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DIELECTRIC RELAXATION MODES IN LIQUID CRYSTALLINE MIXTURE

Mixture of two liquid crystalline compounds (which do not exhibit antiferroelectric or ferrielectric phase separately) shows ferrielectric phase in a broad temperature range. The dielectric spectroscopy technique was used for investigation of collective molecular motions in the mixture. Two relaxation modes were detected in the ferrielectric phase and the soft mode in the SmA phase. The temperature dependence of the parameters of the dielectric relaxation modes are presented and discussed.*

Keywords: Ferrielectric phase, Goldstone mode, soft mode.

1. INTRODUCTION

A lot of new antiferroelectric liquid crystalline compounds have been synthesized after discovery of chiral antiferroelectric phase. The mixtures with induced antiferroelectric phase have been prepared. These new liquid crystalline antiferroelectric materials show various chiral smectic phases and subphases. The general phase sequence during cooling can be as follows: Isotropic→SmA*→SmC^*_α→SmC*→SmC^*_β→SmC^*_γ→SmC^*_A→SmI*→SmI^*_A→Crystal (using the notation proposed by Lagerwall et al. [1]). The structure of chiral smectic subphases could be described by the clock model [2] with three- and four-layer unit cell for SmC^*_γ and SmC^*_β phases respectively. The SmC^*_β as the SmC^*_A phase has an antiferroelectric nature [3].

The unit cell of ferrielectric $Sm C^*_\gamma$ consists of two synclinic and one anticlinic layers which give net electric polarization, but lower than in the ferroelectric phase [2]. The $Sm C^*_\gamma$ exhibits one polar mode with low relaxation frequency, which indicates that the response is due to collective fluctuations in the phase angle, e.g. a distortion of the $Sm C^*_\gamma$ helix [1]. In this phase, two dielectric relaxation modes were observed in some cases [4-6].

Pandey et al. [7] report the experimental verification of two theoretically predicted dielectric modes in the $Sm C^*_\alpha$ phase, one connected with the helicity of the $Sm C^*_\alpha$, and the second similar to the soft mode.

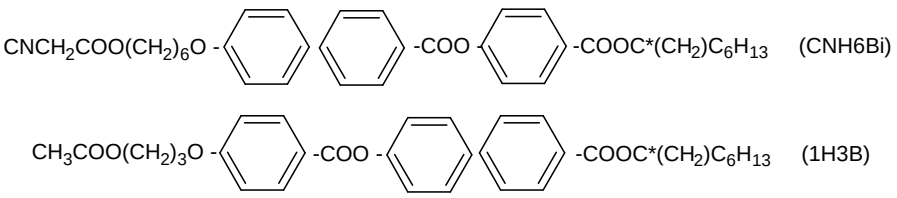
Broadband dielectric spectroscopy has often been used to study the molecular and collective molecular relaxations in ferroelectric liquid crystalline materials [1,8,9]. The experimental information concerning the dielectric relaxation modes, especially in ferrielectric subphases, are still needed.

In this work, dielectric study of a bicomponent mixture (3:7) of liquid crystalline compounds has been performed. The investigated mixture possesses a ferrielectric subphase over a broad temperature interval.

Other mixtures of the same compounds were investigated dielectrically [10-12]. It was shown [10,11] that the mixture (5:5) exhibits antiferroelectric phase in a broad temperature range near the room temperature, which suggests a possibility of some optoelectronic applications.

