have lower values of birefringence in THz range than in visible range. In most cases, increase the length of molecules causes the increase in the value of birefringence. Values of absorption coefficients are below 20 1/cm for all measured liquid crystals. The most of them have maxima of absorption around 1 THz for ordinary ray, and around 1.5 THz for extraordinary ray.

Acknowledgments

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References

[1] Göbel, T., Meissner, P., Gaebler, A., Koeberle, M., Mueller, S. and Jakoby, R., in *Proceedings of the Conference on Lasers and Electro-Optics and Conference on Quantum Electronics and Laser Science Conference*, Baltimore, Maryland, 2009, art. no. 5224708,

[2] Chen, C.-Y., Tsai, T.-R., Pan, C.-L. and Pan, R.-P. (2003). *Applied Physics Letters 83* (22), 4497–4499.

[3] Lin, Ch.-J., Lin, Ch.-H., Li, Y.-T., Pan, R.-P., and Pan, C.-L. (2009). *Photonic Technology Letters 21*, 11.

[4] Vieweg, N., Jansen, Ch., Khaled Shakfa, M., Scheller, M., Krumbholz, N., Wilk, R., Mikulics, M. and Koch, M. (2010). *Optics Express 6097*, *18*, 6.

[5] Pan, R.-P., Hsieh, Ch.-F., Pan, C.-L. and Chen, Ch.-Y. (2008). *Journal of Applied Physics 103*, 093523.

[6] Tsai, T.-R., Chen, Ch.-Y., Pan, C.-L., Pan, R.-P. and Zhang, X.-Ch. (2003). *Applied Optics 42* (13), 2372–2376.

[7] Enikeeva, V. A., Makarov, V. A., Ozheredov, I. A. and Shkurinov, A. P. (2007), in *Proceedings of the Conference Digest of the Joint 32nd International Conference on Infrared and Millimetre Waves, and 15th International Conference on Terahertz Electronics*, 2007, art. no. 4516591, pp. 480–481.

[8] Wilk, R., Vieweg, N., Kopschinski, O., Hasek, T. and Koch, M. (2009). *Journal of Infrared, Millimeter, and Terahertz Waves 30* (11), 1139–1147.

[9] Wilk, R., Ph.D. thesis, Universität Carolo-Wilhelmina zu Braunschweig, 2007.

[10] Pałka, Norbert and Trzcinski, Tomasz, in *Proceedings of SPIE - The International Society for Optical Engineering 79380*, San Francisco, California, USA, 2011, art. no. 79380L.

[11] Lee, Y.-Sh., *Principles of Terahertz Science and Technology* (2009). Corvallis, Oregon 97331, USA.

[12] Vieweg, N., Shakfa, M. K. and Koch, M. (2011). *Optics Communications 284* (7), 1887–1889

[13] Vieweg, N. and Koch, M. (2010). *Applied Optics 49* (30), 5764–5767.