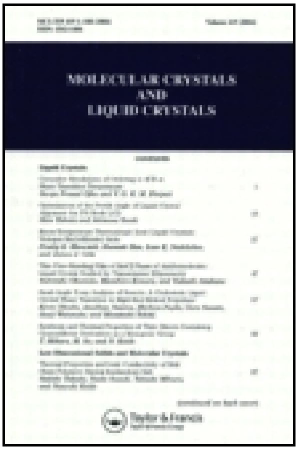

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ZLI-1695 Liquid Crystal Anisotropy Characterization in the Near Infrared by Generalized Ellipsometry

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ZLI-1695 LIQUID CRYSTAL ANISOTROPY CHARACTERIZATION IN THE NEAR INFRARED BY GENERALIZED ELLIPSOMETRY

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One key point for an advantageous use of liquid crystals in optical devices for telecom applications is a proper design and simulation capability. For this purpose it is mandatory to know the optical behaviour of these materials at the wavelength of interest, i.e. the transparency windows of the optical fibers in the Near-IR region. To this aim, we have applied Generalized Ellipsometry, an extension of standard ellipsometry that allows optical characterizations of anisotropic thin films, for investigating liquid crystal samples. The optical anisotropy of the ZLI-1695 liquid crystal was measured as a function of the wavelength in the spectral range from 300 to 1700 nm. Comparing our experimental data with those reported by the manufacturer (Merck) at a single wavelength, we have also estimated the ordinary and extraordinary refractive indices spectra.

Keywords: liquid crystals; ellipsometry; near infra red; optical anisotropy; refractive index; Jones matrix

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INTRODUCTION

Accurate measurements of the material's optical parameters are always a first and important step in the design of photonic devices. Presently a large research effort is devoted to the design and realisation of photonic devices, especially in the telecom field, in view of transferring the light signals processing functions from electronics to optics. The ultimate goal would be achieving so called all-optical processing that would avoid multiple conversion of the data carrying signals. Many technologies and different materials are running the challenge towards this goal and material science research can play in it a decisive role. Amongst these materials, liquid crystals (LC) have a peculiar position: they have been so far almost disregarded and considered too exotic for telecom applications mainly due to high scattering losses and slow response time. However, their potentialities have proved to be so appealing, for instance because of huge electro-optic coefficient and ease of integration, that many material scientists have started to think at them as a very good candidate in that challenge. Customized liquid crystalline materials have been designed and developed with many attractive features that can overpass the previously mentioned drawbacks, however the major commercial application of LC in flat panel display technology has driven all LC material research and characterization in the visible wavelength range. As matter of fact, there is a lack of information and characterization about LC's in the near infra-red (NIR) region that is exactly the wavelength range of telecom interest. This is the motivation for this work of measuring the refractive indices spectra of a LC material from the visible up to 1700 nm and of establishing a simple a reliable technique for further samples measurements.

Different methods exist for measuring the refractive index of a solid or liquid material, the most common being based either on total internal reflection [1] or on leaky guided waves (the m-lines method) [2] or on ellipsometry. A comprehensive comparison among different techniques for refractive index measurements is out of the scope of the present paper, but we want to underline here that LC sample have some peculiarities that render them difficult to analyze, whichever technique is employed. In fact, they are strongly anisotropic; because of their liquid nature they cannot be easily set into self-standing films and usually need glass substrates; both principal refractive index values of LC are in the same range of most glasses refractive index; LC's need to be properly aligned for obtaining a monocrystalline behaviour. All these difficulties can explain the lack of data for LC refractive indices, especially at NIR, however we aim to demonstrate that ellipsometry can be conveniently used to obtain these data, even though with support of additional experimental measurements. Moreover, once remaining obstacles will be removed (and some research groups are working on that), this technique can be usefully exploited for measurements at industrial level, where fast and quasi-automatic procedure are mandatory.

