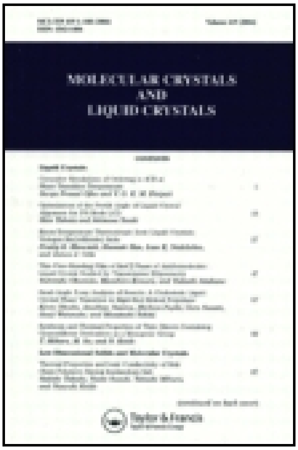

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Dielectric Response in the Smectic A and Smectic C* Phases of a Ferroelectric Liquid Crystal, 12CN5(R*)

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DIELECTRIC RESPONSE IN THE SMECTIC A AND SMECTIC C* PHASES OF A FERROELECTRIC LIQUID CRYSTAL, 12CN5(R*)

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This paper reports the results of the dielectric relaxation studies performed in the Smectic A (SmA) and Smectic C (SmC*) phases of the ferroelectric liquid crystal, 12CN5(R*) in the frequency range 5 Hz to 13 MHz. Planar orientation used throughout the study was achieved by rubbed polyamide coating on the surfaces of the dielectric cell. Transition temperatures determined from the derivative of the dielectric permittivity agrees with that obtained using thermal polarizing microscopy. The dielectric spectrum in the SmA phase shows single relaxation, whereas the SmC* phase has two relaxations, viz., the low frequency Goldstone mode and the high frequency soft mode. Special attention was paid to the study of the low frequency Goldstone mode relaxation. From the Cole-Cole plots, the temperature dependence of dielectric strength ($\Delta\varepsilon$), the relaxation frequency (f_R) and the distribution parameter (α) relevant to the Goldstone mode have been estimated. The relaxation frequency follows the Arrhenius relation in the asymptotic regions far from the transition. Results of the bias-dependent dielectric measurements of the Goldstone mode relaxation have also been presented.*

Keywords: arrhenius plots; cole–cole plots; dielectric relaxation frequency; ferroelectric liquid crystals; goldstone and soft mode

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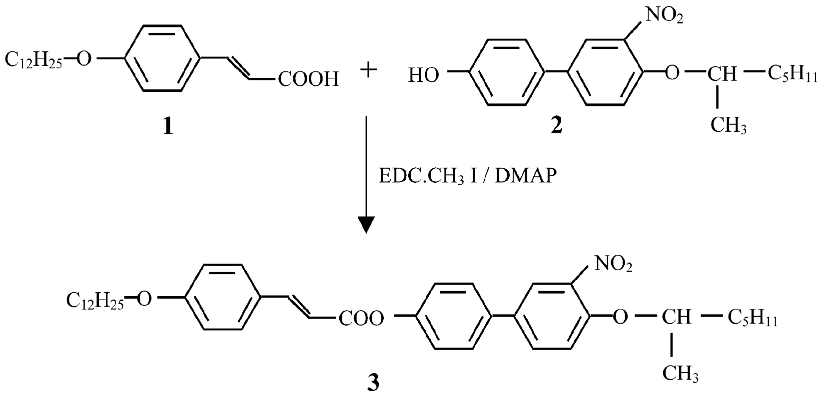
INTRODUCTION

Recent years have seen an upsurge in interest of ferroelectric and chiral smectic C* phases in liquid crystals (LCs). Confined SmC* liquid crystal layers have particularly advantageous properties which can be used to achieve fast light modulators, with various applications in optical signal processing and optical communication systems [1–3]. The surface stabilized geometry allows the suppression of the intrinsic helix of ferroelectric liquid crystals (FLCs) and produces two stable states with opposite spontaneous polarization [4]. These states can readily be switched with a time constant of a few microseconds by applying relatively small constant external electric field.

The electro-optic effects in LC devices arise from the coupling between dielectric anisotropy and/or the polarization (spontaneous or induced) with applied electric field [5]. In general, the switching of LC molecule in these devices takes place in the LC volume whereas their position at the solid-LC interface remains to a larger extent unchanged. Dielectric relaxation spectroscopy is one of the basic and extensively used methods for studying the dynamics of FLCs. In this communication, the results of the dielectric studies in a FLC with SmA and SmC* phases are presented and in particular the dielectric relaxation corresponding to the Goldstone mode is discussed.