2. EXPERIMENTAL

The mixture (3:7) of liquid crystalline compounds presented below (which do not exhibit antiferroelectric phase separately) was studied. The molecular structure of the components is presented below:



The investigated compounds were synthesized and the mixture was prepared in the Institute of Chemistry, Military University of Technology (Warsaw, Poland). The phase sequences for the two compounds are as follows: Cr→ SmA^*→Iso for 1H3B and Cr→SmC^*→ SmA^*→Iso for CNH6Bi [13]. The phase sequences in the investigated mixture [13]:

$$Cr\ 18\text{-}19.5^oC \rightarrow SmC^*_\gamma \rightarrow 52\ ^oC \rightarrow SmA^* \rightarrow 105\ ^oC \rightarrow I$$

The dielectric measurements were performed for the liquid crystal mixture placed between two parallel glass plates with 5x5mm gold electrodes. The sample thickness was d = 5μm. We used standard cells, commercially available from AWAT Warsaw. The cells used give planar orientation. The measurements were carried out with Solartron 1260A Impedance Analyser with Chelsea Dielectric Interface in the frequency range 10^{-1}Hz ÷ $5\cdot10^5$ Hz. The measuring sinusoidal signal (0.1V) was applied nearly perpendicularly to the director of smectic layers.

For fitting the experimental results the Havriliak-Negami equation in the following versionwas used:

$$\varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' = -i\left(\frac{\sigma_0}{\varepsilon_0\omega}\right)^n + \sum_{k=1}^{m}\left\{\frac{\Delta\varepsilon_k}{\left[1+(i\omega\tau_k)^{\alpha_k}\right]^{\beta_k}} + \varepsilon_{\infty k}\right\}$$

where: σ_0 – dc conductivity, $\Delta\varepsilon$ – the dielectric strength, τ – the relaxation time, α – the width parameter, β – the asymmetry parameter, ε_∞ – the permittivity for infinite frequency.
All the presented experimental results were obtained during cooling.

3. RESULTS AND DISCUSION

The temperature dependencies of various dielectric parameters of the investigated mixture suggest that in the temperature range between 25°C and 52°C the ferrielectric $Sm C^*_\gamma$ subphase exists in cooling process. It shows two different temperature dependencies of the dielectrics parameters in the lower temperature region and in the higher temperature region.

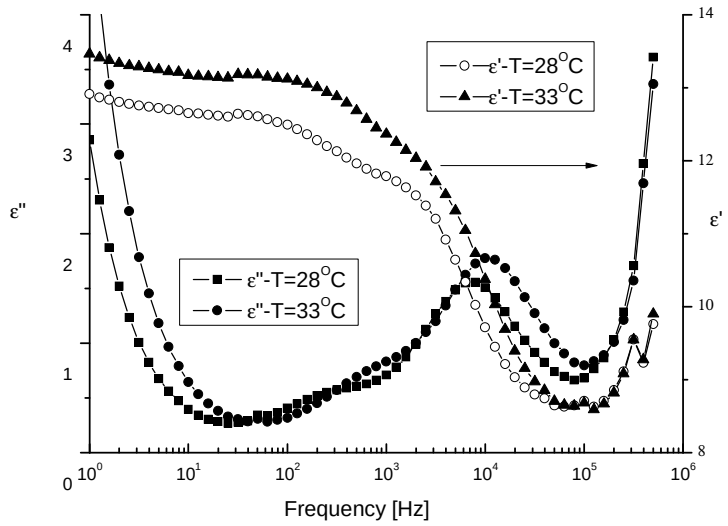


Fig. 1. Dielectric spectrum of the investigated mixture at chosen temperatures for two relaxation modes in the ferrielectric phase

In the lower temperature range between 25°C and 35°C two relaxation processes are observed in the $\mathrm{Sm}C^*_\gamma$ subphase but in the higher temperatures' 35°C-52°C, only one relaxation peak is detected. The dielectric response in these two temperature regions is shown in Fig. 1 and Fig. 2 respectively. Fig. 1 shows two relaxation processes: the first one in the 100 Hz region, and the second one in the kHz region. The relaxation frequency ν_R and the dielectric strength $\Delta\varepsilon$ of the relaxation mode were obtained by fitting the experimental results with Havriliak-Negami equation. An example of the fitting procedure for the low-frequency mode (LRM) and high-frequency mode (HRM) in lower temperature region is presented in Fig. 3 for example. The values ν_R and $\Delta\varepsilon$ obtained from the fitting for both peaks are presented in Fig.4. The relaxation frequency changes from 200Hz up to about 800Hz with the temperature increasing from 25°C up to 32°C for LRM mode. The dielectric strength of this mode also increases with increasing temperature. The dielectric strength changes from $\Delta\varepsilon = 1$ at 25°C up to about $\Delta\varepsilon = 2.2$ at 32°C.