Ellipsometry is by far a well-established technique to explore the surface and thin film optical properties of a large variety of solid and liquid materials [3]. More recently, standard Spectroscopic Ellipsometry (SE) has been extended to Generalised Ellipsometry (GE) in order to evaluate similar and additional optical information, as for instance the three dimensional orientation of anisotropic material like Liquid Crystals (LC) [4]. In fact, SE describes isotropic structures that reflect (or transmit) light maintaining its polarisation, so that Jones matrices, $J_{r,t}$ defined in the next Section, are diagonal.

Biaxial and uniaxial materials reveal nonvanishing off-diagonal elements instead. GE allows the determination of all the complex Jones matrix elements, also known in this case as Mueller matrix elements, thus proving to be suitable for structures containing at least one anisotropic layer.

From an experimental point of view, SE and GE are based on measurement of two physical quantities: the relative phase change, Δ, and the relative amplitude change, Ψ, suffered by incident light when reflected (or transmitted) by a layered structure. These parameters are linked to the reflection (or transmission) coefficients, r_{pp}, r_{ss}, r_{ps}, r_{sp} (t_{pp}, t_{ss}, t_{ps}, t_{sp}) for *p*-, *s*-, and cross-polarizations respectively, through Fresnel equations:

$$\begin{aligned}\tan\Psi_{ps}\cdot e^{i\Delta_{ps}} &= \rho_{ps} = \frac{r_{ps}}{r_{pp}}\\ \tan\Psi_{sp}\cdot e^{i\Delta_{sp}} &= \rho_{sp} = \frac{r_{sp}}{r_{ss}}\\ \tan\Psi\cdot e^{i\Delta} &= \rho = \frac{r_{pp}}{r_{ss}}\end{aligned} \tag{1}$$

In the isotropic case, these equations reduce just to the third one.

These coefficients are directly related to the optical response of the surface: the Ψ's and Δ's spectra depend on the refractive indices of the layers, on their thickness and, in the case of anisotropic films, on the orientation of their optical axis (of course, they depend on any physical parameters that affect the optical behaviour of the material, for instance on temperature).

Anisotropic characterisation is not therefore straightforward, since ellipsometry does not directly measure film parameters, but instead the integral optical response of the whole stack. Once the experimental data are acquired (see Fig. 1, step 1), it is necessary to draw up a multilayer optical model, which carefully describes the sample structure (step 2). Specific software generates theoretical data and unknown parameters, such as thickness or optical constants values, are adjusted in the optical model to best fit the experimental data (step 3). Parameters values are fixed once

