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Mid-infrared refractive indices of the nematic mixture E7

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E7 is a room temperature nematic liquid crystal mixture with a high positive dielectric anisotropy and a high chemical stability. Because of its relatively high nematic-to-isotropic transition temperature, it is suitable for mid-infrared laser applications, where the absorption of laser light is not negligible and gives rise to a certain heating of the medium. In this paper we give a measurement of the refractive indices of the liquid crystal E7 at a wavelength of $10.6 \,\mu\text{m}$ as a function of temperature. An empirical formula to represent the experimental data is also provided.

1. Introduction

E7 is a mixture of 4-pentyl-4'-cyano-biphenyl and terphenyl. It is a widely used room temperature nematic liquid crystal. The literature reports some experimental results concerning the optical anisotropy and refractive indices in the visible spectral region [1-3]. However very few experimental results concern the mid-infrared spectral region [4]. This type of liquid crystal is a good candidate for mid-infrared laser applications where the CO₂ laser ($\lambda = 10.6 \,\mu\text{m}$) is commonly employed. Its high clearing temperature allows the employment of relatively high power lasers without inducing the nematicto-isotropic transition. In fact a problem that arises when mid-infrared laser light is used is the local heating of the liquid crystal film due to the laser light. The heating is due to the relatively high absorption coefficients of liquid crystals at these wavelengths, specifically, $\alpha_e = 5.5 \times 10^{-3} \,\mu\text{m}^{-1}$ and $\alpha_o = 4.0 \times 10^{-3} \,\mu\text{m}^{-1}$ for the extraordinary and ordinary rays, respectively [4]. For these reasons we believe that further characterization of the optical properties of E7 at these wavelengths is important for future applications considering the wide use of CO₂ lasers for industrial and medical applications. The experiment has been performed using an optical technique based upon refraction of a midinfrared laser beam by a wedge-shaped liquid crystal cell. A very sensitive new type of infrared video-camera has been employed as a detector. With this camera it is possible to obtain very good quality images of the Gaussian shaped laser beam even at very low values of laser power. This avoids the heating of the medium in

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the zone where the laser beam passes through the liquid crystal, preventing the formation of an unwanted temperature gradient within the liquid crystal film that could lead to thermally induced effects and to incorrect temperature measurements.

2. Description of the experimental apparatus

The experimental set-up is shown in figure 1. Our light source is a c.w. CO_2 laser that operates on the fundamental Gaussian mode at a wavelength of 10.6 µm (line P20). The laser light is polarized along the horizontal plane by means of a Brewster window placed inside the laser cavity. A beam condenser formed by two ZnSe lenses placed in a confocal configuration allows us to obtain a quite narrow laser spot on the video-camera of a diameter of approximately 2 mm. The laser radiation is polarized at 45° with respect to the horizontal plane by means of a wire grid polarizer and passes through a liquid crystal cell filled with the liquid crystal E7 (Merck). The easy axis of the sample is in the horizontal plane and the first plate of the cell (i.e. the first encountered by the laser beam) is perpendicular to the wave vector of the incident laser radiation (see figure 2, first plate labelled A). The cell is composed of two ZnSe windows, 2 mm thick, kept in a wedge-shaped configuration by means of two spacers of different thickness. The alignment of the NLC molecules is planar and is obtained by coating the inner surfaces of the windows with PVA (a polymer) and rubbing the surfaces with a soft cloth. The alignment was checked by means of a polarizing microscope. The angle formed by the two windows of the NLC cell was evaluated by an optical method, giving the value $\theta = 1.013^{\circ} \pm 0.005^{\circ}$. The first ZnSe window of the cell (window A in

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Figure 1. Experimental apparatus: (1) total reflecting mirror, (2) gas tube containing CO₂, (3) Brewster window, (4) out-coupling mirror, (5) beam condenser, (6) mirrors, (7) wire grid polarizer, (8) liquid crystal wedged cell and thermostat, (9) temperature controller, (10) pyroelectric video-camera, (11) personal computer. Ray R_{ref} is the reference beam, emerging from the empty wedge. R_o and R_e are the ordinary and extraordinary rays appearing when the LC is inserted into the wedged cell.

figure 2) was placed perpendicular to the incoming infrared laser beam. To do this a visible He-Ne laser beam was superimposed on to the infrared beam. The orientation of the cell was then adjusted until the beam reflected by the first surface of window A was sent back on itself. The infrared laser beam passes through the wedge and reaches an infrared pyroelectric videocamera (Spiricon Pyrocam III, model PY-III-C-A) interfaced with a personal computer. The pixel size is 85 µm, and the distance between two adjacent pixels is 15 µm. The camera is also provided with sophisticated software that allows an averaging procedure to reduce the noise. The software shows, in real-time, the shape of the Gaussian profile of the detected spot, providing the position of the peak. The camera is mounted upon a micrometric translating stage in order to change the camera position in a very precise way across the observation plane π along the X-axis (see figure 1). The temperature of the sample is controlled by means of a thermostat with an accuracy of $\Delta T = 0.1^{\circ}$ C. The sensing surface of the camera detector was placed perpendicular to ray R_{ref} (see figure 1) by means of a procedure analogous to that used for the liquid crystal cell. The distance L = 1.558 m between the cell and the detector array of the camera, which plays an important role in our measurements, was evaluated with a precision of 0.06%.

