July 1998

ELSEVIER

Materials Letters 36 (1998) 76–80

MATERIALS LETTERS

Use of mirage effect for the detection of phase transitions in liquid crystals

K. Rajasree [a,*], V. Vidyalal [a], P. Radhakrishnan [a], V.P.N. Nampoori [a], C.P.G. Vallabhan [a], A.K. George [b]

[a] *Opto-Electronics Laboratory, International School of Photonics, Cochin University of Science and Technology, Cochin-682 022, India*
[b] *Physics Department, College of Science, Sultan Qaboos University, P.O. Box 36, Postal Code 123, Muscat, Oman*

Received 10 September 1997; revised 5 December 1997; accepted 17 December 1997

Abstract

The phenomenon of single beam mirage effect, otherwise known as photothermal deflection (PTD) effect using a He–Ne laser beam has been employed to detect phase transitions in some liquid crystals. It has been observed that anomalous changes in amplitude occur in the PTD signal level near the transition temperature. The experimental details and the results of measurements made in liquid crystals E_8, M_{21} and M_{24} are given in this paper. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Liquid crystals; Mirage effect; Photothermal deflection; Nematic and smectic phases

1. Introduction

It is well known that a phase transition is the change of a thermodynamic state of a substance brought about by the variation in any of the physical variables like temperature or pressure. Usually drastic changes in the physical properties of the material accompany a phase transition. Among the various optical methods used for phase transition studies [1–3], techniques based on thermo-optic effects are found to be ideal as they do not have the same drawbacks of other popular techniques. The photothermal deflection (PTD) otherwise known as the mirage effect is one such method which can be used to determine the phase transition temperatures of the samples with great accuracy and convenience [4–8]. This technique is fully non-contact in nature and therefore, contamination of the samples by attachment of probes or electrodes can be avoided. The present paper describes measurements based on single beam mirage effect for the detection of phase transitions in some cyanobiphenyl liquid crystals. This technique was successfully used earlier to detect phase transition temperatures in some other classes of samples, viz., ferroelectrics, superconductors and organic semiconductors [4,8].

The basic principle involved in this technique is described in detail elsewhere [4] and is briefly as follows: a hot body heats up the surrounding medium so as to generate a refractive index gradient (RIG) directed away from the surface. In our experiment, instead of using a modulated pump beam for heating the sample, as in conventional PTD measurements

* Corresponding author.

PII: S0167-577X(98)00004-4

[5–7], an electrical heating element is used to heat the sample thereby generating the RIG. A laser beam (probe beam) propagating normal to the RIG and parallel to the hot surface suffers deflection from the original beam path (mirage effect) as it is made to pass through the region above the sample surface. The amount of deflection is a function of the magnitude of the RIG in the vicinity of that surface and this in turn will depend on various thermal parameters of the sample as well as the distance between the sample surface and the detector along with the relevant geometrical factors. The magnitude of the beam deflection can be measured using a position sensitive detector (PSD). As the thermal properties of a sample undergo drastic variation at the phase transition temperature it is bound to affect the deflection signal in a measurable way due to the consequential change produced in the RIG.

2. Determination of the phase transition temperature in liquid crystal

A liquid crystal exhibits properties intermediate between a crystalline solid and an isotropic liquid. It is highly anisotropic in some of its properties with a certain degree of fluidity. An exceptional variety of phase transitions is characteristic of the liquid crystalline state.

The study of phase transitions occurring in liquid crystals is very important from a fundamental as well as a practical point of view. Due to the unique behaviour of some of the phases exhibited by liquid crystals, these materials have been the subject of extensive theoretical and experimental studies. Most of the liquid crystals do not melt directly from the crystalline state to the isotropic liquid [9,10]. Instead, they pass through an intermediate phase called a mesophase. In such case, two or more transitions are involved: one at a lower temperature, a transition from crystalline solid to the mesophase, followed by a transition from one type of mesophase to another mesophase or to an isotropic liquid at a higher temperature.

Commonly, phase transitions in which liquid crystalline phases participate are observed using optical microscopy. But in some cases, the optical texture of the liquid crystalline phases show minimum difference so that it is difficult or impossible to distinguish different phase types by microscopic observations. A more objective and detailed study of phase transitions can be performed by calorimetric investigations. In most cases, differential scanning calorimetry (DSC) is used, but in some cases, adiabatic calorimetry or differential thermal analysis (DTA) are used. We describe in this paper yet another method which is simpler and more convenient to use than the conventional methods to detect phase transitions in liquid crystals.