EXPERIMENTAL

The LC was prepared by the esterification of the cinamic acid derivative **1** and phenolic derivative **2** in the presence of 1-(3-(dimethylamino)propyl)-3-ethyl-carbidiimide methiodine (EDC.CH_3I) and (dimethylamino)pyridine DMAP [6] as shown below:



We use the abbreviated name 12CN5(R*) for the LC which is the end-product **3** as indicated above.

An Olympus (BH-2) polarizing microscope in conjunction with a Linkam (TMS 94) heating stage was used for the microscopic textural observations. The cooling and heating rates followed during microscopy are 0.5°C per hour. The polarized thermal microscopic textural observations (focal conic batonnet texture in SmA and threaded marble schlieren in SmC*) suggested [7] the following phase sequence:

$$\text{Crystal} \xrightarrow{-17.0^\circ\text{C}} \text{SmC}^* \overset{96.5^\circ}{\longleftrightarrow} \text{SmA} \overset{119.3^\circ}{\longleftrightarrow} \text{Isotropic}$$

The compound is found to exhibit reproducible phase transition temperatures over repeated runs of heating and cooling cycles.

Commercially available (Devicetech Inc., USA) cells made from two parallel glass plates with separation 10 μm is used for the study. Each plate of the cell consists of thin ITO conductive coating (1-cm^2 effective area) over which a rubbed polyamide film was deposited to induce homogeneous director alignment. Cells with maximum thickness variation lower than 0.5 μm over whole conducting area was used. The LC was introduced into the cell by capillary action in its high temperature isotropic state. The cell was simultaneously observed through the polarizing microscope to ensure the homogeneity of the alignment and to check for any discontinuity. The cell was placed in a specially built oven and the temperature was stabilized to an accuracy of ± 0.1°C with a Linkam (TMS 94) temperature controller. The experimental studies were carried out by heating the sample to an initial temperature corresponding to its isotropic state, followed by its subsequent cooling at a very slow rate (about 0.5°C per hour) to the temperatures corresponding to the liquid crystalline state.

Dielectric investigations were performed in the frequency range 5 Hz to 13 MHz using a Hewlett Packard (HP LF 4192A) Impedance Analyzer along with an HP 16047C Test Fixture. The cell was calibrated with the use of standard organic liquids. The stray capacitance of the cell was found to be less than 0.1% of the cell capacitance filled with LC (at room temperature). The capacitance of the empty cell was found to vary by less than 0.5% within the temperature range of 20–125°C. The capacitance and the dielectric loss of the empty cell are found to be invariant with the frequency (in the range of 5 Hz to 13 MHz).

RESULTS AND DISCUSSION

The temperature variation of permittivity and dielectric loss are studied using 1V oscillating level of 100 kHz frequency. The permittivity is found to increase with decreasing temperature whereas the variation of the dielectric loss is accompanied by a decrease as the temperature is decreased from the isotropic state. The observed rise in permittivity is due to the increasing structural order with enhanced dipole correlation with the decreasing temperature. However, the temperature variation of permittivity is not associated with any sudden increase either at the isotropic-SmA (IA) or SmA-SmC* (AC*) transition temperatures T_{IA} or T_{AC^*}, respectively, as observed in other such samples [8]. We have therefore estimated the temperature derivative of permittivity (relative), and the result is presented in Figure 1. The values of T_{IA} and T_{AC^*} obtained by the present dielectric method agree with microscopic observations.

The frequency variation of permittivity and dielectric loss are studied at different temperatures in the SmA and SmC* phases. It is observed that the loss spectrum exhibits one peak in the SmA phase at around 6 MHz at all temperatures studied (Fig. 2). It may be noted that the dielectric peak shifts to the lower frequency side with decreasing temperature in the SmA phase. The observed temperature shift of the relaxation frequency (f_R) is illustrated in Figure 2. The temperature shift of the dielectric loss peak corresponding to the relaxation frequency is observed to be small when compared to the large frequency span (5 Hz to 13 MHz) of the spectrum. This higher frequency relaxation is related [9] to the dipolar reorientation. It is observed that the present SmA relaxation frequencies fall in the range of reported values in other LC compounds [10,11] although it is on the higher side.

