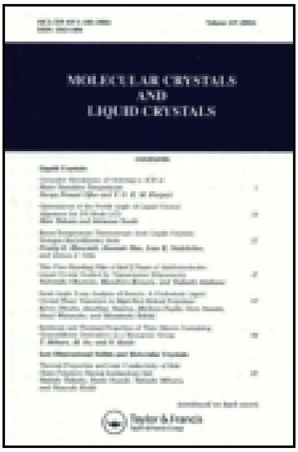

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Dielectric Spectroscopy of a Dichiral Mesogen with a Unique Phase Sequence

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Dielectric Spectroscopy of a Dichiral Mesogen with a Unique Phase Sequence

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Dielectric relaxation behavior of a dichiral mesogenic liquid crystal material, viz. (R,S)-FPPY, having anomalous phase sequence has been studied over a wide range of frequency. Measured dielectric spectra show a new relaxation process, in addition to the usual Goldstone mode, in the SmC phase, which has been assigned to the relaxation process originating from the dichirality of the compound. The overlapping of two molecular modes has been observed in the dielectric spectrum of both isotropic and optically isotropic (IsoX) phases. The present detailed dielectric spectroscopic studies also establish an interesting ferroelectric-like ordering in the unknown SmX* phase.*

Keywords Chirality; dichiral compound; dielectric spectroscopy; liquid crystal; optically isotropic phase

Introduction

Liquid crystals are attractive soft materials both from the viewpoints of fundamental research and their application to electro-optic switching devices. In particular, studies of chirality in liquid crystals are much more striking since because of the introduction of chirality, the twisted structure competes with spatially uniform liquid crystalline orders, resulting in a variety of modulated and frustrated liquid crystal phases such as cholesteric blue phase, twist grain boundary, and smectic blue phases [1,2]. Recently the synthesis of dichiral liquid crystal materials with unusual phase sequences has opened new vistas of research activities in the field of liquid crystals [3–8]. Different types of unusual phase sequences have been predicted and realized experimentally; their thermodynamical and structural properties have also been studied comprehensively. Location of the chiral moieties in the overall molecular structure seems to have a significant effect on the emergence of these chirality-induced frustrated superstructures. An interesting example of the effect of chirality

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Address correspondence to B. K. Chaudhuri, Department of Solid State Physics, Indian Association for the Cultivation of Science, 2A and 2B Raja S C Mullick Road, Kolkata, West Bengal 700032, India. Present Address for B. K. Chaudhuri: Department of Physics, National Sun Yat Sen University, Kaohsiung-804, Taiwan. E-mail: sspbkc@rediffmail.com can be seen in some dichiral mesogens, where the chirality was found to play a leading role in the appearance of the cubic superstructure.

The dichiral material of our present investigation, viz. 2-{4-[(*R*)-2-fluorohexyloxy]phenyl}-5-{4-[(*S*)-2-fluoro-2-methyldecanoyloxy]phenyl}pyrimidine, abbreviated as (*R,S*)-FPPY, exhibits an unusual endothermic transition from an anisotropic smectic phase to an optically isotropic phase (IsoX) [4,6–8]. This dichiral mesogen showing a chirality-induced cubic phase possesses two chiral moieties with different structures at both peripheral ends of the rigid core part. The structure of IsoX phase was found to belong to crystallographic space group I432 based on X-ray diffraction and circular dichroism study [8]. The appearance of the IsoX phase depends, however, on molecular chirality [4]. The reentrant isotropic transition in this system is an interesting phenomenon to support the idea of induced rigidity or conformational ordering: *i.e.*, intermolecular orientational order promoting intramolecular conformational changes.

Due to the critical molecular structure of the dichiral mesogenic compound, the molecular arrangement in different phases and unusual phase behavior in such materials are rather difficult to comprehend. It is well known that dielectric relaxation spectroscopy [9] is an elegant tools to study dipole arrangement as well as the dynamics of both collective and non-collective molecular processes in liquid crystal phases. Hence, dielectric spectrum can be successfully used to identify the phases of such new materials. In order to obtain molecular dynamics in different phases in (*R,S*)-FPPY, in this article, we have carried out detailed frequency and temperature-dependent studies of dielectric relaxation behavior of this typical dichiral compound, elucidating some striking features.