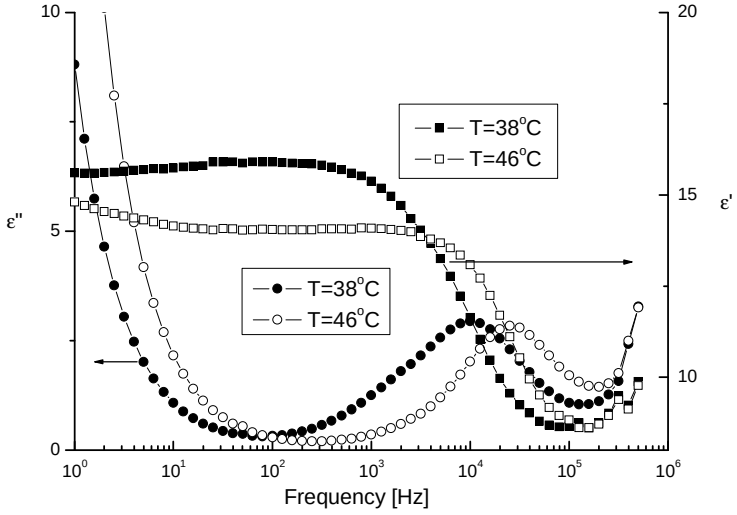


Fig. 2. Dielectric spectrum in higher temperature range of ferrielectric phase

The relaxation frequency of the high-frequency mode (HRM) changes from 6 kHz up to about 10 kHz in the same temperature range. The dielectric strength of this mode is rather constant with changing temperature and equal to about $\Delta\varepsilon = 4$.

In the temperature range between 35°C and 52°C HRM mode was observed only. The values of relaxation frequency and dielectric strength of the this mode is shown in Fig. 5 and Fig. 6 together with all relaxation processes detected in the investigated mixture. The relaxation frequency of HRM mode in this temperature range increasing from about 10 kHz at 35°C to about 50 kHz near phase transition to SmA* phase. Initially the dielectric strength increases from $\Delta\varepsilon = 4$ at 35°C up to maximum $\Delta\varepsilon = 12$ and then slowly decreases up to about $\Delta\varepsilon = 2$ at 52°C.

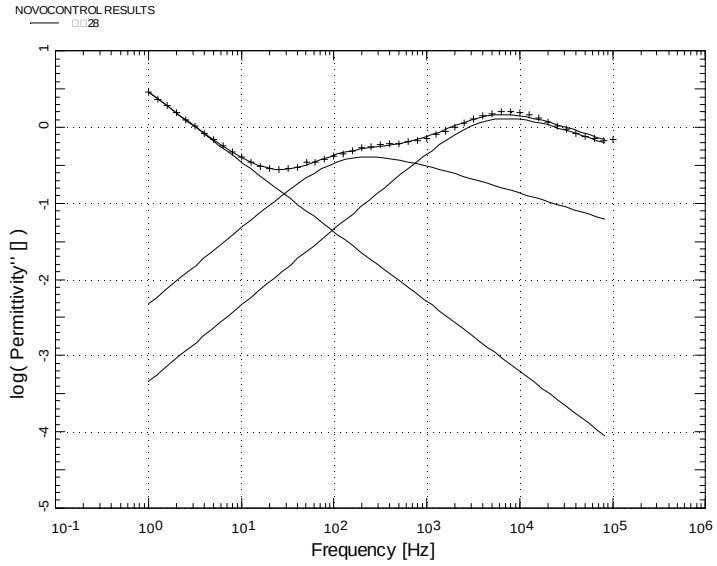


Fig. 3. Fitting procedure to Havriliak-Negami equation for two peaks observed in the ferrielectric phase

