Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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S. -Y. T. Tzeng[a]; C. -N. Chen[a]; Y. Tzeng[b]
[a] Department of Electro-Optical Engineering, National Taipei University of Technology, Taipei 106, Taiwan, ROC [b] Institute of Physics, Academia Sinica, Taipei, Taiwan, ROC

Online publication date: 09 September 2010

To cite this Article Tzeng, S. -Y. T. , Chen, C. -N. and Tzeng, Y.(2010) 'Thermal tuning band gap in cholesteric liquid crystals', Liquid Crystals, 37: 9, 1221 — 1224

To link to this Article: DOI: 10.1080/02678292.2010.492247

URL: http://dx.doi.org/10.1080/02678292.2010.492247

Liquid Crystals,
Vol. 37, No. 9, September 2010, 1221–1224

Thermal tuning band gap in cholesteric liquid crystals

S.-Y.T. Tzeng[a]*, C.-N. Chen[a] and Y. Tzeng[b]

[a]*Department of Electro-Optical Engineering, National Taipei University of Technology, Taipei 106, Taiwan, ROC;* [b]*Institute of Physics, Academia Sinica, Taipei, Taiwan 115, ROC*

(*Received 14 April 2010; final version received 6 May 2010*)

The phase of a liquid crystal (LC) changing from a nematic phase to a cholesteric (Ch) mesophase is achieved by adding different ratios of chiral dopants S811. By studying the transmission spectrum, we are able to measure the helical pitch in cholesteric phase. The pitch in the mixtures of nematic E7 and chiral dopants S811 as a function of the concentration of the dopant and temperature is investigated. The sensitivity of the selective reflection notch of the cholesteric phase to the thermal tuning depends strongly on the ratios of the chiral dopants. It reveals that the influence of temperature is more profound for those cholesteric liquid crystals (CLCs) which exhibit smectic A (SmA) at lower temperatures. When fitted using Keating's formula, the helical pitch calculated from our experimental results lies on the predicted curve. Optimised ratios of the mixture CLCs for the optimised reflection band with the specified wavelength ranging from 467 nm to 2123 nm are suggested.

Keywords: liquid crystal; cholesteric liquid crystal; smectic A; nematic; transition temperature; pitch

1. Introduction

In recent years, significant progress has been made in the use of cholesteric liquid crystals (CLCs) as passive polarising elements in laser cavities [1–10]. CLC materials with a pitch comparable to the optical wavelength can be regarded as a class of one-dimensional photonic crystals exhibiting a wider band gap and narrower line widths for modes closer to the band edge. These properties suggest that CLCs are promising photonic band gap materials for lasing, switching, variable optical attenuator and display applications.

It has long been recognised that the ability to tune the band gap of CLCs in real time would enhance their application to photonics. The selective reflection band is centred at the wavelength, $\lambda_B = nP$, with the width of the band given by $\Delta\lambda = (\Delta n/n)\lambda_B$, where P is the pitch of the chiral liquid crystal and $n = (n_e + n_o)/2$ the average refractive index of the cholesteric planes having a birefringence of $\Delta n = n_e - n_o$, with n_e and n_o being the extraordinary and ordinary refractive indices of the nematic liquid crystal respectively [5]. The dependence of the pitch and average refractive index of the CLC upon light [10, 11], temperature [6–8, 12] and electric field [9, 10, 12] suggest the reflection band can be modulated by these external stimuli.

In this paper we explore the thermal tuning characteristics of a nematic liquid crystal (E7, Merck) doped with a chiral agent (S811) in differing ratios. By measuring the transmission spectra as a function of the temperature, we are able to study the dependence of the helical pitch. Experimentally it has been observed that the pitch shifts dramatically to the long wavelength near infra-red (IR) when the temperature is lowered towards the Ch–SmA by about 0.2°C.

