Journal of the Korean Physical Society, Vol. 32, February 1998, pp. S1066∼S1068

Doping Effect on the Photo-Pyroelectric Properties of Ferroelectric Liquid Crystals

Chang-Jae Yu, Ju-Hyun Lee, Jae-Hoon Kim* and Sin-Doo Lee

School of Electrical Engineering, Seoul National University, Seoul 151-742, Korea

We have studied the doping effect on the photo-pyroelectricity of ferroelectric liquid crystals (FLCs) with nonlinear optical chromophores. For a FLC mixture of SCE 13 doped with 4-dimethylamino-4 nitro stilbenes (DANS), it is found that the paraelectric-ferroelectric (PA-FE) phase transition temperature, T_c, becomes lower with increasing the concentration of DANS. Under a dc bias electric field, the enhancement of the pyroelectricity in the PA phase (above T_c) of the doped SCE 13 is much larger than that in the FE one. The doped FLCs are expected to be useful for thermal detection and imaging applications.

I. INTRODUCTION

The pyroelectricity in ferroelectric liquid crystals (FLCs) [1–4] has attracted great interest in the use of these materials for thermal detection of infrared radiation and infrared imaging. It is a fundamental property of ferroelectric materials and originated from the change in the spontaneous polarization with temperature. The pyroelectric coefficient γ is defined as the rate of change of the spontaneous polarization P_s with temperature T ($\gamma = dP_s/dT$). For high voltage responsivity, a large value of γ/ϵ' is needed [5]. Likewise, the signal-to-noise is governed by γ/ϵ''. Here, the dielectric constant ϵ is given by $\epsilon' + i\epsilon''$. Therefore, a smaller ϵ and a larger γ are required for better figures of merit, i.e., γ/ϵ' and γ/ϵ''. Moreover, temperature independence of these quantities is highly desirable.

Most ferroelectric solids such as $BaSrTiO_3$ and $PbTiO_3$ possess very large values of P_s but show the divergence of ϵ on approaching the critical temperature, T_c, for the paraelectric (PA)-ferroelectric (FE) phase transition. Unlike ferroelectric solids, FLCs exhibit no catastrophic divergent behavior of ϵ at the ferroelectric, smectic C* to the paraelectric, smectic A phase transition. For practical applications, however, the magnitude and temperature dependence of the pyroelectric properties of these materials need to be improved by molecular engineering [6–8].

In this paper, we have studied the doping effect on the photo-pyroelectric properties of a FLC with nonlinear optical chromophores. For SCE 13 (British Drug House) doped with 1 % to 5 % of 4-dimethylamino-4 nitro stilbenes (DANS) in weight, it is found that T_c becomes lower with increasing the concentration of DANS. Above T_c, γ shows a maximum at a certain concentration of DANS (about 2 %) while below T_c, it remains fairly constant. The dielectric constant ϵ is found to be almost independent of the DANS concentration.

II. EXPERIMENTAL

The FLC materials used in this study were the undoped SCE 13 and doped SCE 13 with DANS of 1 % to 5 % in weight. The phase transition sequence of the undoped SCE 13 is as follows: paraelectric smectic A → (60.8 °C) → ferroelectric smectic C* → (−20.0 °C) → crystalline. The sample cell was made of patterned indium-tin-oxide glass substrates (0.8 cm×0.8 cm). The cell thickness was maintained by glass spacers of 10 μm. Two inner sides of the glass substrates were coated with polyimides of 300 Å, followed by rubbing, so that the homogeneous alignment of LC was promoted [9]. The LC was filled in the isotropic state, and cooled into the mesophase. Electric contacts were made directly to the internal surfaces of the glasses to apply an external electric field. The sample cell was mounted in a hot stage (Mettler FP 90) for temperature control, and the temperature fluctuations were approximately 0.05 °C. For uniform alignment of both the FLC molecules and smectic layers, the sample was cooled down at a rate of 0.1 °C/min into the ferroelectric phase.

The pyroelectric response of each sample was measured using the dynamic Chynoweth technique [10]. A laser diode with the wavelength of 830 nm and the intensity of about 100 mW was used as a light source. The sample cell was periodically heated at a frequency of $\omega = 100$ Hz by a chopped light source. The ac pyroelectric current, generated from the sample in response to the heating, was measured with a lock-in amplifier during heating or cooling of the hot stage. The measured current $i(\omega)$ is given by $A\gamma(dT/dt)$ where A is the area of the electrode, and dT/dt is the rate of the heating of the sample which depends on the cell geometry, the