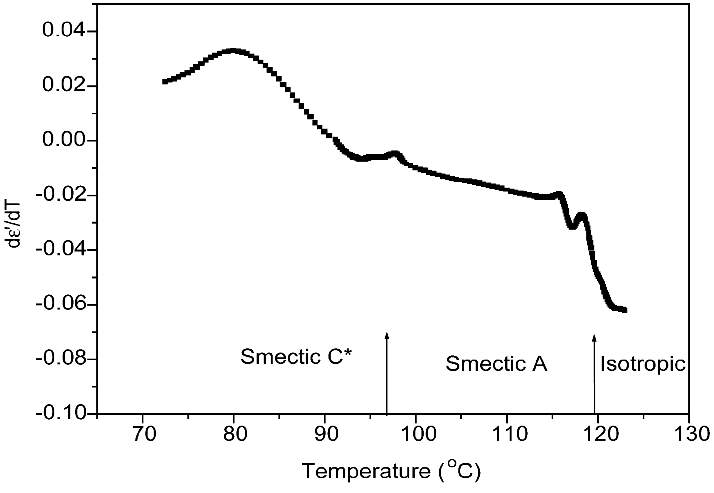


FIGURE 1 Temperature variation of the differential permittivity, dε′/dT studied at a frequency of 100 kHz.

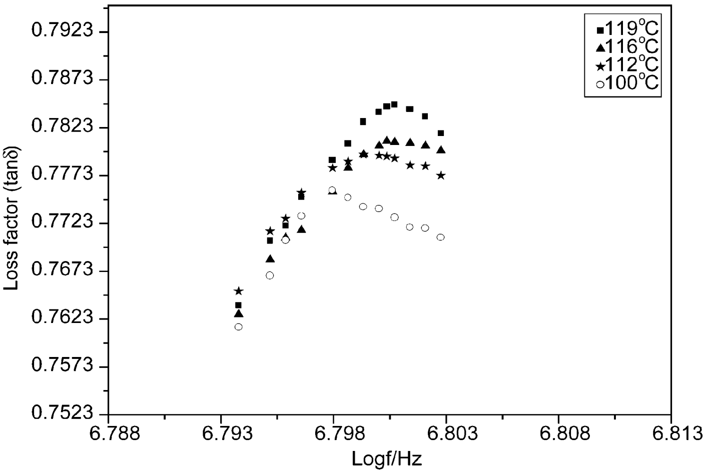


FIGURE 2 Frequency variation of the dielectric loss (in arbitrary units) at different specified temperatures in the SmA phase.

The SmA loss dispersion is found to follow an off-centered Debye mechanism given by the Cole–Cole theory [12]:

$$\varepsilon^*(\omega) = \varepsilon_\infty - \left[\frac{\Delta\varepsilon}{1 + j(\omega\tau)^{1-\alpha}}\right] \tag{1}$$

where $\varepsilon^*(\omega) = \varepsilon'(\omega) - \varepsilon''(\omega)$, the complex dielectric permittivity, $\Delta\varepsilon = (\varepsilon_0 - \varepsilon_\infty)$, the dielectric strength calculated from data of static (ε_0) and high frequency (ε_∞) permittivities, $\omega = 2\pi f$, $\tau = 1/f_R$ and α is the distribution parameter.

The SmA complex dielectric spectrum can be studied [13–15] through the Maier-Saupe and Martin's extended Deby's models. The relaxation frequency has been obtained as a function of frequency using Cole-Cole plots. Figure 3 illustrates the logarithm of the relaxation frequency versus the inverse of the absolute temperature in the SmA phase corresponding to the soft mode. The activation energy 0.11 eV thus estimated for the SmA phase is found to be in quantitative agreement with the reported values [11,16] for FLCs.

The dielectric loss spectrum studied in the SmC* phase is found to exhibit two relaxations, one at around 300 Hz and another at a much higher frequency ~5 MHz. The low frequency relaxation is related to the reorientation of the dipole transverse molecular axis (at the chiral center) [9] to the field (Goldstone mode). The observed dielectric spectrum corresponding to the Goldstone mode is given in Figure 4. As seen from the figure, the helix-related Goldstone mode relaxation in SmC* shifts towards the lower