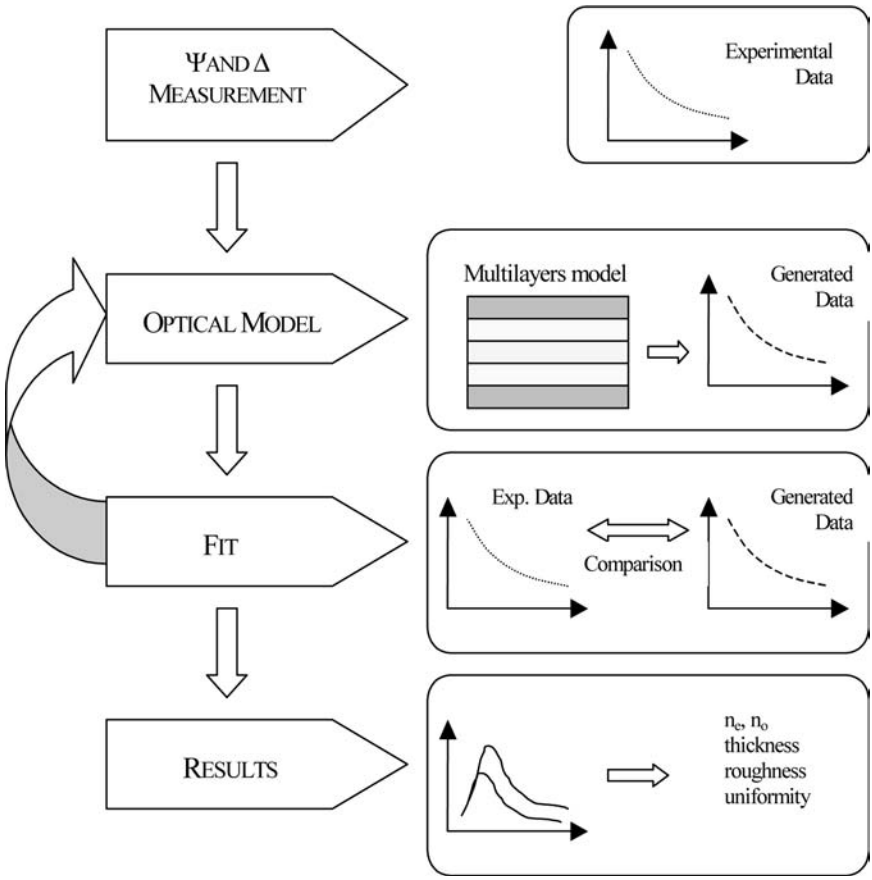

FIGURE 1 (see COLOR PLATE XXXXIII) Spectroscopic GE Analysis Flow Chart.

the iteration process minimizes the difference between experimental and model-generated data (step 4).

In this work, experimental data were measured on a spectroscopic ellipsometer manufactured by the J. A. Woollam Company [5]. A Variable Angle Spectroscopic Ellipsometer (VASE®) was used to perform measurements as a function of both wavelength and angle of incidence, in the spectral range from 300 to1700 nm. This instrument is equipped with an Autoretarder™, which utilizes patented technology to achieve maximum measurement accuracy. Data have been analysed using WVASE32™ software version 3.396.

The investigated samples are BK7 glasses cells filled with ZLI-1695 liquid crystal, by Merck, in both homeotropic and planar alignment.

THEORY

We don't want to give a detailed description of anisotropic GE that can be found elsewhere [6]. We just recall here some basic concepts in order to explain its application in the analysis of complex layered media.

The Jones matrices relate the incident field to the reflected and transmitted ones, their elements provide the complex reflectance (transmittance) coefficients for s- or p-polarised incident light which is reflected (transmitted) into s- and/or p-polarised light:

$$\begin{pmatrix} E_p^{out} \\ E_s^{out} \end{pmatrix} = J_{r,t} \begin{pmatrix} E_p^{in} \\ E_s^{in} \end{pmatrix}$$

where

$$J_r = \begin{pmatrix} r_{pp} & r_{sp} \\ r_{ps} & r_{ss} \end{pmatrix} \text{ and } J_t = \begin{pmatrix} t_{pp} & t_{sp} \\ t_{ps} & t_{ss} \end{pmatrix}$$

As we stated before, in the case of isotropic material we have $n_x = n_y = n_z$ and the Jones matrix will be diagonal

$$J_r = \begin{pmatrix} r_{pp} & 0 \\ 0 & r_{ss} \end{pmatrix}, \ J_t = \begin{pmatrix} t_{pp} & 0 \\ 0 & t_{ss} \end{pmatrix}.$$

But for optically anisotropic samples, the elements of the permittivity tensor are:

$$\left. \begin{array}{l} \varepsilon_x \neq \varepsilon_y = \varepsilon_z, n_x \neq n_y = n_z \\ n_x = n_e \\ n_y = n_z = n_o \end{array} \right\} \quad \textit{Uniaxial}$$

$$\left. \varepsilon_x \neq \varepsilon_y \neq \varepsilon_z, n_x \neq n_y \neq n_z \right\} \quad \textit{Biaxial}$$

where n_e is the extraordinary refractive index and n_o the ordinary one. Off-diagonal elements in Jones matrices represent the conversion of the *p*- and *s*-polarized light into *s*- and *p*-polarized light respectively. The basis of GE is to define and determine three linear independent normalised transmission (reflection) matrix elements once the angle of incidence and light frequency are fixed, see Eq. (1) or the analogous for transmission:

$$\begin{aligned} \tan\Psi_{ps} \cdot e^{i\Delta_{ps}} &= T_{ps} = \frac{t_{ps}}{t_{pp}} \\ \tan\Psi_{sp} \cdot e^{i\Delta_{sp}} &= T_{sp} = \frac{t_{sp}}{t_{ss}} \\ \tan\Psi \cdot e^{i\Delta} &= T = \frac{t_{pp}}{t_{ss}} \end{aligned} \qquad (2)$$

The general transfer matrix **T** is defined as the solution of Berreman's equations [6]. The extension of SE to GE consists in the determination of T, T_{ps} and T_{sp} through regression analysis of experimental data obtained varying the input polarizer azimuth angles and a predefined retardation between the p- and s-modes of the incident light [4].

