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Article

Temperature-dependent Photonic Bandgap of Liquid Crystalline Phases of Smectic and Cholesteric Phases

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ABSTRACT

We report the results of our studies on the physical and optical properties of binary mixtures of cholesteryl nonanoate and 4-n′-pentyl-4′-thiocyanatobiphenyls. Experimentally measured optical anisotropy of refractive indices and helical pitch of liquid crystalline phases helps to study the molecular band gap structure of different liquid crystalline phases, respectively, at different temperatures and at different concentrations.

Key words: Molecular orientation, Refractive indices, Helical pitch, Photonic band gap.

1. INTRODUCTION

Research in the realm of liquid crystals has been a continuum ever since their discovery in 1888. The enduring interest in field of the liquid crystals has been due to their unique electro-optical properties that find utility in a range of optical and photonic applications such as liquid crystal display [1-3] sensors.

Cholesteric liquid crystal is a simple, one-dimensional photonic crystal and has many interesting applications because of their unique properties and simple fabrication process [4-6]. A cholesteric liquid crystal is formed by rod-like molecules whose directors are self-organized in a helical structure. In the planes perpendicular to the helical axis, the liquid crystal directors are continuously rotated along the helical axis. By choosing a high birefringence liquid crystal, the periodic helical structure gives rise to a periodic modulation of the refractive index, which results in a selective reflection band. Within the band, the circularly polarized incident light with the same handedness as the cholesteric helix is reflected while the opposite handedness is transmitted. The frequency range of the reflection band is determined by the ordinary (n_o) and extraordinary (n_e) refractive indices of the liquid crystal and the pitch length (p) of the helical structure. The reflection band edges occur at $\lambda_1=n_op$ and $\lambda_2=n_ep$, where p is the helical pitch length.

A cholesteric liquid crystal cell is typically prepared by doping some chiral agents into a nematic liquid crystal mixture. The fabrication process is quite simple. Moreover, the electromagnetic characteristics of cholesteric liquid crystal photonic band gap can be easily controlled by adjusting the concentrations of liquid crystalline materials; they are influenced by the effect of temperature and electric field [7-13]. Thermo-optical properties have also been widely used to modify the cholesteric liquid crystal photonic band gap frequency range. Temperature-dependent photonic band gap of the liquid crystalline phases depends on the frequency range of birefringence media [14].

In this paper, our aim is to study the molecular structural band gap of liquid crystals depends on the temperature-dependent optical anisotropy of refractive indices and helical pitch. Experimental measured thermo-optical properties of refractive indices and helical pitch help to understand the width of molecular photonic band gap structure which decreases with increasing temperature, respectively, at different concentrations of given mixture. Linear and lateral properties of these materials are used to propose a temperature sensing device, narrow band optical filter, and in many optical systems.

2. EXPERIMENTAL

In the present study, we use the materials, namely, cholesteryl nonanoate (CN) and 4-n′-pentyl-4′-thiocyanatobiphenyls (5BT). Mixtures of 20 different concentrations of CN in 5BT were prepared, and they were mixed thoroughly. Samples were subjected to several cycles of heating, stirring, and centrifuging to ensure homogeneity. Phase transition temperatures of these mixtures were measured with the help of a Gippon-Japan polarizing microscope in conjunction with a hot stage. The samples were sandwiched between the slide and cover slip and were sealed for microscopic observations. The sample whose refractive indices have to be determined is introduced between two prisms of the Abbe refractometer. The combination of prisms containing liquid crystalline material is illuminated by a monochromatic light (λ=5893Å). The refractometer is in conjunction with a temperature bath from which hot water can be circulated to maintain the sample at different temperatures. In the field of view, two lines of demarcation of slightly different polarization are observed. The horizontal polarization corresponds to the ordinary ray and vertical polarization is due to the extraordinary ray. By matching the cross-wire, the refractive indices of the ordinary ray and extraordinary ray are read directly. Measured refractive indices of mixtures using Abbe refractometer are compared with the results obtained by measurement using Goniometer spectrometer [15,16]. Helical pitch measurements were performed by the well-known Grandjean-Cano wedge method [17,18]. The given

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mixture was taken in a wedge-shaped cell treated for homogeneous alignment. The cell is constructed using two indium tin oxide glass substrate, the surfaces of which are coated with polyimide SE-130B. The two glass plates formed a small angle at the wedge. The mixture was cooled slowly (0.2°C/min) from cholesteric to smectic phase, which induces an array of equidistant Grandjean-Cano lines.

2.1. Optical Texture Studies

For the purpose of optical texture studies, the sample was sandwiched between the slide and cover glass and then the optical textures were observed using Gippon-Japan polarizing microscope in conjunction with hot stage. The concentrations range from 5% to 55% of the given mixture and are slowly cooled from its isotropic melt, the genesis of nucleation starts in the form of small bubbles and slowly grow radially, which form a spherulitic texture of cholesteric phase with large values of pitch [19]. On further cooling the specimen, the cholesteric phase slowly changes over to focal conic fan-shaped texture, which is the characteristics of smectic-A (SmA) phase, as shown in Figure 1a. On further cooling the specimen, SmA phase slowly changes over to smectic-C (SmC) phase, as shown in Figure 1b, and hence, this phase is not stable and then changes over to focal conic fan texture with radial striation on the fans [20], which is the characteristic of smectic-E (SmE) phase. At this phase transition, i.e. from SmC phase to SmE phase, it is observed that there is a drastic change in the values of optical anisotropic of the given sample [21,22]. This anomalous behavior is presumably associated with the degree of order of the molecular arrangement in SmE phase and then it becomes crystalline phase at room temperature.