To explain this anomalous behaviour, we adopted the model by Keating and Böttcher [13, 14] to fit the experimental data, obtaining good agreement of the fitting parameter, T_0, with the phase transition temperature characterised by differential scanning calorimetry (DSC) and polarising optical microscopy (POM). Our results show that the influence of temperature is more profound for those doped CLCs which exhibit smectic A (SmA) at lower temperatures and that the temperature dependence of the pitch is consistent with the model prediction [13, 14].

2. Methods

In this paper, the left-hand CLC samples were made by mixing a chiral dopant S811 (Merck) with a nematic liquid crystal E7 (–10 °C to 61°C) in differing ratios from 16 wt% to 27 wt%. The compound was injected into an empty cell made from two glass plates coated with indium–tin oxide (ITO). The cell gap of the CLC samples was 5 μm. The surface of the glass plates was coated with a polyimide and rubbed to promote a homogeneously aligned surface of the cell. CLC cells were mounted in a hot stage and the transmission spectra were recorded using Ocean Optics spectrometers USB4000XR and NIR256-2.5 for the different ranges of the reflection notch. The thermal studies of the phase were made by DSC using TA instruments Q20 at a heating rate of 2°C/min. The

*Corresponding author. Email: sytsay@ntut.edu.tw

ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678292.2010.492247
http://www.informaworld.com

textures of the smectic and cholesteric phase were studied in an Olympus polarising optical microscope with a digital camera Sony SSC-DC50A.

3. Results and discussion

To observe a much wider tuning range, we used two spectrometers (Ocean USB4000XR and NIR256-2.5) for different ranges of the spectra. The sensitivity scope of the spectra in our experiment ranges from 200 nm to 2500 nm. With the prepared CLC cells mounted in a hot stage, the transmission spectra were measured as functions of temperature. Figures 1(a) and 1(b) show the measured transmission spectra of CLCs with a chiral concentration of 21 wt% and 16 wt% for different temperatures. The bandwidth of the spectrum, $\Delta\lambda$, indicated in Figure 1(a) was calculated from the full width at the half maximum of the dip where the minimum transmission was reached. The measured central wavelength, λ_B, was determined by the middle point of the full width at half maximum as indicated in Figure 1(a). It can be seen from Figure 1(a) that the transmission band blue shifts from 2124 nm to the wavelength 680 nm as the temperature is increased from 19.4 to 35.1°C. Beyond this range, the reflection notch is blurred and extinct. The transmission spectrum for CLC with a concentration of 16 wt% blue shifts from 2006 nm to 860 nm as the temperature increases from 12.2 to 39.7°C. Since it is commonly believed that the transmission spectra are attributed to the planar texture of the cholesteric liquid crystal, we can deduce that the mixture E7 + 21 wt% S811 is in Ch phase from 19.4 to 35.1°C and that the mixture E7+16 wt% S811 is in Ch phase between 12.2 and 39.7°C, i.e. the heavier dopant in the mixture, the narrower range of the temperature in the CLC.