Experimental

The chemical structure of the dichiral sample (*R,S*)-FPPY is shown in Fig. 1. The phase sequence on cooling is described as Iso (114°C) SmC* (112°C) IsoX (92°C) SmX* (68°C) Cryst, as determined by DSC [4], where IsoX represents the new optically isotropic phase. The sandwiched type cells were prepared by indium tin oxide (ITO)-coated glass plates following the process discussed in our previous work [10]. Poly vinyl alcohol (PVA) solution was used as the alignment layer. Homogeneously aligned samples are obtained by rubbing the substrates in one direction. The active area and thickness of the cell are about 12 mm^2 and 6 µm, respectively. Temperature of the measuring sample cell was controlled by using Mettler hot stage (FP82) with an accuracy of 0.1°C. A low-frequency impedance analyzer HP 4192A was used to measure the dielectric relaxation spectra. The dielectric permittivity-voltage (ε'-V) hysteresis loops were measured using bias feature of the analyzer in the frequency range of 5 Hz to 13 MHz.

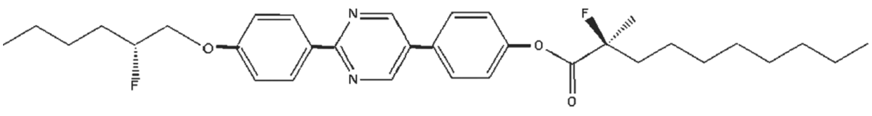

Figure 1. Molecular structure of 2-{4-[(*R*)-2-flurohexyloxy]phenyl}-5-{4-[(*S*)-2-fluoro-2-methyl decanoyloxy]phenyl}pyrimidine ((*R,S*)-FPPY).

Results and Discussion

Figure 2 depicts temperature dependence (during cooling) of the real part of dielectric permittivity (ε') of (*R,S*)-FPPY at various frequencies (viz. 100 Hz, 500 Hz, 1 kHz, 5 kHz, and 10 kHz) for a cell of thickness 6.5 μm. The variation of ε' with temperature as shown in Fig. 2 clearly describes the consequent phase sequence Iso-SmC*-IsoX-SmX* of the material. However, minor deviations as observed in the transition temperatures from those reported earlier [4] might be attributed to the influence of different cell thicknesses [11]. The large ε' in the SmC* phase represents the contribution of the Goldstone mode (GM) [12], indicating the presence of helical structure. The GM contributions dominate at low frequency dielectric response originating from the fluctuation of the azimuthal orientation of the director. When the cooling rate is low, the highly ordered smectic phase is formed perfectly upon cooling from the disordered isotropic phase and then directly transformed into another optically isotropic phase as shown in Fig. 2. This transformation is so fast that it is almost close to thermodynamic equilibrium. The transition temperature from the SmC* to the IsoX phase was found to be not reproducible but depends on the history of thermal treatment. When the sample was kept at a typical higher temperature 113°C in the SmC* phase, it automatically transformed into the IsoX phase and shows the SmC*-IsoX phase transition at this higher temperature (113°C). A direct transition from Iso to IsoX phase was observed on cooling with a slightly higher cooling rate. Such a tendency is in accordance with the fact that the SmC* phase is metastable and eventually transforms to the more stable IsoX phase. It was noted that the temperature range of the SmC* phase is much narrower than that observed from DSC [4]. This discrepancy might be ascribed to the different temperature scan rates used in different measurements. We also note that the width of the SmC* phase largely diminishes as the cell thickness increases (figures not shown). However, the solid-to–liquid crystal phase transition seems to be independent of the thermal history. The phenomenon of thermal hysteresis (inset of Fig. 2) is associated with the presence of metastable state (SmC*) and is a characteristic of the first-order phase transition. There are two theories describing the cause of spontaneous polarization ($\mathbf{P_S}$) in the molecular structure. One is the molecular-statistical theory of ferroelectric ordering in the SmC* phase [13], which claims that spontaneous polarization is caused by specific interactions between the chiral center of the molecule and the polarizable core of the nearest neighboring molecule (chiral and polar interaction). The second one is the indigenous polarization theory [14], which states that the $\mathbf{P_S}$ originates from a statistical biasing of mesogen conformation that derives from steric interaction in tilted smectic layers stacked one over the other. According to these theories, the chiral center and polarizable core are key factors for the emergence of the SmC* phase. The bulky chiral groups in both terminal chains prevent the molecules from packing in a regular herringbone arrangement and the pyrimidine rings pack closely. Due to the strong interaction between pyrimidine moieties, the antiparallel packing of the molecule is stabilized in the SmC* phase giving rise to a high $\mathbf{P_S}$ value in the corresponding phase. The presence of $\mathbf{P_S}$ in the smectic liquid crystal is assumed to be due to a time-dependent coupling of the lateral components of the dipoles of the individual molecules with the chiral environment. Consequently, only the time-averaged projection of the dipole moments along the polar C_2 axis are effective in producing macroscopic $\mathbf{P_S}$. Urbane and Zeks [15] proposed a mean field microscopic model to account for the origin of