3. RESULTS AND DISCUSSION

3.1. Thermo-optical Studies

Results of this investigation are further supported by the optical studies. Temperature-dependent refractive indices are important for practical applications, such as projection displays and thermal-induced photonic band gap tuning. It is highly desirable to predict the refractive indices at the designated operating temperature of a liquid crystal device. The refractive indices for extraordinary ray (n_e) and ordinary ray (n_o) of the given mixture were measured at different temperatures for the different mixtures using Abbe refractometer and precision Goniometer spectrometer. The temperature variations of refractive indices for 45% CN in 5BT are shown in Figure 2. The refractive index of a material can be related to the electric polarizability of the molecules of that medium, so for a medium with anisotropic molecular polarizability where the molecules tend to point in the same direction, the refractive index is expected to be different along different directions as well and hence the refractive index of a material depends on the polarization and propagation direction of light, the material is said to be birefringent. Liquid crystal molecules change their orientations, the refractive index

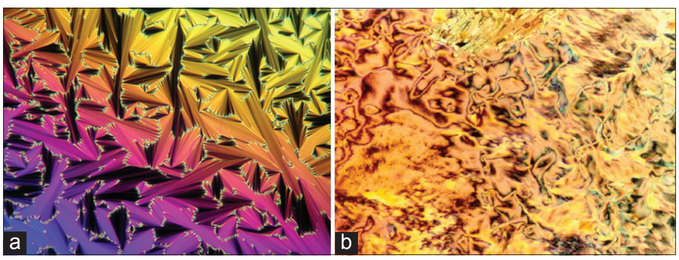

Figure 1: Microphotographs obtained in between the crossed polars, (a) focal conic fan-shaped texture of smectic-A phase (×250). (b) Schlieren texture of smectic-C phase at temperature (×250).

of liquid crystalline materials is satisfied by the total internal reflection condition. When the refractive index of the liquid crystalline material increases, the critical angle is decreased. This is important when working with liquid crystalline samples which have a high index of refraction. It is evident that the thermal non-linearity of liquid crystal refractive indices plays a very important role for some new photonic applications, such as liquid crystal photonic band gap fibers and thermal soliton [23-26]. Several physical models have been developed to describe the temperature effect of liquid crystal refractive indices.

3.2. Molecular Structure of Helical Pitch Layer Measurements on Chiral Nematic and Smectic Phases

Helical pitch of chiral nematic phase has been determined by measuring the distance between the Grandjean-Cano lines as a function of temperature. As the temperature is lowered, the mesophase changes from chiral nematic to smectic phase, spacing between lines is increased, which indicates that pitch of the chiral nematic phase is also increasing. The temperature variation of pitch for the mixture of 45% CN in 5BT is shown in Figure 3. From this figure, it is evident that

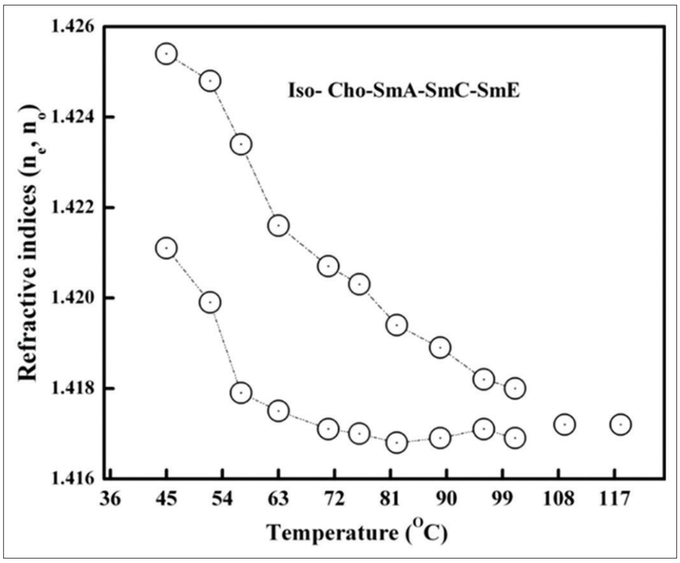

Figure 2: Temperature variations of refractive indices for the mixture of 45% cholesteryl nonanoate in 4-n′-pentyl-4′-thiocyanatobiphenyls.