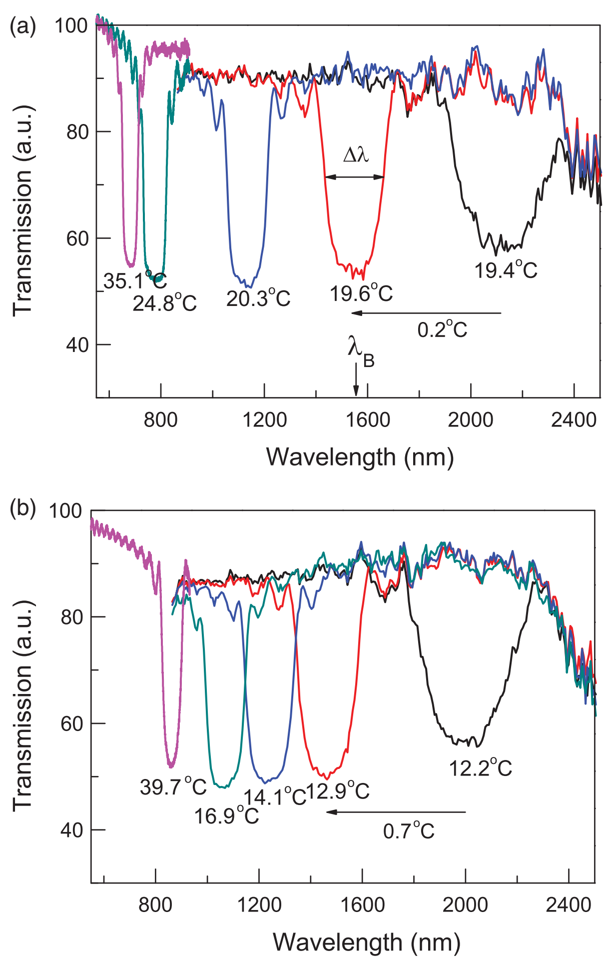

Figure 1. Experimentally measured temperature-dependent transmission spectra of CLCs with different chiral dopant S811 concentrations: (a) 21 wt%; (b) 16 wt% (colour version online).

To explain the temperature variation in Bragg wavelength, λ_B, we explored the temperature dependence of the pitch using the approximation formula $P = (\lambda_B - \Delta\lambda/2)/n_o$, with n_o as a constant [6]. The calculated pitch P vs. temperature is shown in Figure 2, where $n_o = 1.525$ [15]. Based on the information from the experimental reflection notch, the pitch as a function of temperature for CLC cell with S811 for 21 wt%, 25 wt% and 27 wt% in composition is depicted in Figure 2(a). We attempt to fit the experimental data using Keating's theory [13]:

$$P(T) = \gamma \frac{T_0}{T}\left(1 + \frac{\beta}{T - T_0}\right)^2, \tag{1}$$

where T is in K and $T > T_0$. The parameter, β, is a measure of the temperature sensitivity of P at a given temperature above the phase transition temperature, T_0.

The agreement between the theoretical fitted curves (solid lines) and the experimental data appears satisfactory, as shown in Figure 2 where we see that the experimental results lie on the fitted curve given by Equation (1) for concentrations 21 wt%, 25 wt% and 27 wt% in Figure 2(a), and those of 16 wt%, 18 wt% and 20 wt% in Figure 2(b).

The three adjustable parameters, T_0, γ and β, involved for different concentrations of the S811 are listed in Table 1. The transition temperature T_0 increases from 11.3 to 23.6°C with increasing dopant (S811) concentration from 16 wt% to 27 wt%. This is reasonable since the rod-like nature of the chiral dopant in large amounts is likely to promote packing of layers to form a smectic phase. In the more ordered liquid crystal (heavier doped CLC), the higher transition temperature is necessary to provide more Joule heating for phase transition.

The parameter, γ, depends on the anharmonicity factor, interplanar distance and molecular moment of inertia [13]. For the mixtures (E7 + S811) studied, the