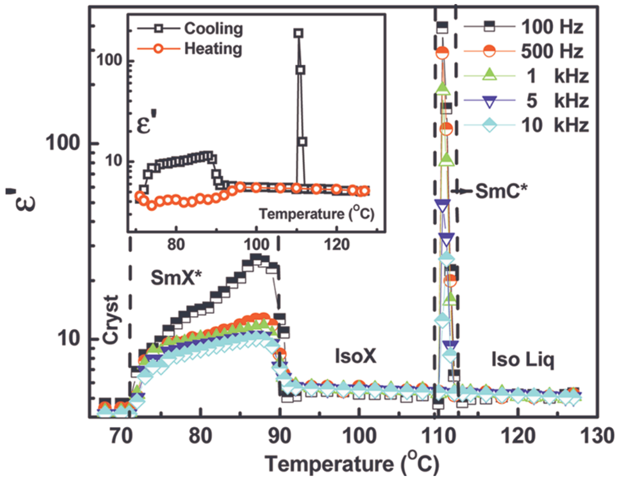

Figure 2. Temperature dependent behavior of the real part of dielectric permittivity (ε') of (*R,S*)-FPPY at different fixed frequencies for a cell of thickness 6.5 µm. Inset shows temperature dependent ε' for heating and cooling runs at 1 kHz.

P_S in the SmC* phase which is compatible with the extended Landau model. They have assumed that the transverse molecular ordering does not originate from the interactions between their transverse dipole moments but is a local property of a molecule that feels the average tilt of neighboring molecules and therefore does not rotate freely around its long axis. In this model it was also assumed that the ordering of the transverse electric dipoles (μ_t) is induced by the tilt via a chiral

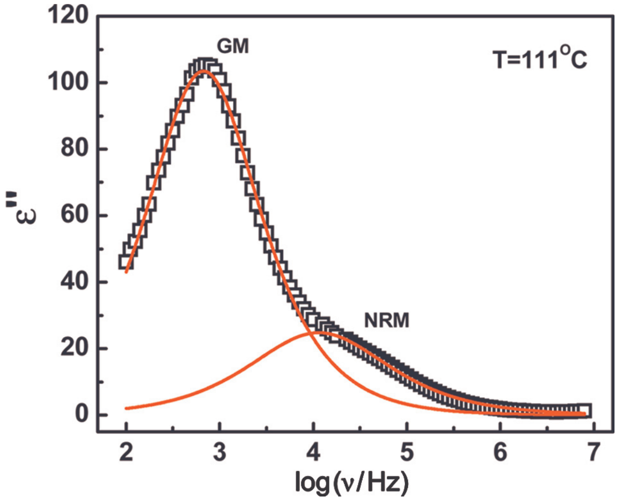

Figure 3. Dielectric spectra of the imaginary parts of the complex permittivity (ε'') of (*R,S*)-FPPY at 111°C (SmC* phase) showing two relaxation process denoted by Goldstone mode (GM) and new relaxation mode (NRM). The solid lines are fits to the Cole-Cole equation (Eq. (3)).

