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APPARATUS FOR OBSERVATION AND MEASUREMENT OF PROPERTIES OF ELECTRO-OPTIC CELLS WITH FERROELECTRIC LIQUID CRYSTALS

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The apparatus for investigation of the behavior of ferroelectic liquid crystals in an electric field and for measurement of their spontaneous polarization is described. Function of the apparatus was tested by observations and measurements properties of several ferroelectric compounds with a high spontaneous polarization.

Introduction

Ferroelectric liquid crystals (FLC) have attracted attention for a long time due to promising use of the materials in various electro-optic devices [1,2]. Research is concentrated especially on preparation of new compounds with ferro- and anti-

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ferroelectric properties and on study of their behavior in an electric field [3,4,5]. Therefore, apparatus for simultaneous visual observation electro-optic cells and measurement of relevant physical properties in the electric field is very useful.

In this article we describe an apparatus whose basic part is a polarization microscope equipped with CCD videocamera, photodetector and special heating/cooling stage. The arrangement enables visual observation and photodocumentation of textures of liquid crystal layers in electrooptic cells and measurement of their optical transmission. The function of the apparatus was tested by observations and measurements of properties of several ferroelectric compounds with a high spontaneous polarization.

Background on the SmC*

The classic FLC's are smectic C-type liquid crystals composed of optically active and dielectrically negative elongated molecules containing usually three aromatic or heterocyclic cores in a rigid central part [6]. At least one chiral substituent has to be attached to the end of the molecule. One or more polar group(s) must be oriented approximately vertically to the long molecular axis creating transverse dipole moment. This fact results in helical smectic C structure (termed as chiral smectic C and abbreviated as SmC*). The tilt direction turns from one layer to the next in the bulk SmC* phase with spatial periodicity $p/2$ (p is the helicoidal pitch). Such structure belongs to monoclinic point group C_2 without the mirror plane symmetry operation. Twofold axis allows the existence of a permanent dipole moment parallel to the C_2 axis and each smectic layer possesses a spontaneous polarization (P_s) in the plane of that layer.

Due to the chirality SmC* phase, the orientation of the P_s changes from layer to layer, according to a helix in the direction of the layer normal. Thus, the overall polarization in the bulk SmC* is zero. From the outside the material appears to be non-polarized. To be able to use the polarization in the operation of a display, the helix must be suppressed.

The helical structure of the SmC* phase can be unwound either in an electric field or by the elastic unwinding of the spontaneous helix by surface interactions. In the second case, planar orienting boundary conditions tend to unwind the phase and so called Surface Stabilized Ferroelectric Liquid Crystal (SSFLC) structure arises if the cell gap is thin enough, i.e. smaller than the helical pitch (typical values are in the order of 2 μm). All the molecules and accordingly also the molecular dipoles are arranged parallel in one direction. Then, the overall polarization is directed either upwards or downwards along the normal to the electrodes. Both states are stable as long as no electric fields of opposite polarity are applied, i.e. the SSFLC structure is bistable. Just this property is mainly used in ferroelectric liquid crystal displays.

Equipment

For investigation of liquid crystals for electrooptical applications it is desired to use apparatus allowing simultaneously to observe textures of their thin layers, to measure temperatures of phase transitions and to investigate an influence of an electric field on optical properties in broad temperature range. For these purposes we used microscope NU2 (Zeiss) in arrangement for observation in polarized light which is equipped with special temperature stage (from –20 °C to + 170 °C). All observations and picture documentation were performed using Color CCD videocamera (COHU 2252-1050), Color monitor (Sony), Videocopy processor (Mitsubishi P90), Time lapse VCR (Mitsubishi HS5440) and a Digital photocamera (Nikon Coolpix 950). Optical transmission measurements were carried out using photodetector (photoelectric cell or photomultiplier tube) and digital storage oscilloscope (Tektronix 5110+5D10 Waveform Digitizer). Software Lucia (LIM) was used for image analysis.

The primary source of a.c. electric voltage for electro-optic cells was Function Arbitrary Waveform Generator (Hewlett-Packard 33120A) whose output voltage was amplified to peak-peak value as much as 150 V_{pp}.