Owing to the absence of resonances in the whole explored range, the wavelength dependence of LC ordinary and extraordinary refractive indices can be quite well represented by the Cauchy dispersion model:

$$n_{o,e}(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

with the usual meaning of A, B and C parameters [7], so that in this case fulfilling the step 2 in Figure 1 flow chart is an easy task.

A very important point to be considered in order to assign a degree of confidence and accuracy to the final results obtained for the searched parameters values is the correlation amongst estimated parameters. In fact, a high correlation amongst two parameters, e.g. the thickness of one layer and its refractive index, implies that one of the two values must be determined by a different and independent measurement and the regression analysis repeated maintaining fixed this parameter value.

EXPERIMENTAL AND ANALYSIS RESULTS

To determine the LC anisotropy and estimate the ordinary and extraordinary refractive indexes, the following multilayer stack have been considered: BK7 glass substrate, SiO_x thin film, thin surface roughness layer, biaxial LC film, thin surface roughness layer, SiO_x thin film, and BK7 glass substrate. We checked our general optical model by filling the empty cell with water and looking for film parameters (i.e. thickness and refractive index). Results obtained are in very good agreement with those of literature.

The investigated LC samples are two ZLI-1695 liquid crystal (from Merck) cells with different alignments. In the first one DMOAP surfactant on the glass substrates induced homeotropic alignment and in the second one a vacuum deposition at oblique incidence of SiO_x thin film induced planar alignment, both prepared in clean room. Samples homogeneity has been controlled by polarisation microscopy. We assumed that all LC samples investigated refer to planar uniaxial configurations.

Measurements on LC cells have been made in the transmission mode at incident angles between $-45°$ and $+45°$ in the spectral range 300–1700 nm. It should be noted that transmission measurements allow accurate measurements of optical anisotropy Δn in the whole spectral range, while the two refractive indices n_e and n_o remain closely correlated so that a different measurement is needed for their actual values determination. The most appropriate would be using the same VASE® instrument for GE in reflection, but the presence of a very thick first layer (that is the glass substrate of the LC cell) may avoid reaching the required precision. Overcoming this problem requires a specific design of the cell geometry and assembly, which is in progress.

The amount of experimental data obtained in each experiment is very large owing to the number of physical variables varied during every single measurement round, incident light polarization, phase retardation among them, angle of incidence, wavelength. For each experimentally recorded curve a corresponding software-generated curve can be plotted at the end of the fitting process. As an example, in Figure 2 we report few curves, experimental and software-generated, obtained for Ψ and Δ versus wavelength at different incidence angles, in the case of the homeotropic cell. The parameters fit looks so good that experimental and generated curves are almost always indistinguishable. Experimental data are processed by the WVASE32™ software on the basis of the chosen optical model. As a final result we show in Figures 3a,b the Δn spectra obtained for the planar cell and the homeotropic cell, respectively. These results are neither consistent with the value provided by Merck ($\Delta n = 0.0625$ @ 589 nm), nor among each other: in fact, the two cells containing the same LC material should exhibit the same optical anisotropy, which is not the case shown in Figure 3. There are evident reasons for this apparent failure of the GE method. Some are inherent to the sample preparation, as thickness non-uniformity, filling factor, very large thickness of the glass substrates, and very poor index contrast between different layers. Some others are connected with the large number of free parameters involved in calculations:

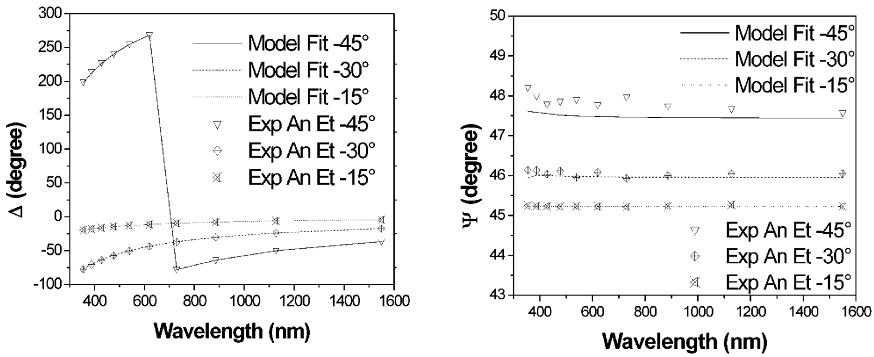

FIGURE 2 Experimental and generated data for Ψ, and Δ, in case of LC homeotropic cell.

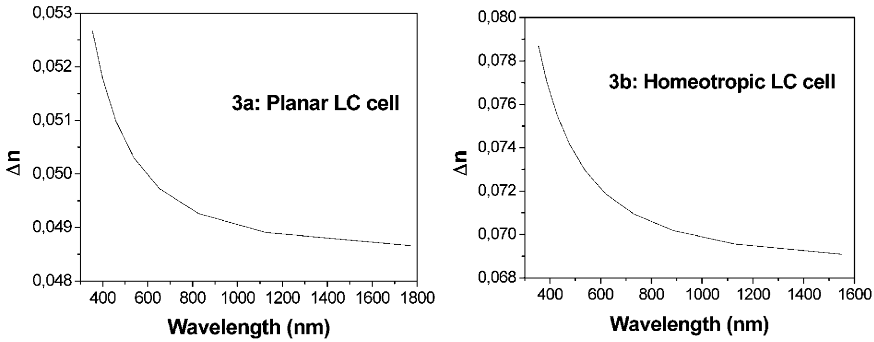

FIGURE 3 Optical anisotropy spectra for LC planar cell and LC homeotropic cell, respectively.

LC film thickness, ordinary refractive index, extraordinary refractive index, aligning film thickness, in-plane orientation angle, out-of-plane tilt angle. The ex-post correlation analysis showed that a non negligible correlation avoided the simultaneous determination of all the parameters values with the wanted accuracy. Thus, we kept fixed some parameters, as we knew them by independent measurements, moreover we took advantage of the WVASE32™ software utility that allows different experiments' data to be linked together and fitted with single materials' parameters. We measured cell thickness before filling it with the LC by interference fringes method, using a spectrometer, obtaining $d = 1.70$ μm, for the LC planar cell, and

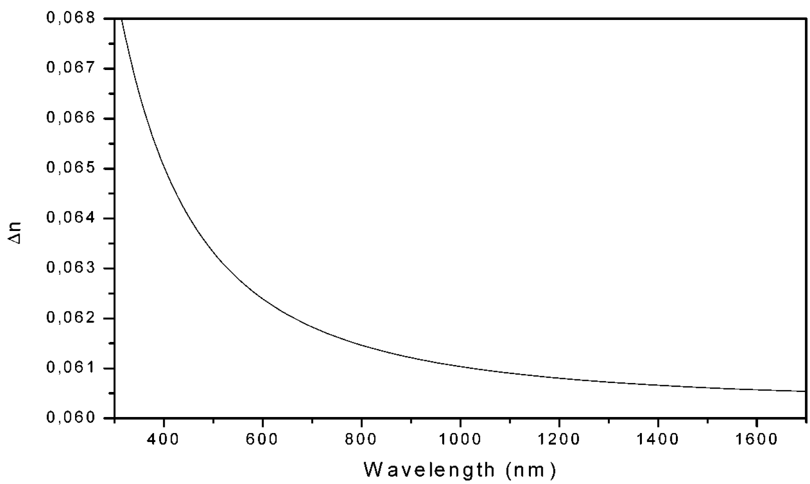

FIGURE 4 Optical anisotropy spectrum of ZLI-1695.