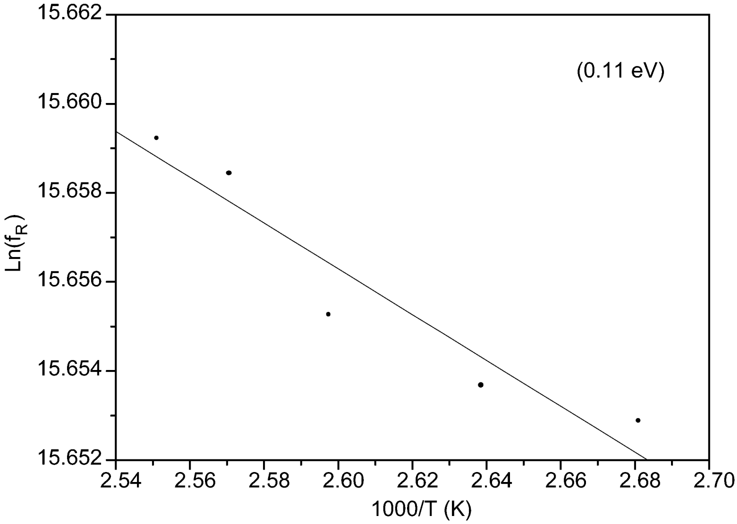


FIGURE 3 Temperature variation of the relaxation frequency (Arrhenius plot) for SmA phase corresponding to soft mode.

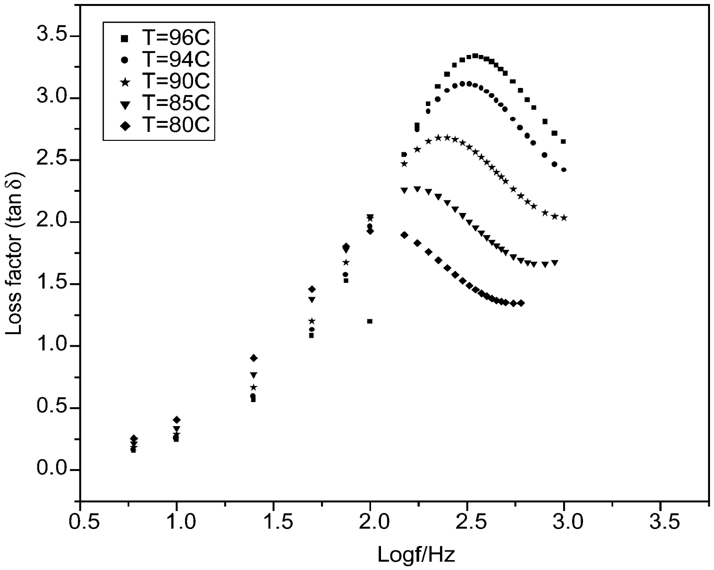


FIGURE 4 Variation of dielectric loss (Arbitrary units) at different specified temperatures corresponding to the low frequency Goldstone mode relaxation.

frequency side with decreasing temperature. However, the high frequency soft mode relaxation peak at ~5 MHz shifts to the high frequency side with decreasing temperature (Fig. 5). The relaxations observed for the higher frequency (~5 MHz relevant to the tilt angle fluctuations) are found to correspond to the soft mode. This corresponds to the polarization of the long molecular axis to the field. It is found that the tilt-related relaxation frequencies agree with the reported [8,10,11] range of relaxation frequencies in other FLC compounds exhibiting a tilted C phase.

The observed loss peak at around 300 Hz is related to Goldstone mode relaxation relevant to the SmC* helix formed due to the correlation of transverse dipole situated at the chiral center. The Cole-Cole plots for the Goldstone mode relaxation are drawn at different temperatures. It may be observed that the dielectric strength ($\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$) decreases with decreasing temperature (Table 1). The α-parameters determined from Cole-Cole plots of SmC* phases in Goldstone mode relaxations demonstrate the relative confinement of liquid crystal transverse dipole in the helix matrix with decreasing temperature.

A relative study of the temperature variation of the relaxation frequencies across AC* transition (i.e., a high frequency relaxation in the SmA named as soft mode; a low frequency and a high frequency corresponding to the Goldstone and soft modes in SmC* phases, respectively) are carried out by plotting them in Figure 6. As expected [17], the relaxation frequency

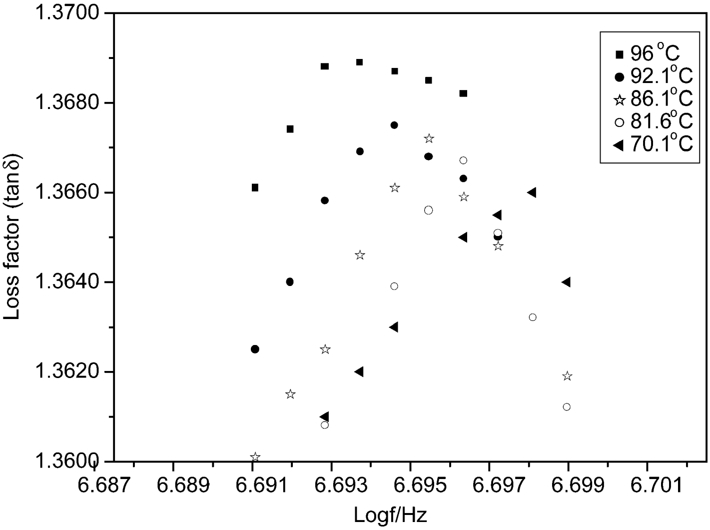


FIGURE 5 Variation of dielectric loss at different specified temperatures corresponding to high frequency soft mode relaxation.