Phase Transitions

The sequences of phases and transition temperatures were determined by polarizing light microscopy observing sample textures on sample heating (4 °C min^{-1} or less) except the tabulated temperature value between *Cr* and SmC* which represents sample undercooling capability.

Heating/Cooling Stage

A special copper cell provided with two opposite glass windows had electrical heating for temperature range from ca +50 °C to +170 °C. For temperature range from –20 °C to +50 °C a liquid is used streaming through the cell from the Refrigerated and Heating Circulator (Julabo F 25). Glass electro-optic cells were situated inside a central cavity with diameter 30 mm and height 4 mm in which constant temperature with an accuracy ±0.05 °C was maintained. The sample temperature was independently measured by means of a Pt100 resistor element inside the cavity. The all copper cell was mounted on a special X-Y movement stage.

Electro-Optic Cell

The electro-optic cell consisted of two 2 mm thick glass plates (typically 20×30 mm^2) recovered with ITO transparent electrodes, which were separated by Mylar spacers or nickel wires of calibrated thickness or diameter (typically 20 or 40 μm). The electrodes were coated with unidirectionally rubbed PVA layers to obtain strong planar anchoring.

A special electrode pattern was made by etching in order to have a well-defined overlapping area (about 25 mm^2).

Spontaneous Polarization

The spontaneous polarization values were determined from P(E) dependence (see Fig. 3) in the form of a hysteresis loop detected during ferroelectric switching in an a.c. electric field.

The display on an oscilloscope of the ferroelectric hysteresis loop is a conventional method for ferroelectric investigations. In the experimental study one employs Sawyer-Tower capacitance bridge set-up [7] whose basic circuit is shown in Fig. 1. The application of a large sine-wave voltage to a linear or non-polar dielectric material results in a current flow, which varies sinusoidally with time. By comparison, a typical non-linear or polar dielectric material will have a current flow with contributions from dipolar switching in the material usually in the form of current peaks. The electrical non-linearity is often displayed as a function of the driving signal rather than as a function of time. An integrating linear capacitor C_0 is placed in series with the polar material. The value of C_0 is chosen to be large enough so that most of the voltage drop in the circuit will occur across the polar material and thus the voltage at point x is a close approximation to the voltage across the polar dielectric material. The voltage V_p developed across C_0 due to current i is

$$V_p = \frac{1}{C_0}\int i\,dt$$

and hence the voltage at point y is proportional to the charge q flowing through the polar material. By connecting points x and y to the plates of an oscilloscope one can obtain the q versus V characteristics of the polar dielectric material (see Fig. 2a). Digital memory oscilloscopes are readily available to record and also evaluate the hysteresis loop.

Unfortunately, with samples exhibiting higher electric conductivity (which is mostly the case of liquid crystals) it is not possible to use simple Sawyer and Tower circuit shown in Fig. 1. In such case a loop has rounded ends and terminal lines are not horizontal (Fig. 2b). This makes it impossible to determine accurately, by extrapolation, the correct value of the spontaneous charge Q_s.

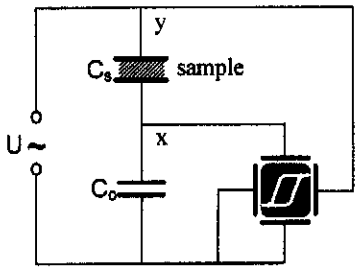


Fig. 1 The principle or the Sawyer-Tower bridge method for measurement of spontaneous ferroelectric polarization

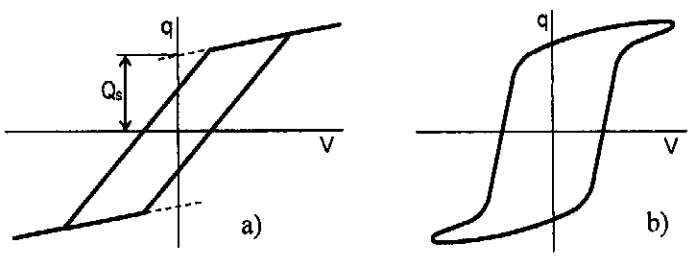


Fig. 2 Hysteresis loops due to nonconducting sample (a) and due to conducting sample (b)