3. Description of the experiment and results

A nematic liquid crystal is a chemical compound containing molecules that are rod shaped. If the liquid crystal is in the nematic phase all the molecules tend to align in a preferred direction called the 'easy axis' [5]. A well aligned nematic liquid crystal sample is a highly anisotropic optical medium characterized by two different refractive indices, called the ordinary n_0 and extraordinary n_e refractive indices [4, 6, 7]. A laser beam, polarized at 45° with respect to the easy axis of the liquid crystal, splits itself into an 'ordinary' ray and an 'extraordinary' ray. Measuring the angle between these rays with respect to the situation where the NLC is absent, we obtain the two refractive indices of the liquid crystal by means of the laws of refraction. The point at which ray R_{ref} (see figure 1), emerging from the empty wedge, encounters the observation plane π , which is perpendicular to R_{ref}, is determined experimentally by translating the camera along the X-axis by means of the micrometric translator, until the peak of the spot is exactly in the centre of the detector matrix. The cell is then filled with the liquid crystal and the two refracted beams R_o and R_e appear. The camera is now moved in order to bring the centre of the sensor matrix exactly in to alignment with the peak corresponding to the ordinary beam. The displacement X_0 from the point O is recorded. This procedure is repeated for the extraordinary spot, recording its distance X_e from point O. The accuracy of the measurement of X_{o} and X_{e} is estimated to be 200 µm. From geometrical considerations (see figure 2) we can obtain the two indices of refraction using:

$$n_{\rm o} = \frac{\sin(\theta + \delta_{\rm o})}{\sin \theta}, \quad n_{\rm e} = \frac{\sin(\theta + \delta_{\rm e})}{\sin \theta}$$
(1)

where θ is the angle of the wedge formed by the two ZnSe plates, and δ_o and δ_e are the angles formed by the two beams R_o and R_e with respect to the beam R_{ref} emerging from the wedge when the NLC is absent (see



Figure 2. Liquid crystal wedged cell. The angle between the two ZnSe plates has been exaggerated for illustrative purposes. The infrared laser beam encounters first the substrate A. When the wedge is empty only ray R_{ref} emerges; when the wedge is filled, the ordinary and extraordinary rays R_o and R_e appear. The angles formed by R_o and R_e with R_{ref} are called δ_o and δ_e .

figure 2). We note that the lateral shifts of beams R_o and R_e with respect to R_{ref} at the output of plate B are smaller than 15 µm. These shifts are much smaller than the experimental accuracy of the measurements of X_o and X_e and thus can be disregarded here. From elementary geometry it follows

$$\delta_{\rm o} = \tan^{-1}(X_{\rm o}/L), \quad \delta_{\rm e} = \tan^{-1}(X_{\rm e}/L)$$
 (2)

so that

$$n_{\rm o} = \frac{\sin\left[\theta + \tan^{-1}(X_{\rm o}/L)\right]}{\sin\theta}, \quad n_{\rm e} = \frac{\sin\left[\theta + \tan^{-1}(X_{\rm e}/L)\right]}{\sin\theta}$$
(3)

Each measurement has been repeated many times, changing the temperature of the sample in order to reconstruct the temperature dependence of the refractive indices. Every time the temperature was changed, 20 min was allowed for thermal equilibration of the sample. In figure 3 we show the measured extraordinary refractive index (open circles), the ordinary refractive index (solid dots) and the average refractive index $\langle n \rangle = (2n_{\rm o} + n_{\rm e})/3$ (stars) as a function of the reduced temperature $T_{\rm R} = T - T_{\rm c}$, where T is the temperature of the sample and $T_c = 58^{\circ}C$ is the nematic-to isotropic transition temperature. The uncertainty in the estimation of each value of the refractive indices has been estimated to be $\delta n = 0.007$ for both the ordinary and extraordinary indices. The experiment has been repeated four times in order to test the reliability of the experimental results. The average refractive index is well represented by the same straight line, both in the anisotropic and in the isotropic phase.

In figure 4 we report the optical anisotropy $\Delta n = n_e - n_o$ as a function of the reduced temperature. In order to help the reader to extract the experimental



Figure 3. Extraordinary refractive index n_e (open circles), ordinary refractive index n_o (solid dots) and average refractive index $\langle n \rangle = (2n_o + n_e)/3$ (stars) as a function of the reduced temperature $T - T_c$. The figure shows also the fit of the curves by means of equations (4) and the fit of the average refractive index by a linear regression.



Figure 4. Optical anisotropy $\Delta n = n_e - n_o$ as a function of the reduced temperature $T - T_c$ (open circles). The figure shows also the curve fitted using equations (4) (solid line).

values we fitted the curves of the refractive indices and of the optical anisotropy by means of the empirical expressions

$$\begin{cases} n_{\rm e} = 1.59523 \times (1.03643 - T_{\rm R})^{0.016428} \\ n_{\rm o} = 1.51785 \times (0.774891 - T_{\rm R})^{-0.00480856} \\ \Delta n = 0.0989065 \times (0.212431 - T_{\rm R})^{0.199407} \end{cases}$$
(4)

for $T_{\rm R} = T - T_{\rm c} < 0$. These functions have no physical meaning but represent only a convenient way to recover the experimental results. These curves are shown in figures 3 and 4. Our experimental results agree quite well with those reported by Mansfield [8] that are published in [4], in which no mention is made of the measurement method. These latter results are, to our knowledge, the only published experimental results concerning this particular liquid crystal at the wavelength considered here.

4. Conclusions

The refractive indices and optical anisotropy of the nematic liquid crystal mixture E7 have been measured at various temperatures at the wavelength $10.6 \,\mu$ m. An experimental technique based upon refraction by a nematic wedge has been used. We used a new kind of highly sensitive infrared video–camera as the infrared detector, allowing the use of low laser power in order to avoid heating effects induced by the laser beam.

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