3. Experimental set-up

The schematic diagram of the experimental set-up utilizing a single beam mirage effect is shown in Fig. 1. A chopped laser beam with a Gaussian cross-section (half power beam width = 0.84 mm) from a stabilized 5-mW He–Ne laser is made to pass the heated sample surface at a grazing distance of 0.42 mm. The sample is enclosed in a chamber with appropriate windows to avoid air convection which may cause erratic fluctuations of the probe beam. The specimen, in the form of a film of liquid crystal with a free surface, is in contact with a sample holder which is heated by an electrical heating element (cartridge type) attached to a temperature controller.

The PSD consists of a step index multimode optical fiber with a core diameter of 80 μm (cladding 120 μm) with a polished tip and coupled to an

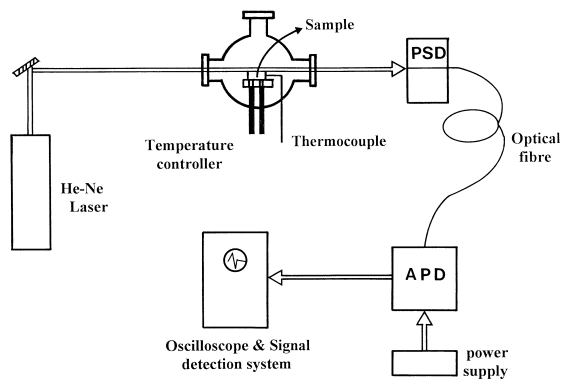

Fig. 1. Schematic diagram of the experimental set-up using the single beam method.

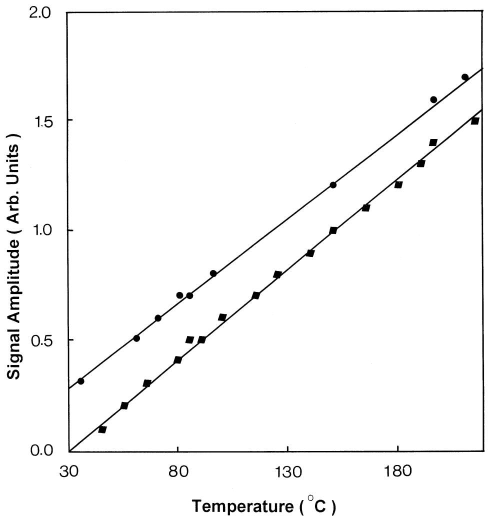

Fig. 2. The plot of the signal vs. temperature for the heating element. (● Heating; ◆ Cooling).

avalanche photo diode (Thorn EMI Si APD type S30500) at the other end. The output of the APD is monitored across an appropriate load resistance using a digital AC voltmeter. The fiber tip is mounted on an XYZ translator. Initially, at room temperature, the chopped probe beam is adjusted to fall on the polished tip of the fiber to get a maximum signal (v_0) from the APD detector corresponding to the center of the beam. As the sample is heated, (at a rate of $\sim 0.5°C/min$) the probe beam gets deflected and the PSD output (v_t) is reduced. The difference ($v_0 - v_t$) is taken as the deflection signal. A plot of deflection signal vs. temperature in the case of the sample holder itself is given in Fig. 2. The temperature of the heated surface is measured using a thermocouple. As the rate of heating is small, the lag in the thermocouple reading is not appreciable for thin samples.

4. Results and discussion

The cyanobiphenyl liquid crystals used here as specimens are E_8, M_{21} and M_{24} (BDH Chemicals). This class of liquid crystals are known to be more stable than most other liquid crystals and as a result they are less likely to undergo chemical changes during use and accumulate impurities [10]. Measurements were carried out in the nematic (N), smectic A (S_A) and isotropic (I) phases of these samples and reproducible results were obtained in each case. The S_A–N, N–I transition temperatures (T_{AN} and T_{NI}) and the melting temperature (T_M) of these samples were also studied using the present single beam mirage set-up. Figs. 3–5 display the mirage signal amplitude as a function of temperature for E_8, M_{21} and M_{24}, respectively. Transitions are indicated by clear and sharp variations in the deflection signal amplitude at different temperatures. This anomalous behaviour in the signal obviously arises due to the rapid change in thermal parameters like specific heat and thermal conductivity of the material during phase transitions.