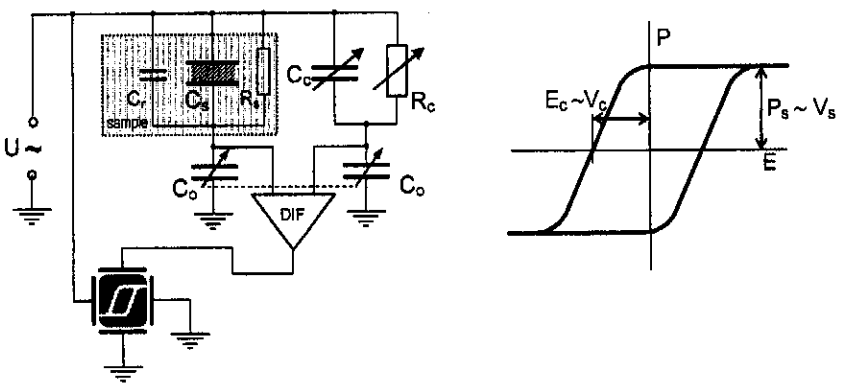


Fig. 3 A standard mesuring Diamant bridge for studying the ferroelectric polarization in chiral smectic liquid crystals, and a compensated hysteresis loop on the screen of the digital storage oscilloscope

These difficulties outlined above have been surmounted in the method initiated by Diamant *et al.* [8] using an additional compensation of the resistance and residual capacitance of the sample. A second Sawyer and Tower circuit containing an adjustable compensation resistor R_c and capacitor C_c has been added (see Fig. 3). The resultant voltage from the bridge thus formed is fed to the Y

plates of the oscilloscope by a differential amplifier. Adjusting R_c to equal the sample resistivity R_s removes the rounded ends of the displayed hysteresis loop.

The residual capacitance C_r of the sample cell can be compensated and measured by adjusting C_c to produce a hysteresis loop ending in horizontal lines. One then obtains the compensated loop, Fig. 3, giving an undistorted display of the spontaneous polarization only. Coercive electric field E_c and P_s can be easily determined as

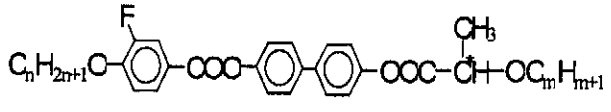
$$E_c = \frac{V_c}{d} \qquad \text{and} \qquad P_s = \frac{V_s C_0}{S}$$

where S is the surface area of the sample, d the thickness of the sample. V_s and V_c can be directly measured from the hysteresis loop on the screen of the digital storage oscilloscope.

The loop was observed at various amplitudes (up to 10^7 V m^{-1}) and frequencies (5-250 Hz) of the sine or triangular electric field. The range of the field strengths applied was limited by the breakdown voltage and the range of frequencies — by the possibilities of compensating the dielectric losses, and conductivity. For too high measuring field strengths the hysteresis loop will be distorted in a characteristic way due to electrohydrodynamic flow phenomena in the cell [9]. On heating sample upwards of the temperature of transition to the smectic phase A, to the chiral nematic phase or an isotropic phase the hysteresis loop vanishes.

Results and Discussion

The function of apparatus was tested by determination of sequences of phases and transition temperatures in mesogenic substances of common formula [10].



Values of spontaneous polarization at different temperatures are also presented. The phase sequences, phase transition temperatures and the spontaneous polarization values P_s for the investigated compounds are summarized in Table I.

All the compounds studied exhibit only enantiotropic SmC* phases with ferroelectric properties. The phase transitions seem to be of the first order characterised by a phase coexistence region and temperature hysteresis. Temperature stability of the SmC* phase slightly decreases and melting point slightly increases with increasing number carbon atoms m in chiral centre. This effect can be explained in terms of the steric influence of an end chain branching on

molecular packing.

The values of P_s measured in the SmC* phases exhibit continuous increase on cooling. No saturation is observed. For several *F n/m* substances the temperature dependence of P_s is shown in. Fig. 4.