TABLE 1 Cauchy Coefficients

Cauchy coefficients	Ordinary	Extraordinary
A	1.457	1.517
B	$4.9 \cdot 10^{-4}$	$5.7 \cdot 10^{-4}$
C	$5.3 \cdot 10^{-5}$	$5.8 \cdot 10^{-5}$

d = 10.63 μm for the homeotropic one. Also we kept fixed the birefringence value Δn = 0.0625 (@ 589 nm) provided by Merck. The resulting Δn spectrum obtained with these constraints is reported in Figure 4.

A similar reasoning could be applied to the evaluation of the ordinary and the extraordinary refractive indices. Using as fixed parameters n_e and n_o values provided by Merck @ 589 nm, $n_e = 1.534$ and $n_o = 1.471$, we were able to fit the A, B and C parameters of Cauchy formula for both indices; the fitted values are reported in Table 1 and the corresponding curves in Figure 5. However, it should be noted that correlation among fitted parameters is not completely negligible in this last fit so that a more reliable refractive index spectrum is demanding a GE measurement in reflection as envisaged previously. A reason for this could be find in the previously mentioned problems connected with LC sample preparation and especially in the low refractive index contrast between glass substrate and LC material.

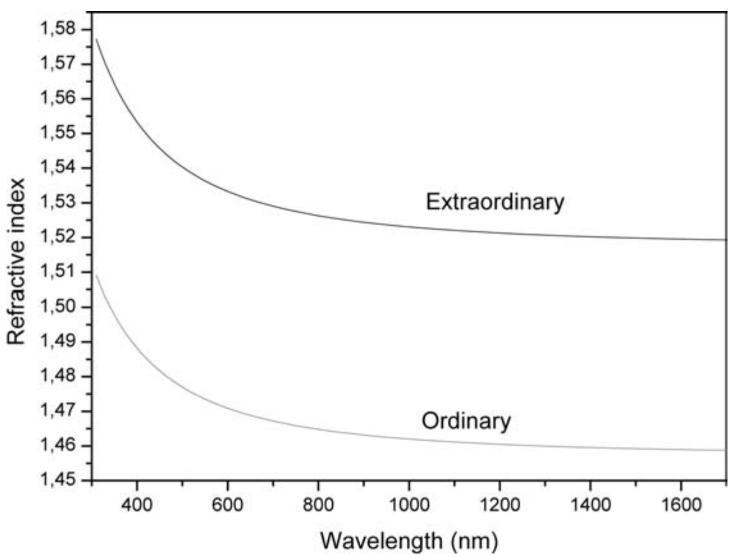

FIGURE 5 Estimated refractive indices spectra.

CONCLUSIONS

We have used Generalised Ellipsometry to measure optical anisotropy of the nematic LC ZLI-1695, from 300 to 1700 nm. We have also given an estimate to the ordinary and extraordinary refractive indices spectra. Ellipsometric transmission measurements were carried out with a commercial spectroscopic ellipsometer with automated phase retardation function between the two orthogonal polarizations that made possible anisotropic measurements with a high accuracy. At normal incidence the technique provides in-plane refractive index difference as well as in-plane optical axis orientation. Varying the angle of incidence the technique is sensitive to out-of-plane index difference and out-of-plane optical axis tilt orientation. Implementing a different cell geometry and assembly, spectroscopic ellipsometric measurements in reflection can be performed also on LC cells, in order to obtain a direct and accurate estimate of the two refractive indices in the whole range from visible to Near Infra-Red. All these capabilities, and a very simple and quick experimental procedure, render GE a very powerful tool for investigations about optical and orientational parameters of liquid crystalline materials, with the additional very important feature to give spectroscopic informations in a range that include all the telecom windows in the NIR region. In our opinion, ease and quick availability of these data can promote the design and realization of photonic devices based on LC's for telecom applications, which presently are often far from optimization being based on materials production and characterization performed in the visible range for display applications.

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