The following transition temperatures are observed on heating:

$$E_8:\ \text{Nematic} \xrightarrow{T_{NI}=70.0°C} \text{Isotropic liquid},$$

$$M_{21}:\ \text{Crystal} \xrightarrow{T_M=55.0°C}$$

$$\text{Nematic} \xrightarrow{T_{NI}=73.5°C} \text{Isotropic liquid},$$

$$M_{24}:\ \text{Crystal} \xrightarrow{T_M=54.0°C} \text{Smectic A} \xrightarrow{T_{AN}=67.5°C}$$

$$\text{Nematic} \xrightarrow{T_{NI}=80.5°C} \text{Isotropic liquid}.$$

Note that T_M for E_8 is not reported here since E_8 is a room temperature liquid crystal which melts much below room temperature to form a nematic phase. The phase transition temperatures determined using the present technique agree well with those reported earlier [11,12]. Samples which do not undergo any phase transition do not exhibit any anomalous variation in the signal amplitude in this temperature region (Fig. 2). The two separate curves in Figs. 3–5 correspond to the data when the sample is heated and cooled. There is a slight displacement between the heating and cooling curves due to the thermal effect of the substrate in which the sample was kept. It does not have any physical significance with respect to the properties of the sample. The hysteresis phenomenon which is typical for most ferroelectric crystals is also observed on cooling the heated sample as is clear from Figs. 3–5.

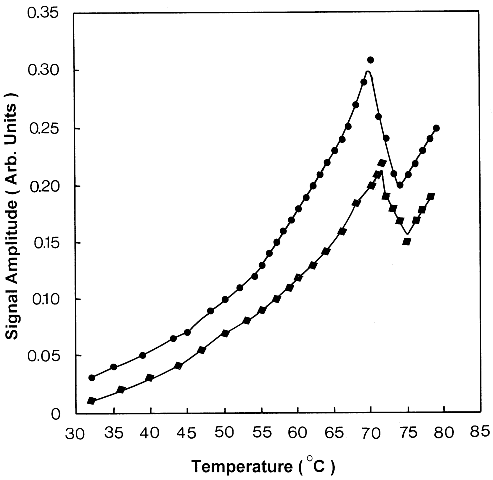

Fig. 3. The plot of the signal vs. temperature for liquid crystal E_8. $T_{NI} = 70.0°C$ (● Heating; ♦ Cooling).

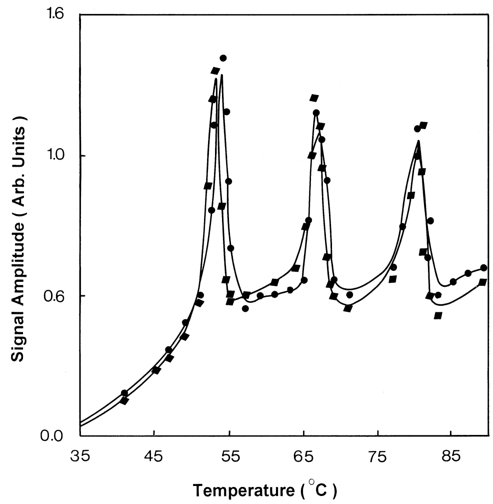

Fig. 5. The plot of the signal vs. temperature for liquid crystal M_{24}. $T_M = 54.0°C$, $T_{AN} = 67.5°C$, $T_{NI} = 80.5°C$ (● Heating; ♦ Cooling).

In many cases, the transition from crystalline to liquid crystalline state can be super cooled, i.e., the liquid crystalline phase may exist as a metastable phase below the melting temperature. For the transition from isotropic liquid to liquid crystal as well as for transitions between several liquid crystalline phases, super cooling (or over heating) effects are in general not observed. As expected, at the nematic–isotropic transition temperature, T_{NI}, a maximum in amplitude is observed precisely at the same temperature for both heating and cooling (Figs. 3–5). On the other hand, super cooling occurs in the nematic phase below the melting point T_M and solidification occurs at a lower temperature. It is obvious from Fig. 4 that the liquid crystal has changed to solid phase $\sim 5°C$ below T_M.

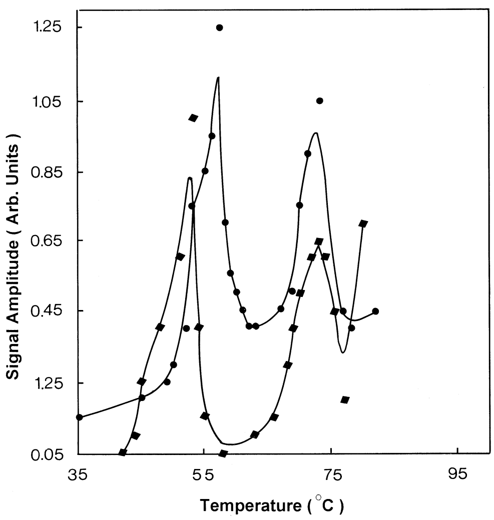

Fig. 4. The plot of the signal vs. temperature for liquid crystal M_{21}. $T_M = 55.0°C$, $T_{NI} = 73.5°C$ (● Heating; ♦ Cooling).