TABLE 1 Temperature Variation of the Relaxation Frequency (f_R), Relaxation Time (τ), Dielectric Strength ($\Delta\varepsilon$) and Distribution Parameter (α) in the SmC* Phase Relevant to the Goldstone Mode

Temperature T(°C)	Relaxation frequency f_R (Hz)	Relaxation time τ (ms)	Dielectric strength $\Delta\varepsilon$	Distribution parameter α
96	350	2.86	136	0.031
94	300	3.33	132	0.035
90	250	4.00	128	0.042
85	175	5.71	112	0.050
80	100	10.0	116	0.071

of the soft mode in the SmA and SmC* phases and the relaxation frequency of the Goldstone mode in the SmC* phase show degeneracy at T_{AC^*}.

It is also simultaneously observed that the spontaneous polarization mediated helix fluctuations are found to be influenced by the applied voltage across the plates of FLC cell. Increasing applied bias voltage from 0 to 35 V across the cell plates is found to result in decrease of dielectric loss amplitude corresponding to Goldstone mode. Goldstone mode relaxation

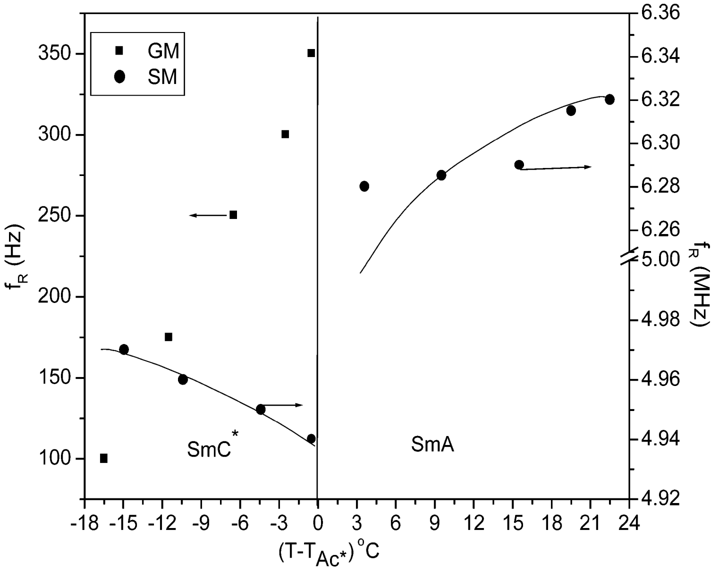


FIGURE 6 Temperature variation of the relaxation frequency (soft mode and Goldstone mode) across AC* transition.

frequency is found to decrease with increasing bias. However, soft mode relaxation dielectric loss remains invariant. The decreasing loss of amplitude in the Goldstone mode with increasing bias is found to occur due to the suppression of the polarization helix (unwinding). The polarization helix stabilization conditions defined by the coupling of transverse dipole moment over the SmC* layers is found to depend on the applied voltage. The variation of the loss peak corresponding to Goldstone mode relaxation observed in SmC* phase (at 95.5°C) is given in Figure 7 for different applied voltages. This shift of f_R Goldstone mode dispersion is found to agree with the reported results in other FLC compounds [18].

As seen from Figure 6, the dielectric loss peak value decreases effectively with temperature, while bias plays marginal influence to reduce the loss. The observed variation of the Goldstone mode relaxation frequency (Fig. 8) with applied bias is found to follow similar trend to that of Arrhenius (temperature) shift of Goldstone mode relaxation in SmC*. Hence the shift of Goldstone mode relaxation with bias is presented in Arrhenius-like reduced plots (*i.e.*, log f_R *vs.* 1000k/eV, where k is the Boltzmann constant, e is the charge of electron and V is the applied voltage) in Figure 9. The Goldstone mode relaxation activation energies which may be