(a_1) and a non-chiral (a_2) interaction represented by the potential viz.

$$V(\psi) = -a_1\theta \cos\psi - a_2\theta^2 \cos 2\psi \tag{1}$$

Assuming that the order parameter of the molecular long axis is 1, the angle ψ describes the orientation of μ_t in the plane perpendicular to the molecular long axis, being $\psi = 0$ when μ_t points parallel to the direction of $\mathbf{P_S}$. The chiral term tends to align the transverse dipoles in the direction where $\psi = 0$, producing a polar order. The non-chiral term has two minima, viz. $\psi = 0$ and $\psi = \pi$, producing a quadrupolar order. The quadrupolar ordering is much larger than the dipolar ordering in the SmC* phase. For the present investigation, due to the large overlapping of the core moieties as well as the chiral groups, the coefficient a_1 increases, forming the metastable SmC* phase. The rich and new phase sequence observed in the compound undoubtedly originates from the nature of the chiral chains. The presence of an intermediate isotropic phase in the phase sequence of the material underlines the frustration of the system. The competing interaction at the boundary of the helically ordered chiral SmC* phase and disordered IsoX phase is responsible for the observed frustration of the investigated sample.

In order to study the rotational motions of the molecules, dielectric relaxation spectra were obtained at various temperatures. The complex dielectric permittivity $\varepsilon^*(\omega, T)$ can be expressed by the standard relation, viz.

$$\varepsilon^*(\omega, T) = \varepsilon'(\omega, T) - i\varepsilon''(\omega, T) \tag{2}$$

where $\varepsilon'(\omega, T)$ and $\varepsilon''(\omega, T)$ are, respectively, the real and imaginary parts of the dielectric constant: ω is the angular frequency, and T is the temperature of the system. We have measured $\varepsilon^*(\omega, T)$ of the bulk material in the frequency range 10 Hz to 13 MHz confined within homogeneously aligned ITO-coated glass plates. The material shows two clear molecular relaxation processes in the anisotropic SmC* phase for the probing field applied parallel to the director, as shown in Fig. 3. Analysis of the spectra was performed by fitting the imaginary part using Havriliak and Negami function [16] as described below.

$$\varepsilon^*(\omega, T) = \varepsilon_\infty = \sum \frac{\Delta\varepsilon_k}{[1 + (i\omega\tau_k)^{\beta_k}]^{\alpha_k}} \tag{3}$$

where ε_∞ is the high frequency limit of dielectric permittivity, $\Delta\varepsilon_k$ is the dieletric strength, τ_k ($=1/2\pi\nu$) is the relaxation time, and ν is the characteristic frequency of the kth absorption process. The exponents α_k and β_k are, respectively, the symmetric and asymmetric broadening parameters. $\alpha_k = 1$ and $\beta_k = 1$ correspond Debye function; for $\alpha_k = 1$ and $0 < \beta_k \leq 1$ we have the Cole-Cole function [17] and for $\beta_k = 1$ and $0 < \alpha_k \leq 1$ we have the Cole-Davidson function [18]. The relaxation process in our sample is found to be Cole-Cole type. The high-frequency mode denoted as new relaxation mode (NRM) in Fig. 3 could be related to some internal degrees of freedom associated with the dichirality of the material. By fitting the imaginary parts of Eq. (3) to the experimental points, the dielectric parameters for the above mentioned two modes in the SmC* phase have been calculated as shown in Table 1. In general, for soft mode, a rapid change of relaxation frequency is observed near the transition. But in our case, near the transition the relaxation frequency of this high-frequency mode is found to be temperature invariant. Hence, the NRM might not be related to the soft mode. In this case, we could not detect the