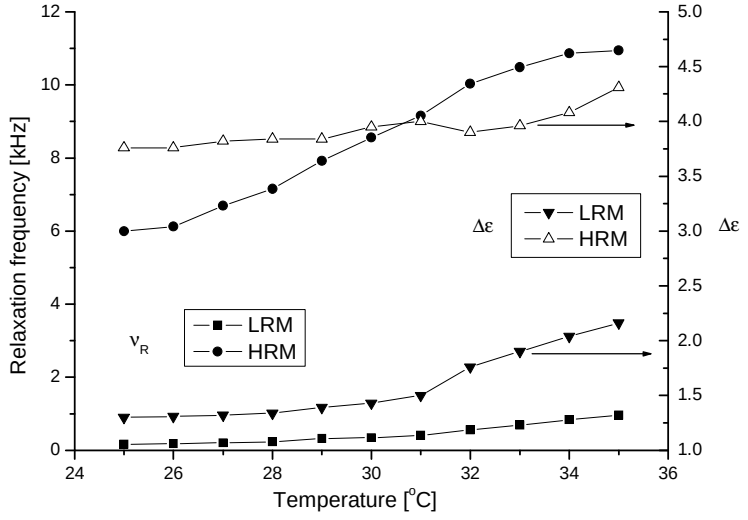


Fig. 4. Temperature dependence of the relaxation frequencies and the dielectric strength of ferrielectric phase

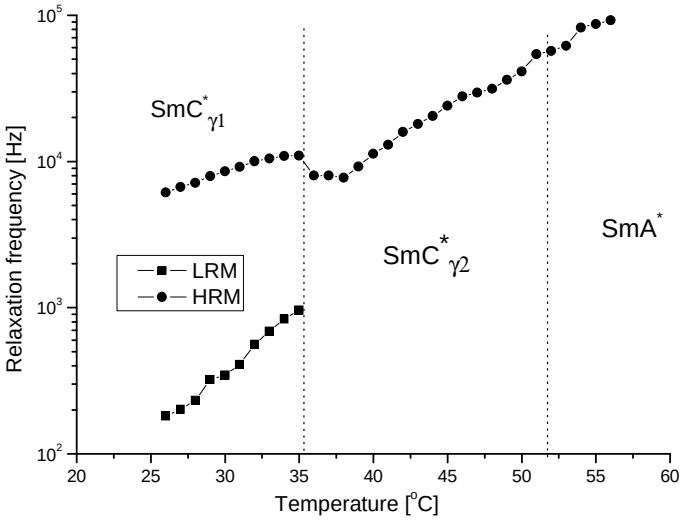


Fig. 5. Temperature dependence of the relaxation frequency in the ferroelectric and SmA*phases

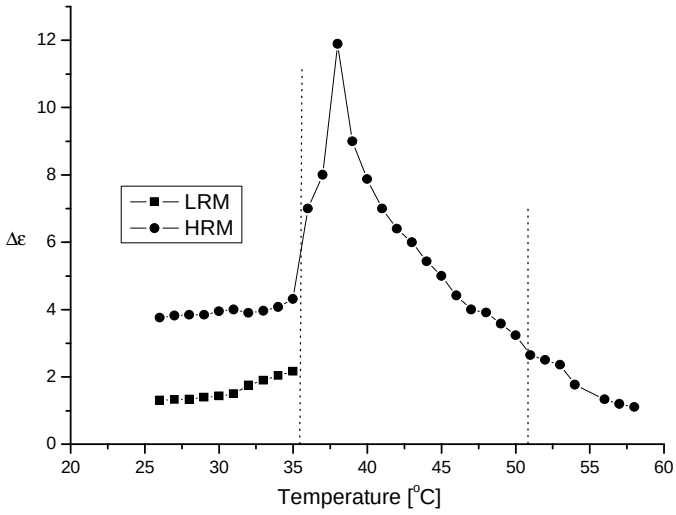


Fig. 6. Temperature dependence of the dielectric strength in the ferroelectric and SmA* phases