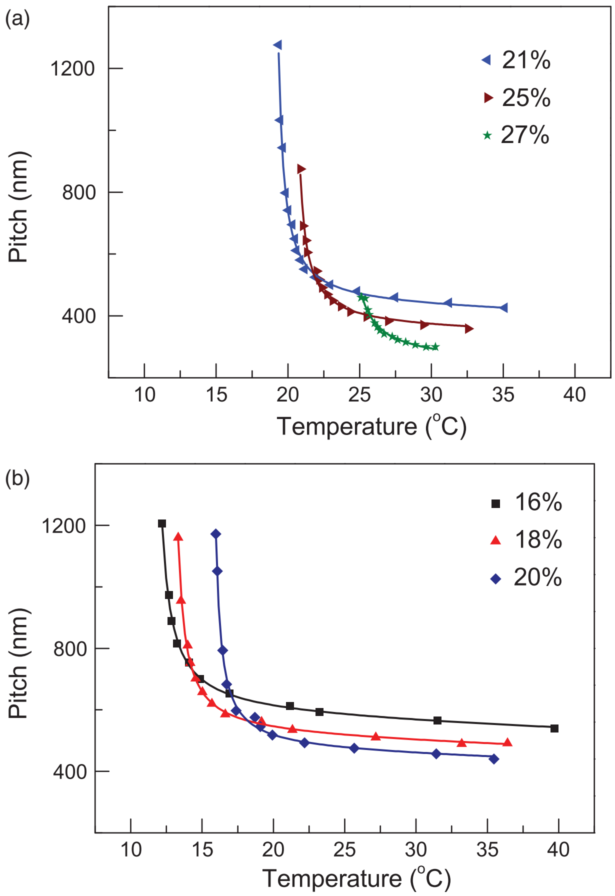

Figure 2. Pitch of CLCs vs. temperature with different chiral dopant S811 concentrations: (a) 21 wt%, 25 wt% and 27 wt%; (b) 16 wt%, 18 wt% and 20 wt%. Symbol: experimental data; solid line: fitted curve by Keating model (colour version online).

Table 1. Fitted parameters of different compositions.

S811 (%)	T_0	γ (nm)	β (K)
16	284.5K (11.3°C)	582.9	0.3685
18	285.8K (12.6°C)	515.7	0.3102
20	288.6K (15.4°C)	466.2	0.2861
21	292.0K (18.8°C)	430.9	0.3601
25	293.4K (20.2°C)	361.3	0.3466
27	296.8K (23.6°C)	256.7	0.5314

anharmonic contributions between close neighbours are relatively directly enhanced by the chiral agent such that the relative twist angle of the nearest neighbours increases as the chiral agent concentration is increased. Hence the pitch over which the twist repeats itself is shortened for the heavily doped CLC. It also reflects on the fitted parameter, γ. As listed in Table 1, γ decreases from 582.9 nm to 256.7 nm as S811 increases from 16 wt% to 27 wt%.

The texture of the LC phases of the mixtures was studied under POM with a digital camera. The

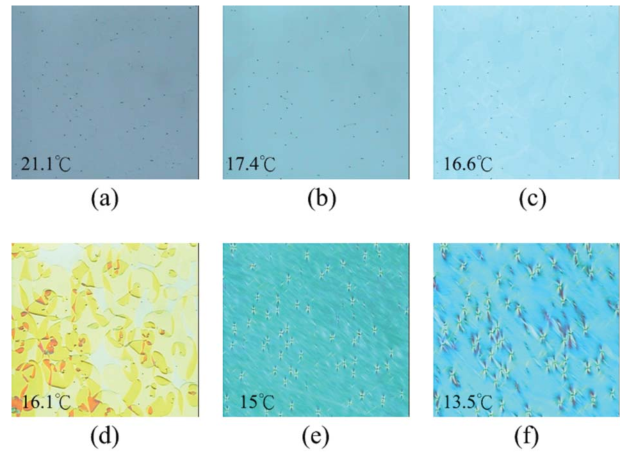

Figure 3. Photographs (a)–(f) of the mesophase of CLCs with 20 wt% chiral dopant S811 taken at different temperatures (colour version online).

microphotographs of the texture of CLC with 20 wt% chiral dopant S811 at different temperatures are shown in Figure 3. The mixture is in the isotropic phase above 45°C; as the temperature is lowered to 35°C the sample becomes transparent and is in the planar texture. Further lowering the temperature to 21.1°C, 17.4°C and 16.6°C makes the sample more and more transparent as shown in Figure 3(a), Figure 3(b) and Figure 3(c) respectively. At 16.1°C we saw a texture resembling that of twist grain boundary (TGB) phase [6], as shown in Figure 3(d) respectively. Further cooling of the sample to 15°C, which is close to the Ch–SmA transition temperature T_0 (15.4°C) fitted by Equation (1) [13], reveals a texture similar to that of the smectic phase [6, 12] as shown in Figure 3(e). Figure 3(f) clearly shows the smectic liquid crystalline phase seen at an additional lower temperature (13.5°C). We studied the phase behaviour of the other five mixtures with concentrations from 16 wt% to 27 wt% under POM. The photographs obtained suggest that they follow the same phase sequence as the sample with a concentration of 20 wt%. The transition temperatures read from the microphotographs of the mesophases are consistent with those fitted by Equation (1).