Table 1. Dielectric strength ($\Delta\varepsilon$), relaxation frequency (ν_c), and distribution parameter (α) in SmC* phase of ((*R,S*)-FPPY) for goldstone mode (GM) and the newly observed relaxation mode (NRM)

Temperature (°C)	$\Delta\varepsilon_{GM}$	ν_{CGM} (Hz)	α_{GM}	$\Delta\varepsilon_{NRM}$	ν_{CNRM} (Hz)	α_{NRM}
111	256.459	675.676	0.133	75.0160	1.1×10^4	0.256
111.5	48.641	787.402	0.112	17.248	1.1×10^4	0.272

soft mode. Due to the metastability of the SmC* phase, we could not, however, detect the actual behavior of dielectric strength and relaxation frequency of the modes in the SmC* phase.

The frequency-dependent dielectric permittivity for the present sample at isotropic (Iso) and optically isotropic (IsoX) phases are shown in Fig. 4. In both the phases thermally activated relaxations have been found in the kHz region. In Iso and IsoX phases, the dielectric spectra show the overlapping of two high-frequency modes. Because the frequency component also depends on temperature, the higher frequency relaxation cannot be attributed to ITO or any artifact. To deconvolute the effect of high-frequency relaxation, the field dependence of dielectric spectrum has been studied. It is observed that applying a bias field of 1.5 volt/μm the two relaxation processes separated out. The corresponding feature is shown in Fig. 5. The Cole-Cole fittings of the observed two modes show high-frequency relaxation. The temperature dependence of the relaxation has been performed in the IsoX phase with 1.5 volt/μm applied bias. The log $\nu_c \cdot 1000/T$ plots of the two modes are found to be linear and thus should follow the Arrhenius equation as shown at the inset of Fig. 5. We might not get the proper activation energy of the two modes because the deconvolution of two modes has been done in the presence of bias fields. But the nature of the graphs confirms the molecular origin of the two relaxations. Also, because the same overlapping of modes has also been found in Iso phase, the modes

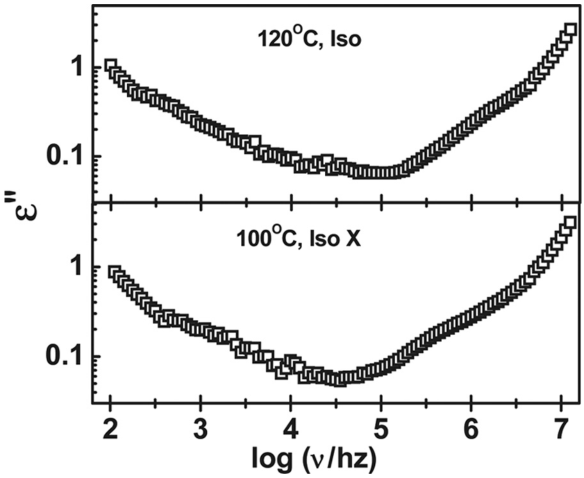

Figure 4. Dielectric spectra of the imaginary parts of the complex permittivity (ε'') of (*R,S*)-FPPY at 100°C (IsoX phase) and 120°C (isotropic phase) showing overlapping of two modes in high-frequency regime.