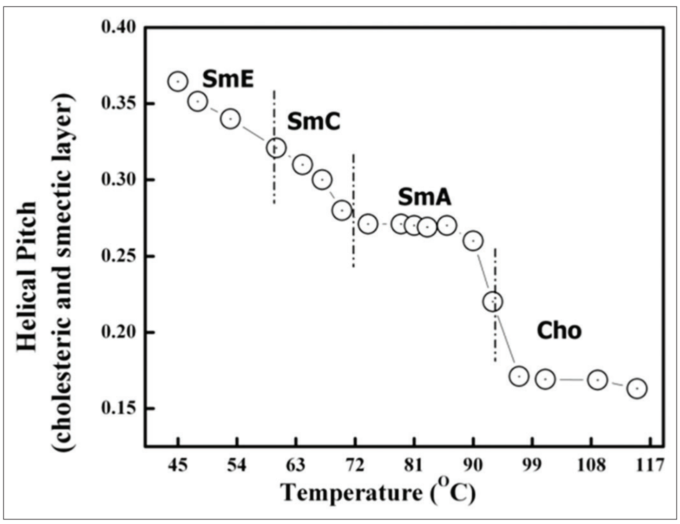

Figure 3: Temperature variations of pitch for the mixture of 45% cholesteryl nonanoate in 4-n′-pentyl-4′-thiocyanatobiphenyls.

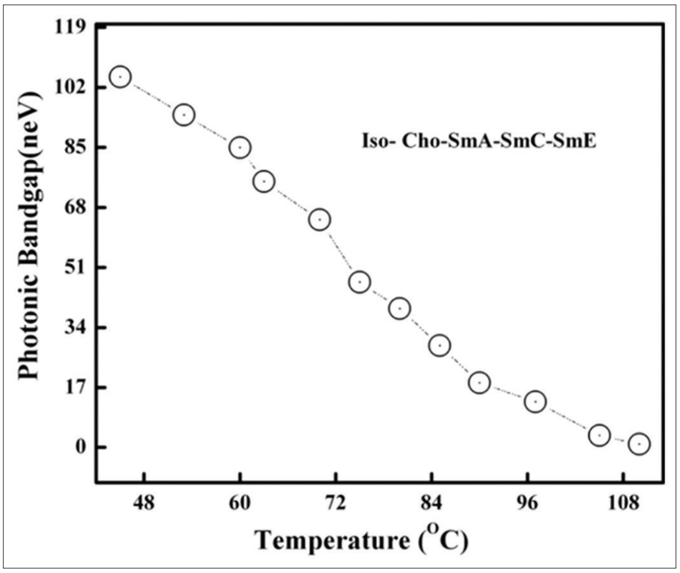

Figure 4: Temperature variation of photonic band gap for the mixture of 45% cholesteryl nonanoate in 4-n′-pentyl-4′-thiocyanatobiphenyls.

the variation of pitch from chiral nematic to smectic phase is smooth and continuous. However, gradually, the value of pitch increases from 0.17 to 0.19 μm on cooling the sample from chiral nematic to smectic phase. The value of pitch increases steeply and reaches a maximum of 0.37 μm at chiral nematic to smectic phase transition. In this study, we have noticed that the sequence is isotropic-chiral nematic-SmA-SmC-SmE phases on cooling [27,28]. Pitch is continuous at the chiral nematic-smectic phase transition in spite of rather energetic transition. The pitch increases on cooling to smectic phase and it diverges on approaching the SmA, SmC, and SmE phases. This divergence is related to the second-order transition. It exhibits a steep decrease and it is close to chiral nematic phase which are usually the characteristics of the second-order phase transition of SmA, SmC, and SmE phase, respectively, at different temperatures. Therefore, it follows to predict: How the molecular structures of chiral dopant molecules are related to the existence of helical twisting power. A small change in structure can lead to large changes in macroscopic helical twisting power [29,30]. These large changes apparently arise because the chiral solute molecules with slightly different shapes can induce significant differences in local orientational order of the solvent molecules around them. Hence, helical twisting power calculations are necessary to have a twisted nematic solvent. This, in turn, induces different amounts of twist in the bulk solvent. Therefore, it is clear that theoretical method can predict helical twisting values.

3.3. Anisotropic Molecular Layer Structure of Photonic Band Gap

Temperature variation of photonic band gap for the mixture of 45% CN in 5BT is shown in Figure 4. From the figure, we have observed that increase in temperature of given material causes a decrease in photonic band gap, for which in this region, the conductivity also decreases. In this study, the temperature-dependent photonic band gap of material is estimated at different concentrations of given molecules, which shows different molecular structures and they have induced a phase separation and aggregation of the chiral molecules. If we increase the temperature, which makes the sample more and more transparent, the planar helical structures become more uniform. Increasing the temperature causes increase in pitch, which clearly tells that the segregations of molecular layers decrease [11-13,31]. Temperature-dependent optical birefringence, helical pitch, and nano molecular self-assembled aggregation of the molecules and optical band gap are attractive to demonstrate the scientific technological potential applications such as optical switches, filters, and waveguides.

4. CONCLUSIONS

Microscopic investigation of given mixture shows the existence of conventional chiral nematic and chiral-induced smectic phases for different concentrations, respectively, at different temperatures. Molecular photonic band gap structures of liquid crystalline phases depend on temperature of optical anisotropy of refractive indices and helical pitch. Experimentally measured thermo-optical properties help to understand the width of molecular photonic band gap structure decrease with increasing temperature, respectively, at different concentrations.

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