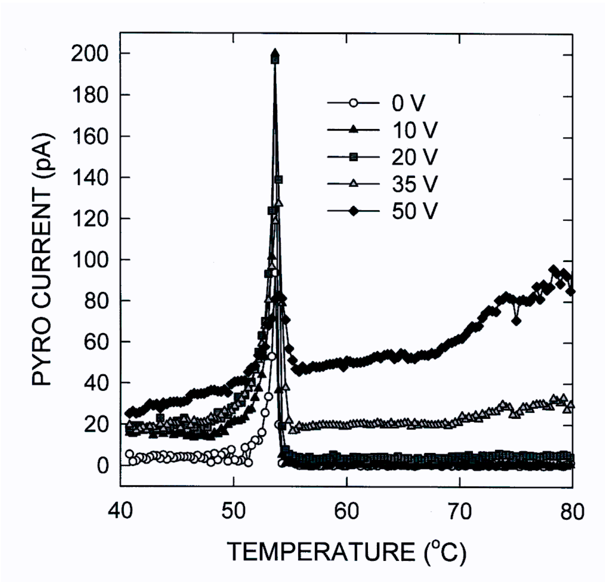

Fig. 1. The photo-pyroelectric currents of a doped SCE 13 with 2% of DANS in weight as a function of temperature at various dc bias electric fields.

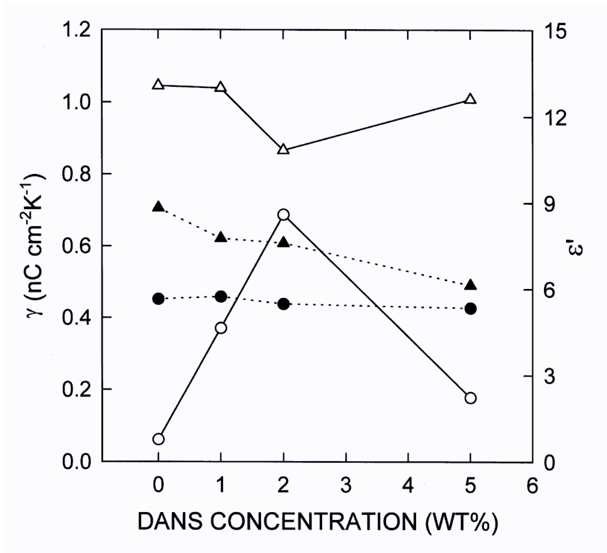

Fig. 3. The pyroelectric coefficient γ and the dielectric constant ϵ' at $(T - T_c) = \pm 5$ °C as a function of the doping concentration of DANS in weight. The open and filled symbols denote γ and ϵ', respectively. The circular and triangular symbols represent the data measured at $(T - T_c) = 5$ °C and at $(T - T_c) = -5$ °C, respectively.

absorption of the light, and the thermal relaxation time with the cell walls. Since the quantity AdT/dt is not known, a calibration procedure must be adapted for the spontaneous polarization P_s. For the undoped SCE 13, the measured value of $P_s = 20.4$ nC/cm^2, using a triangular wave method, at 41.0 °C was used for calibrating the current i.

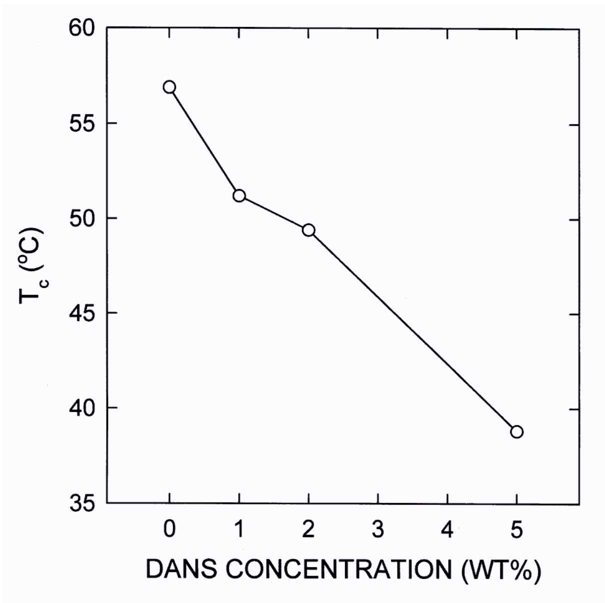

Fig. 2. The variations of the paraelectric-ferroelectric phase transition temperature T_c with the doping concentration of DANS in weight.

III. RESULTS AND DISCUSSION

Figure 1 shows the pyroelectric currents of the doped

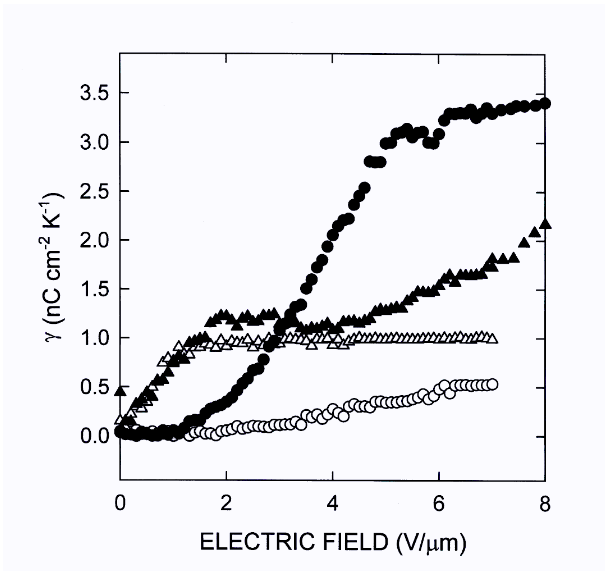

Fig. 4. The pyroelectric coefficient γ of the undoped SCE 13 and the doped SCE 13 with 2% of DANS in weight at $(T - T_c) = \pm 5$ °C as a function of the bias field. The open and filled symbols denote the undoped SCE 13 and the doped SCE 13, respectively. The circular and triangular symbols represent the data measured at $(T - T_c) = 5$ °C and at $(T - T_c) = -5$ °C, respectively.