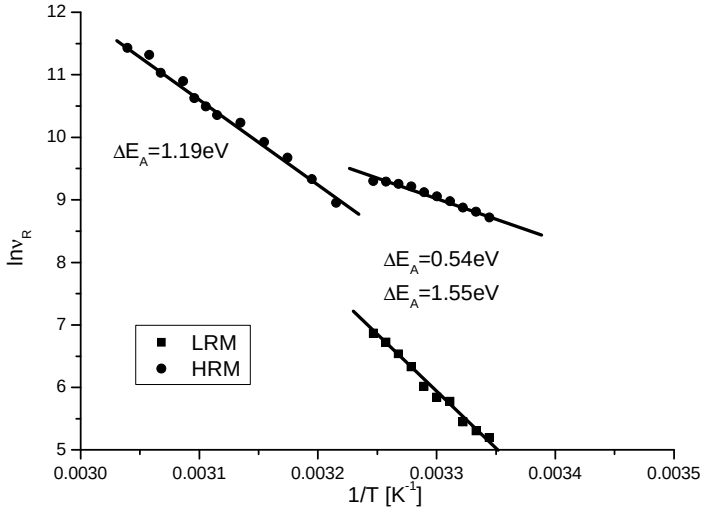


Fig. 7. Arrhenius plots for the relaxation processes in the ferrielectric phase

As shown in the Fig. 7, all relaxation modes observed in the ferrielectic phase exhibits Arrhenius-like temperature dependence. The activation energy of the HRM process in the higher temperature range is equal to $\Delta E_A = 1.19$eV and $\Delta E_A = 0.54$eV in the lower temperature range of ferrielectric phase existing. It suggests some structural difference in these parts of the ferrielectric phase. The activation energy of LRM is rather high and equal to $\Delta E_A = 1.55$eV.

No influence of the biasing voltage on HRM mode has been registered up to 2V/5μm, but a rapid increase of dielectric strength in the range 2V/5μm to 6V/5μm has been detected.

The possible interpretation of HRM mode is that it is a collective relaxation mode related to phase angle fluctuation, i.e. a distortion of the $\mathrm{Sm}\,C^*_\gamma$ helix [1,14-16], so called ferrielectric Goldstone mode.

The LRM mode observed in the investigated mixture in the frequency region 100 Hz is similar to SLM (surface layer mode) observed by Bourny et al. [5] and Sarmento et al. [6]. These authors suggest that the relaxation process is apparently related to the existence of visible disclination lines. Jaradat et al. [17] suggest a relation between the ferroelectric structure and surface interactions. It is not possible to observe the disclination lines in our case unfortunetly due to gold electrodes used. However both, relaxation frequency range and that the mode is registered in ferrielectric phase suggest that we observe the surface layer mode.

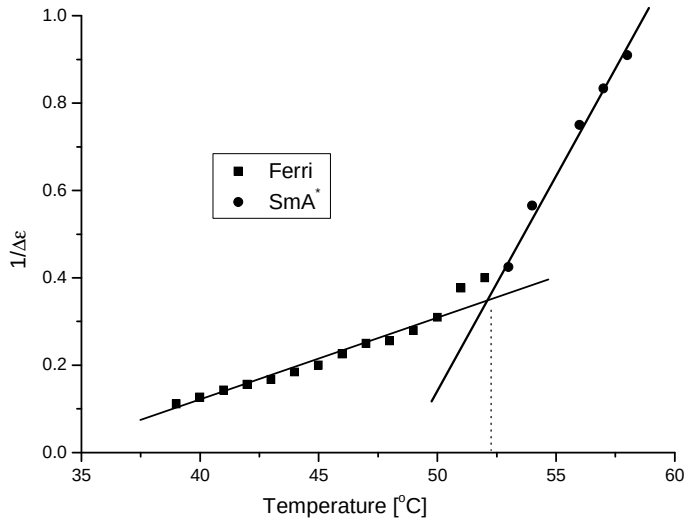


Fig. 8. Temperature dependence of the inverse of the dielectric strength in the SmA* and the ferrielectric phases

