Broad temperature range ferrielectric liquid crystal with subwavelength helix pitch

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Abstract. The ferrielectric liquid crystal (FerriLC) phase with the helix pitch $p_h$ of about 100 nm was revealed in a broad temperature range from -3°C to +35°C in a mixture containing an achiral smectic-C (SmC) biphenylpyrimidine and two non-mesogenic chiral diesters of 4,4''-terphenyl dicarboxylic acid.

1. Introduction

The phenomenon of ferrielectricity began to be considered more than sixty years ago as an inherent property of a specific phase state of polar crystals [1]. To date, it has been well proven that a common property of ferrielectric phases, which are intermediate between ferroelectric and antiferroelectric phases, is the presence of nonequivalent subsystems of oppositely directed dipoles [2]. The same statement is also true for the ferrielectric phases of polar smectic liquid crystals [3, 4].

Until now, ferrielectric phases in polar liquid crystals have been observed and investigated experimentally mainly in the chemical class of (R)- and (S)-1-Methylalkyl 4'-4''-n-Alkoxybenzoyloxy) biphenyl-4-carboxylates [3 - 7]. Ferrielectric phases were observed at temperatures above 60°C, and their existence temperature range has been varied from 2°C [6] to 12°C [4], depending on the molecular structure. The main efforts of researchers were devoted to proving the existence [3 - 6] and the classification of ferrielectric phases in liquid crystals on the basis of various theoretical approaches [6 - 8].

We have developed a multicomponent chiral smectic liquid crystal with a rather broad temperature range of the ferrielectric phase, from -3°C to +36°C. Below is a description of this result, including data on the chemical composition of the mixture and evidence of the presence of a broad-temperature range ferrielectric phase.
2. Results and discussions

The chemical structure of the developed three-component mixture, called as FerriLC-1, in which the ferrielectric phase is observed in the temperature range from -3°C to +36°C, is shown in Table 1.

Table 1. Chemical structure of the FerriLC-1 mixture.

| Entry | Liquid crystal components | Concentration, % weight |
|-------|---------------------------|-------------------------|
| 1     | \( \text{H}_{13}\text{C}_8 \text{C}_6 \text{H}_{11} \) | 49.7                    |
| 2     | \( \text{F}_2\text{C} \text{(S)} \text{O} \text{C} \text{C}_6 \text{O} \text{C} \text{C}_6 \text{H}_{13} \text{C}^\text{F}_3 \) | 38.9                    |
| 3     | \( \text{H}_2\text{C} \text{O} \text{C} \text{C}_6 \text{O} \text{C} \text{C}_6 \text{H}_{13} \text{CH}_3 \text{O} \text{C} \text{C}_6 \text{H}_{13} \text{COOC}_6\text{H}_9 \) | 11.4                    |

The FerriLC-1 mixture contains an achiral smectic-C biphenylpyrimidine [9] as the SmC host (see Table 1, entry 1) and two chiral non-mesogenic dopants shown in Table 1, in entry 2 (description of this structure syntheses was published in [10]) and in entry 3 (the structure was published in [11, 12]). A mixture of the same three components that are shown in Table 1 but with a different percentage of these components has already been investigated earlier in work [13], where it was shown that with a weight ratio of the components of 52%, 39%, 9% in entries 1 - 3 of Table 1, respectively, the mixture was a smectic C* ferroelectric liquid crystal.

Now we claim that at the concentrations of the mixture components indicated in Table 1, a broad-temperature ferrielectric phase appears in the mixture. This statement is confirmed by the shape of the hysteresis loop, typical for ferrielectrics (see Figure 1). The hysteresis loop shape shown in Figure 1 is observed over a temperature range of -3°C to +36°C, which can be seen in the inset to Figure 1.

![Figure 1](image-url)

**Figure 1.** Macroscopic polarization \( P \) of a 107 µm FerriLC-1 based cell versus triangular electric field \( E \) of 2 \times 10^{-2} \text{ Hz} frequency applied to the cell; the insert shows the temperature dependence of coercive field \( E_c \).
Static hysteresis loops of FerriLC-1 based cells were measured at the applied triangular voltage with frequency $2 \cdot 10^{-2}$ Hz to exclude the influence of viscous torque on the voltage coercivity and on the loop shape [14 - 16]. The FerriLC-1 layer thickness in electro-optical cells was around 107 µm, and the hysteresis loops measurements were carried out via measurements of polarization reversal currents and their subsequent integration according to the well-known method described in detail [16].

The pitch $p_0$ of the FerriLC-1 helix measured by the known method [17], turned out to be less than 120 nm in the entire temperature range of the ferroelectric phase existence (see Figure 2), that is, several times less than any wavelength in the visible spectral range. The spontaneous polarization $P_s$ of the FerriLC-1 mixture is observed up to the temperature about of 110°C, Figure 2. It means that within the temperature interval $36°C < T < 110°C$ other polar phases exist: either smectic C* phase or other ferrielectric phases predicted in [7, 8]. However, we have not yet completed the identification of these phases by now.

![Figure 2. Temperature dependencies of the helix pitch and spontaneous polarization of the FerriLC-1 mixture.](image)

3. Conclusion

A ferrielectric phase with a subwavelength helix pitch ($p_0 < 120$ nm) was discovered in the temperature range from -3°C to + 36°C in the mixture of achiral smectic C biphenylpyrimidine with two non-mesogenic chiral compounds.

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