With respect to the large variety of phase transitions in liquid crystals, the matter of determining their nature (i.e., first or second order) arises. It is known that melting as well as *N–I* transitions in liquid crystals are first order in nature with occurrence of relative changes in several thermal parameters. At the *N–I* transition, however, these quantities are usually an order of magnitude smaller than those at the melting point [13]. This is apparent from Figs. 4 and 5 where the signal amplitude is smaller in magnitude at T_{NI} than that observed at the T_M. The S_A–N transition has recently been the subject of a large number of investigations, the main reason being that it can be a first or second order transition. According to the microscopic theory of McMillan [14], the phase transition S_A–N can be first as well as second order depending on the ratio T_{AN}/T_{NI}. When this ratio is < 0.87, S_A–N should become second order. In the present case for M_{24}, $T_{AN}/T_{NI} = 0.84$ which indicates that the transition is second order. However, the ratio is very close to that required for a first order transition ($T_{AN}/T_{NI} > 0.87$) and of course is the reason for the large signal amplitude at T_{AN} (Fig. 5).

In the present studies, instead of the measurement of signal fluctuations at the transition temperature as we had observed in the case of $BaTiO_3$ and Triglycine sulfate [4], clear enhancement in the signal amplitude occurs during the phase transition. It must be remembered that the specimen in this case is a thick film which apparently reduces the mirage signal fluctuations. In addition to this, the magnitude of the RIG developed at the transition points in the case of liquid crystals is fairly large so that the corresponding variation in mirage signal are also quite large.

5. Conclusions

From the above results, it is concluded that the anomalous change in signal amplitude observed in single beam mirage effect is a very good indicator of the occurrence of phase transitions in materials like liquid crystals. The single beam mirage set-up is found to be more sensitive than the dual-probe configuration and moreover, the single beam set-up also avoids a pump beam which requires more complex set-up as described by earlier investigators [5–7]. The technique based on the mirage effect is much simpler compared with direct measurements of the temperature dependence of the dielectric constant, index of refraction, etc. The technique, besides being of low cost and easy to construct, is also non-contact. Since the optical fiber is used in the detector system the method is useful for telemetric measurements as well as for multiplexed transmission of data. However, one clear disadvantage of the technique is that the signal cannot be related to a single, well defined, thermal property.

Acknowledgements

The authors are grateful to the Department of Science and Technology (GOI) and MHRD for financial assistance.

References

[1] H.D. Megan, Ferroelectricity in Crystals, Methun, London, 1957.
[2] C.N.R. Rao, K.P.R. Pisharody, Progress in Solid State Chemistry, Vol. 10, Pergamon, Oxford, 1975.
[3] J.B. Goodenough, J.M. Longo, Crystallographic and Magnetic Properties of Perovskite and Perovskite Related Compounds, Vol. 4a, Landolt–Bornstein New Series, Group III, Springer-Verlag, Berlin, 1970.
[4] K. Rajasree, V. Vidyalal, P. Radhakrishnan, V.P.N. Nampoori, C.P.G. Vallabhan, Meas. Sci. Technol. 4 (1993) 435.
[5] K.C. Tsui, P.C.W. Fung, H.L. Tam, G.O. Walker, J. Phys. Chem. Solids 52 (1991) 979.
[6] A. Hadj-Sahraoui, G. Louis, B. Mangeot, P. Peretti, J. Billard, Liq. Cryst. 115 (1989) 579.
[7] A. Hadj-Sahraoui, G. Louis, B. Mangeot, P. Peretti, J. Billard, Phys. Rev. A. 44 (1991) 5080.
[8] K. Rajasree, V. Vidyalal, P. Radhakrishnan, V.P.N. Nampoori, C.P.G. Vallabhan, J. Thomas, V.N. Sivasankara Pillai, unpublished.
[9] G.H. Brown, W.G. Shaw, Chem. Rev. 57 (1957) 1049.
[10] J.L. Fergason, Sci. Am. 211 (1964) 76.
[11] A.K. George, K.P. Mohandas, Phys. Chem. Liq. 30 (1995) 233.
[12] K.P. Mohandas, A.K. George, J. Chem. Phys. 96 (1992) 4779.
[13] W.H. de Jeu, Physical Properties of Liquid Crystalline Materials, Gordon & Breach, New York, 1980.
[14] W.L. McMillan, Phys. Rev. A 4 (1971) 1238.