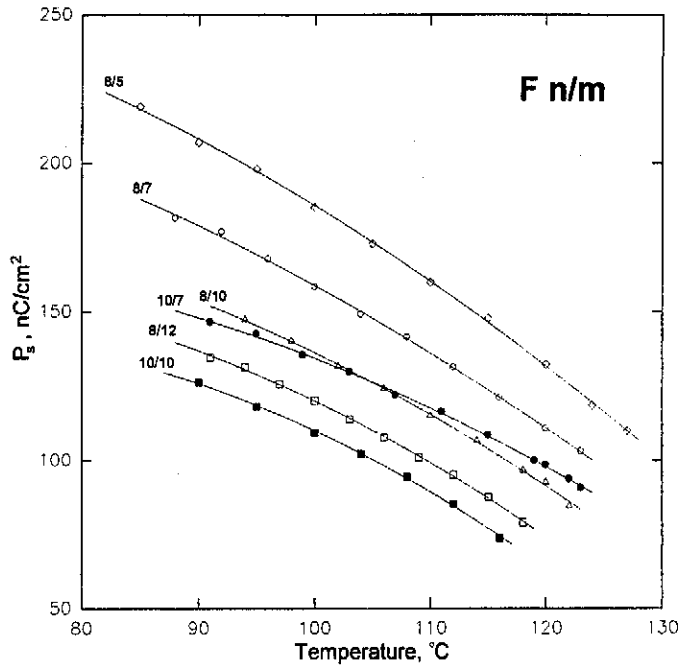


Fig. 4 Temperature dependence of the spontaneous polarization P_s for the homologous series *F n/m* [10]

Table I Phase transition temperatures (°C) and spontaneous polarization P_s for the homogeneous series *F n/m*

F n/m	M.P.	Cr		SmC*		Iso	P_s nC cm^{-2}
8/5	89.0	●	85	●	131.5	●	127
8/7	90.5	●	87	●	128.5	●	115
8/10	96.5	●	92	●	126.5	●	100
8/12	97.5	●	91	●	123.0	●	92
10/7	91.5	●	88	●	130.0	●	98
10/10	93.5	●	86	●	122.5	●	83

P_s is the spontaneous polarization in the SmC* phase at temperature 10 °C below the clearing temparature. M.p. – melting point; Cr – crystal; SmC* – chiral smectic; Iso – isotropic liquid; (●) – the phase exists; (-) – the phase does not exist

In Table I the values of P_s at temperature 10 °C below the clearing temperature are given for comparison. The spontaneous polarization decreases with increasing number of carbon atoms *n, m* in terminal alkyl chains of the molecule.

Conclusion

The described apparatus allows to simultaneously observe a behavior of thin liquid crystal layers in an electric field and to measure main characteristics of ferroelectric liquid crystals in a broad temperature range. The bridge experimental setup is suitable for routine measurements of spontaneous polarization of new substances.

Acknowledgements

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References

[1] Lueder E.: *Liquid Crystal Displays*, Wiley & Sons, Ltd., Chichester, 2001.
[2] Pirkl S.: Sdělovací technika **60**(10), 8 (1997); **60**(11), 6 (1997).
[3] Pirkl S.: Chem. Listy **80**, 449 (1986).
[4] Takezoe H., Takanishi Y.: in The *Chirality in Liquid Crystals* (Kitzerow H-S., Bahr C., Eds.), pp. 251–295, Springer-Verlag, New York, 2001,.
[5] Hird M., Goodby J.W., Hindmarsh R., Lewis R.A., Toyne K.J.: Ferroelectrics **276**, 219 (2002).
[6] Lagerwall S.T.: *Ferroelectric and Antiferroelectric Liquid Crystals*, VCH Verlag, Weinheim, 1999.
[7] Sawyer C.B., Tower C.H.: Phys. Rev. **35**, 269 (1930).
[8] Diamant H., Drenck K., Pepinski R.: Rev. Sci. Instr. **28**, 30 (1957).
[9] Kai S., Hashimoto K., Ose K., Imasaki M.: Mol. Cryst. Liq. Cryst. **130**, 143 (1985).
[10] Hamplová V., Bubnov A., Kašpar M., Pirkl S., Glogarová M.: 7th European Conference on Liquid Crystals, P138, Jaca, Spain, 2003.