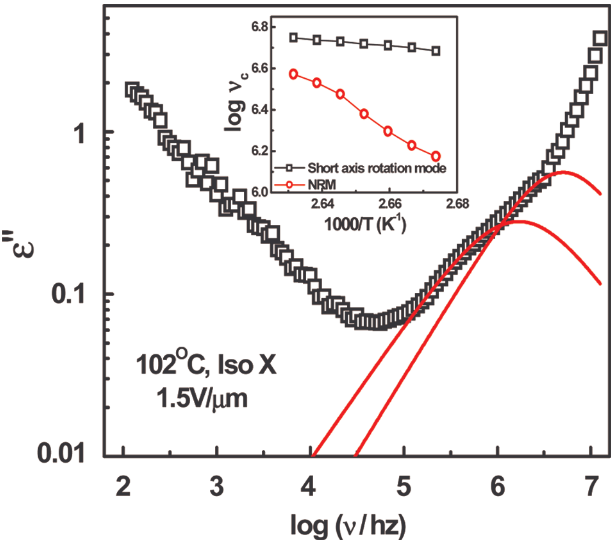

Figure 5. Dielectric spectra of the imaginary parts of the complex permittivity (ε'') of (*R,S*)-FPPY at 102°C (IsoX phase) in presence of 1.5 V/µm bias field (the two modes being separated under a bias field). The solid lines are fits to the Cole-Cole equation (Eq. (3)). Inset shows the $\log \nu_c \cdot 1000/\mathrm{T}$ plot in presence of a 1.5 V/µm bias field.

must be of molecular origin and thus non-collective type. The field-dependent study in isotropic phase is not performed because the dielectric breakdown voltage is very small in the isotropic phase and thus the application of bias in the isotropic phase might damage our cell. A relatively high-frequency mode must be attributed due to the short axis rotation of the liquid-crystalline molecules. The consistently observed relatively low-frequency mode might be attributed to the dichirality of the molecules and thus corresponds to the NRM earlier found in the SmC* phase.

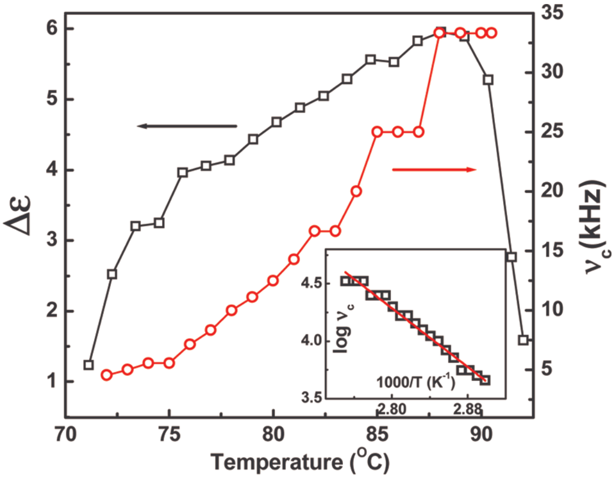

Figure 6. Temperature dependence of dielectric strength ($\Delta\varepsilon$) and relaxation frequency (ν_c) in the SmX* phase of (*R,S*)-FPPY. Inset shows the fitting according to an Arrhenius formula.

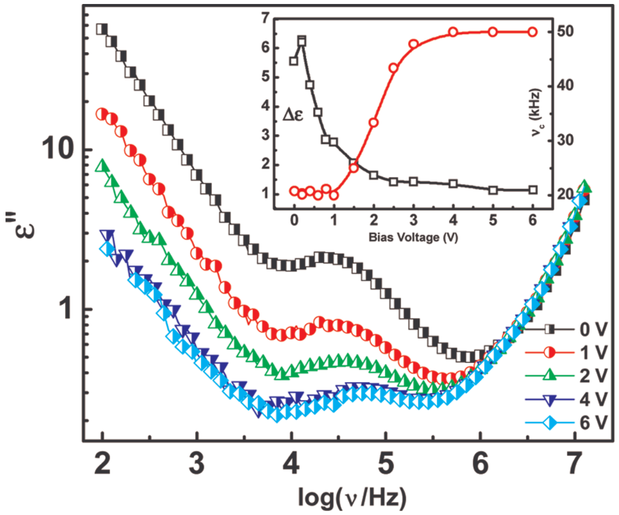

Figure 7. Dielectric spectra of the imaginary parts of the complex permittivity (ε'') of (*R,S*)-FPPY at 85°C (SmX* phase) for different applied voltage. Inset shows the voltage dependence of dielectric parameters obtained by fitting the experimental points to the Cole-Cole equation (Eq. (3)).

The relaxation frequency of NRM is found to be lower for SmC* phase compared to that of the IsoX phase, which might be due to hindered rotation of the molecules in the helically ordered phase.