SCE 13 with 2 % of DANS as a function of temperature for various bias electric fields. As expected, the pyroelectric current exhibits a divergent behavior at the PA-FE phase transition. The dielectric divergence was found to be less profound than the pyroelectric response at the transition. The qualitative features of the undoped SCE 13 were quite similar to this doped sample except for the enhanced pyroelectric response in the PA state under a relatively high bias voltage. Above a certain bias voltage ($\geq$ 35 V), the dipole moment of the individual DANS molecule seems to experience reorientation in the PA state. This is reflected in the pyroelectric current at temperatures above 70 °C as shown in Fig. 1.

The effect of the DANS concentration on T_c is shown in Fig. 2. T_c decreases linearly with increasing the concentration. This indicates that the tuning of the pyroelectricity and its temperature range can be controlled by the concentration of an appropriate doping agent. Fig. 3 shows γ and ϵ', measured at $(T - T_c) = \pm 5$ °C, as a function of the DANS concentration. In the FE phase, γ remains fairly constant while it has a maximum at a certain concentration (about 2 %) of DANS in the PA phase. This may be attributed to the subtle change in the intermolecular interactions between the DANS molecules in the FLC environment [11,12].

Fig. 4 shows γ of the undoped SCE 13 and the doped SCE 13 with 2% of DANS in weight at $(T-T_c) = \pm 5$ °C as a function of the bias electric field. Under a dc bias field, it is clear that the pyroelectricity of the doped SCE 13 is greatly enhanced above a certain field strength (about 5 V/μm) in the PA as well as in the FE phases. In the PA phase of the doped SCE 13, γ stays constant in the low field regime, increases almost linearly with the field, and becomes eventually saturated in the high field regime. This manifests itself the reorientation process of DANS in the FLC medium; hindered rotation, partial reorientation, and complete reorientation. It may be then concluded that considerable improvement in pyroelectricity of FLCs can be anticipated with structural modifications of the constituent molecules or introduction of a proper dopant into them.

IV. CONCLUDING REMARKS

We have studied the doping effect on the photo-pyroelectric properties of FLCs with nonlinear optical chromophores. It was found that the paraelectric-ferroelectric phase transition temperature becomes lower with increasing the concentration of the dopant. The material figures of merit can be tuned by controlling the doping concentration and a dc bias electric field. Over conventional ferroelectric solids, doped FLCs have several advantages such as non-catastrophic divergence of the dielectric constant near the phase transition. These materials seem promising for the use in the area of thermal detection and imaging of infrared radiation.

ACKNOWLEDGMENTS

This work was supported in part by the Ministry of Education of Korea through BSRI-97-2415.

REFERENCES

* Present address: Department of Physics, Kent State University, Kent, OH 44242, USA.

[1] L. J. Yu, H. Lee, C. S. Bak and M. M. Labes, Phys. Rev. Lett. **26**, 388 (1975).

[2] A. M. Glass, J. S. Patel, J. W. Goodby, D. H. Olson and J. M. Geary, J. Appl. Phys. **60**, 2778 (1986).

[3] Y. Kim, J. -H. Kim, S. -D. Lee and G. Park, Ferroelectrics **156**, 43 (1994).

[4] J. W. O'Sullivan, Yu. P. Panarin and J. K. Vij, J. appl. Phys. **77**, 1201 (1995).

[5] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics* (Clarendon, Oxford, 1977).

[6] A. Kocot, R. Wrzalik, J. K. Vij and R. Zental, J. App. Phys. **75**, 728 (1994).

[7] B. Helgee, T. Hjertberg, K. Skarp, G. Andersson and F. Gouda, Liq. Cryst. **18**, 871 (1995).

[8] R. E. Geer, J. Naciri, B. R. Ratna and R. Shashidhar, Appl. Phys. Lett. **69**, 1405 (1996).

[9] J. S. Patel, G. W. Goodby and T. M. Leslie, Ferroelectrics **59**, 137 (1984).

[10] A. G. Chynoweth, J. Appl. Phys. **27**, 78 (1956).

[11] M. Lim, B. Park, S. -Y. Eom and S. -D. Lee, Mol. Cryst. Liq. Cryst. **280**, 159 (1996).

[12] B. Park, M. Lim, J. -H. Lee, J. -H. Kim and S. -D. Lee, Ferroelectrics **179**, 231 (1996).