The LC phases of the mixtures of S811 and E7 were studied by DSC. The results of all the compositions studied by DSC are shown in Figure 4. For compositions with S811 <19 wt%, the phase transitions (from SmA to CLC) are not obvious in Figure 4(a) and so, to see the variation of the heat flow clearly, the region indicated by the dashed box, is enlarged in Figure 4(b).

Based on the hot stage POM data, we can characterise the SmA and CLC phases in Figure 4. The observed transition temperatures (from SmA to CLC) for the mixtures of E7 and dopant S811 with

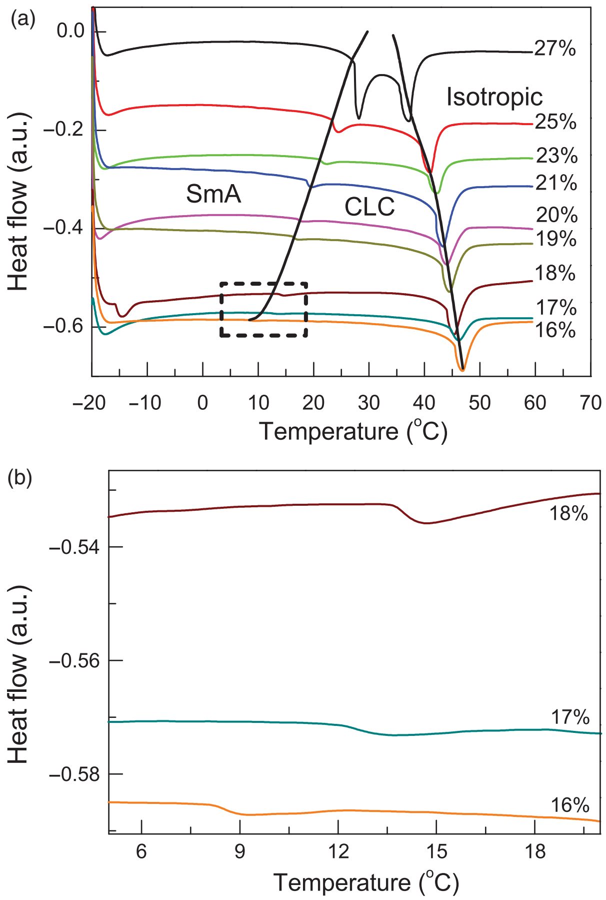

Figure 4. Differential scanning calorimetry study of CLCs with different chiral dopant S811 concentrations (colour version online).

different compositions agree with the fitted parameters, T_0, listed in Table 1. When the mixture was in the texture of Ch phase, the reflection notch was observed as shown in Figure 1. As expected, the temperature range of the Ch phase decreases with an increase in S811.

4. Conclusions

From the microphotographs of the phase texture by POM and the DSC study of the six mixtures investigated, it can be seen that all display SmA at the low temperatures. This is consistent with the predicted SmA–Ch transition temperature, T_0, fitted by Keating's model.

Our results indicate that the composition of the chiral dopant in the mixture plays a vital role in phase transition. We obtained six optimised ratios of the chiral dopant (S811) in a liquid crystal (E7), which present the cholesteric phase at 10°C to 40°C and offer a thermal tunable pitch ranging from 1276 nm to 300 nm.

Acknowledgements

The authors wish to thank Professors J.J. Wu and Y.J. Jen for fruitful discussions. The authors are indebted to Professor T.J. Wang for assisting in establishing the thermal stage and C.F. Tsai for operating differential scanning calorimetry. This work was supported partly by National Science Council of the Republic of China under contract No. NSC 96-2112-M-027-001-MY3.

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