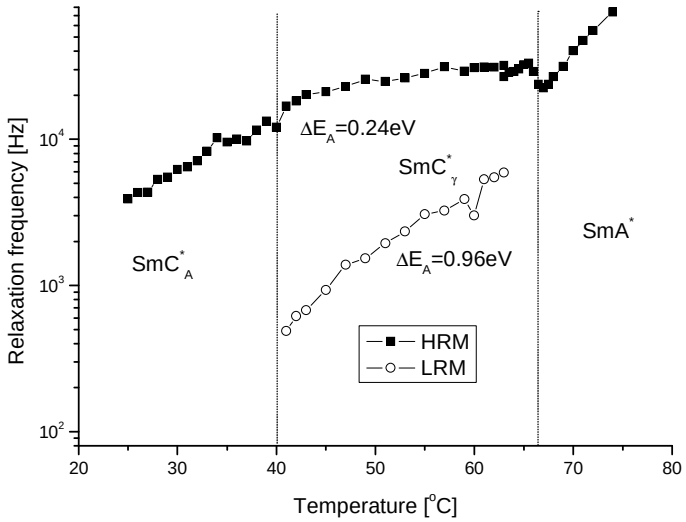


Fig. 9. Temperature dependence of relaxation frequency in the mixture (5:5) investigated earlier [11]

Similar low-frequency and high-frequency modes were detected in the mixture (5:5) in the temperature range from 40°C to 66.5°C, (Fig. 9) [11]. The frequency range of LRM and HRM are similar for the two mixtures, but the dielectric strength of the modes in the (5:5) mixture is lower. Both the (5:5) mixture and (3:7) mixture the activation energy of high-frequency modes are smaller than the activation energy of low-frequency relaxation modes.

In the SmA^* phase the soft mode appears (Fig. 6 and Fig. 7). The relaxation frequency is greater than 50 kHz and increases with increasing temperature. The dielectric strength $\Delta\varepsilon \approx 3$ near the ferrielectric phase and decreases with increasing temperature. The inverse of the dielectric strength vs. temperature shows linear dependence (Fig. 8).

4. CONCLUSIONS

- In the $Sm C^*_\gamma$ phase of investigated mixture well defined relaxation process in the kHz region was detected in the whole temperature range of this phase, but with different dielectric characteristic (with different activation energies) in the two temperature range 25°C÷35°C and 35°C÷52°C. This is probably a collective mode existing in the ferrielectic phase, so called ferrielectric Goldstone mode.

- In the temperature range 25°C÷35°C in the $Sm C^*_\gamma$ phase another process was detected, so called surface layer mode, related to visible disclination lines.

- In the SmA^* phase the soft mode was observed. The temperature dependence of the reciprocal of dielectric strength shows linear dependence.

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PROCESY RELAKSACJI DIELEKTRYCZNYCH W CIEKŁOKRYSTALICZNEJ MIESZANINIE

Streszczenie

W pracy przedstawiono dielektryczne charakterystyki ostatnio zsyntetyzowanej ciekłokrystalicznej mieszaniny, w której faza ferrielektryczna występuje w szerokim przedziale temperatur. Badania dielektryczne przeprowadzono w komórce o złotych elektrodach i uporządkowaniu planarnym. Otrzymano temperaturowe zależności inkrementu dielektrycznego i częstości relaksacji występujących procesów relaksacyjnych w poszczególnych fazach. W fazie ferrielektrycznej w niższych temperaturach zarejestrowano, oprócz ferielektrycznego Goldstone modu występującego w całym przedziale występowania fazy ferroelektrycznej, dodatkowo proces relaksacyjny w obszarze częstości 0.2-0.8 kHz. Proces ten jest analogiczny do zaobserwowanych procesów przez Bourneya związanych z widocznymi liniami dysklinacyjnymi na powierzchni ciekłego kryształu.