The present dielectric spectroscopic investigation also reveals a high-frequency relaxation mode as well as a low-frequency contribution in the SmX* phase. As shown in Fig. 6, we have obtained the relaxation frequency and dielectric strength of the high-frequency process in the entire temperature range of the unknown SmX*

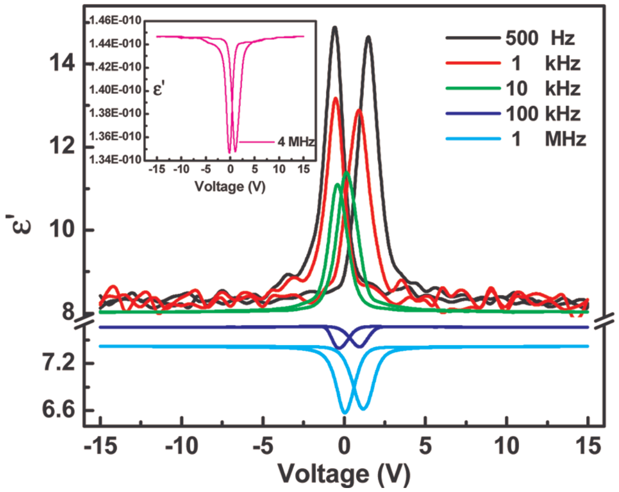

Figure 8. Dielectric permittivity-voltage (ε'-V) hysteresis at different probing frequency at 85°C (SmX* phase) of (*R,S*)-FPPY. Inset shows the high-frequency ε'-V plot showing the absence of re-entrant hysteresis, confirming the absence of a molecular mode.

phase. This relaxation mode is found to be non-collective type showing Arrhenius behavior with an activation energy 22.27 $kJK^{-1}mol^{-1}$ (inset of Fig. 6). This mode might be considered as the NRM, which is also observed in Iso, IsoX, and SmC* phases. As expected from our earlier experimental results in IsoX and Iso phases, it is obvious to get this NRM as non-collective type; *i.e.*, of molecular origin. In order to obtain proper mode characteristics, the field-dependent dielectric relaxation measurements have also been performed in the entire SmX* temperature range as depicted in Fig. 7. It has been found that with the increase of field strength, the obtained high-frequency mode is suppressed and the relaxation frequency saturates with the application of a critical field shown in the inset of Fig. 7. This high-frequency mode is considered to be associated with the high-frequency NRM found in the other phases of the material and might be attributed to the internal degrees of freedom related to the dichirality of the material. The low-frequency relaxation process in the SmX* phase might be due the contribution of a Goldstone like mode with a very high dielectric strength and very low relaxation frequency, which is beyond the range of our measurement window of HP4192A.

As shown in Fig. 8, a ferroelectric-like switching behavior is evident from the dielectric permittivity-voltage (ε'-V) hysteresis behavior in the SmX* phase of the present dichiral compound. The interesting inversion of the ε'-V hysteresis curves observed above 60 kHz is attributed to the high-frequency sign change of dielectric biaxiality [19]. The high-frequency ε'-V plot is shown in the inset of Fig. 8. However, unlike the MIC-0406 system [20], the re-entrant inversion of ε'-V hysteresis is not observed in the present case due to the absence or hindrance of molecular mode due to the short axis rotation in the SmX* phase.

Conclusion

To conclude, we have performed a detailed dielectric study (10 Hz to 13 MHz) of a dichiral compound with exclusive phase sequence. The metastability of the SmC* phase can be interpreted on the basis of the interaction arising between the cores and hence chiral parts of the adjacent dichiral molecules. Other than the well-known Goldstone mode, a new relaxation mode has been detected in the SmC* phase. This new mode is assigned to be due to some internal degrees of freedom associated with the dichirality of the material. The overlapping of two molecular modes related to the overall rotation around the molecular short axis and NRM has also been characterized in the isotrotic and optically isotropic IsoX phases. Also, the molecular origin of NRM has been characterized in SmX* phase. Interestingly, from our present dielectric spectroscopic study, the presence of a ferroelectric-like switching behavior in the SmX* phase has also been established.

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