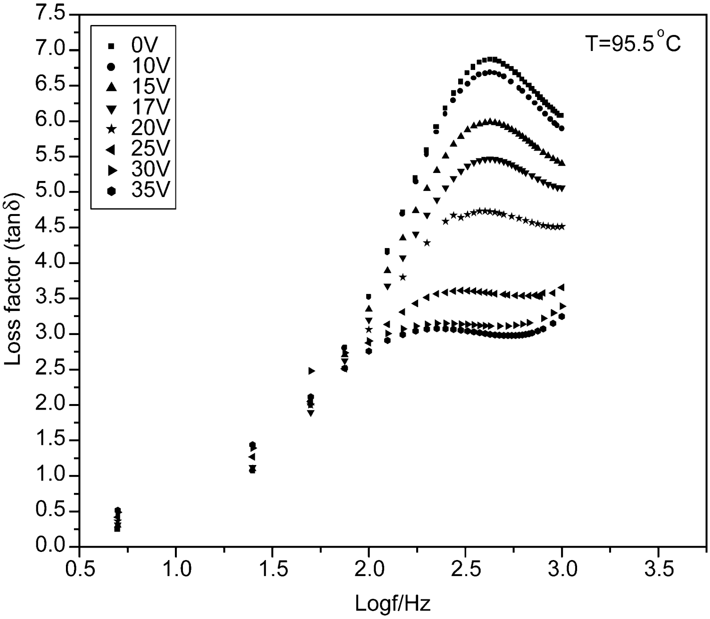


FIGURE 7 Bias voltage variation of frequency Goldstone mode loss spectrum (arbitrary units) in the SmC* phase at 95.5°C.

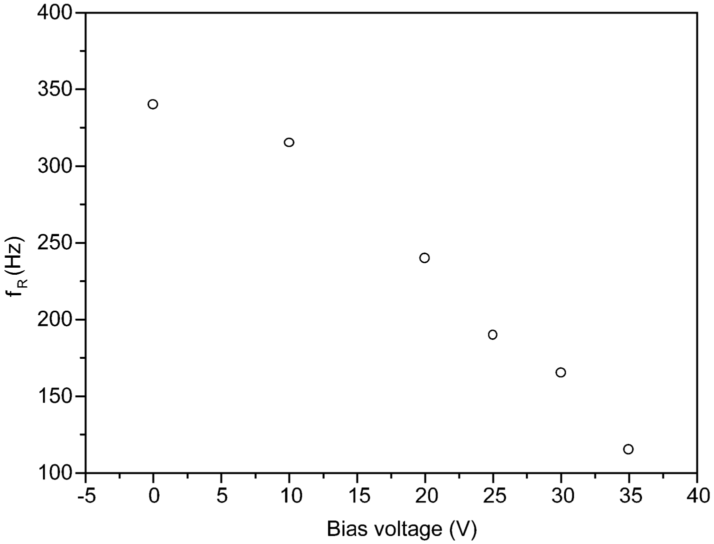


FIGURE 8 Variation of the relaxation frequency of Goldstone mode with applied bias voltage at the temperature of 95.5°C

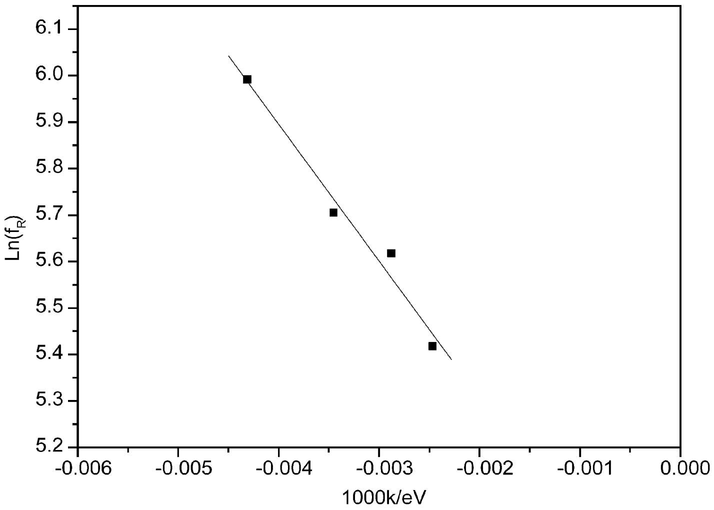


FIGURE 9 Reduced bias Arrhenius like plots for the Goldstone mode relaxation in SmC* phase.

estimated from reduced bias plots will reflect the response of transverse dipole contribution from the chiral center to the external electric stimulus.

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