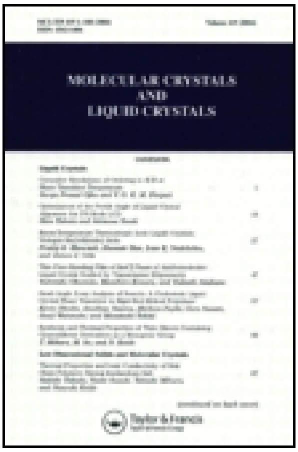

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Changes in the Dielectric Parameters of an Antiferroelectric Material (Racemic Mixture) Due to Electron Beam Irradiation

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Changes in the dielectric properties of an electron beam irradiated antiferroelectric material (racemic mixture) filled dielectric cell have been determined by the dielectric spectroscopy. The material has phase sequence of I-SmC-SmC$_A$-Cr. Goldstone mode could not be detected in the SmC phase due to the destruction of the helix. All the transition temperatures (except SmC$_A$-Cr) and transverse component of the permittivity of the irradiated sample increase due to irradiation. Relaxation frequencies of the modes in the SmC$_A$ phase decrease due to irradiation.

Keywords Antiferroelectric material; dielectric permittivity; dielectric spectroscopy; electron beam irradiation; relaxation frequency

1. Introduction

Antiferroelectric Liquid Crystals (AFLCs) have become important materials because of their attractive properties for display applications [1–6]. These materials are important due to their tri-state switching behavior, easy dc compensation, microsecond response, hemispherical viewing angle (in-plane switching geometry), grey scale capability and the absence of ghost effects [1–6].

Study of the different types of irradiations on various materials has been an important issue because of the drastic changes in the physical properties of the irradiated materials [7–13]. Nuclear reactors and space radiations are the main sources

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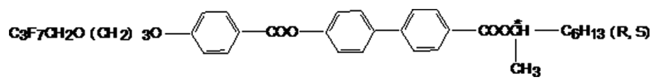

Figure 1. Molecular structure of the AFLC material (racemic mixture of R, S components).

of the radiations. The devices made up of various liquid crystalline materials are often used in radiation prone areas. When these devices are used in such an environment occasionally for a long time, various types and doses of radiations may affect the physical properties of these devices and cause malfunctioning. Preliminary studies on some of the liquid crystalline materials suggest that generally phase transition temperatures of the various liquid crystalline phases are reduced [7–13], transition enthalpies and entropies are also decreased [9,10] due to which stability of the phases is affected. AC and DC conductivities are increased due to which dielectric response of the material is degraded. In some of our earlier work, we have found that for some basic nematic materials (5CB, 8CB and 6CHBT) various display parameters can be optimized with appropriate dose of electron irradiation [11–13]. Hence it becomes important to study the effect of various types and doses of irradiations on liquid crystalline materials including ferroelectric and antiferroelectric liquid crystals. In the present work we have irradiated the AFLC (Racemic Mixture) material (shown in Fig. 1) by electron beam and studied the changes in various properties. Mixture possesses SmC and SmC_A phases.

We are using SmC and SmC_A in the place of $SmC^*$and SmC_A^* phases because in the racemic mixture, chirality vanishes.

2. Experimental Methods

The irradiation experiments were carried out at the 7 MeV linear electron accelerator (LINAC) set up at the Bhabha Atomic Research Centre (BARC), Mumbai, India [14]. Electron pulses of 2 μs duration were used. In order to irradiate the sample, firstly the pure material is filled in a gold coated planar aligned cell of thickness 8.9 μm and then the dielectric data is acquired. After taking the dielectric data, the cell is placed in the path of the electron beam of 7 MeV energy in the crystal phase of the material. The transition temperatures of the pure sample were determined by differential scanning calorimeter (DSC), polarized light microscopy (PLM) and dielectric spectroscopy while that of the irradiated sample was determined by the dielectric spectroscopy. Dielectric spectroscopy is established tool to obtain precise transition temperatures [15].

Dielectric data were acquired by using a Newtons 4th Limited (N4L's) Phase Sensitive Multimeter (model PSM-1735) coupled with Impedance Analysis Interface (model IAI-1257) in the frequency range of 1 Hz to 35 MHz. The temperature of the sample was controlled with the help of a hot stage (Instec model HS-1) having an accuracy of ±0.1°C and temperature resolution of 3 mK. To analyze the measured data, the dielectric spectra have been fitted with the generalized Cole-Cole equation [16–18]. Further details about the experimental techniques used for the dielectric measurements are described in some other publications [11–13, 17,18].

3. Results and Discussion

The different phase transition temperatures and the phase sequence of the pure material are obtained by DSC and typical thermograms are shown in Figure 2.

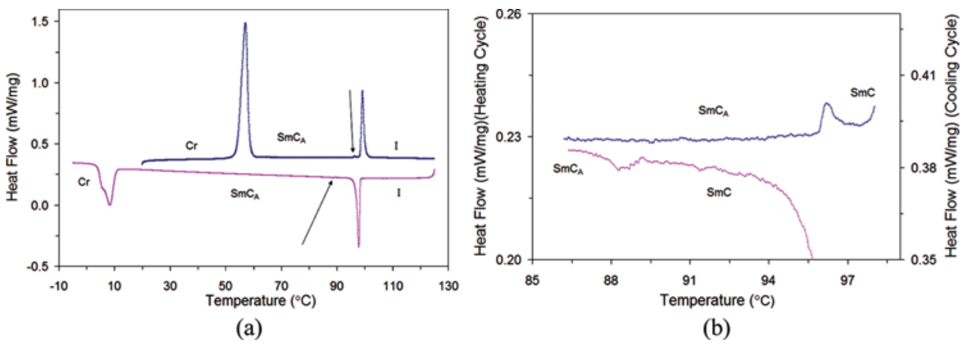

Figure 2. DSC thermograms at the scan rate of 5°C/min (upper is heating and lower is cooling) for the pure material showing (a) Cr-SmC$_A$, SmC$_A$-Cr, SmC$_A$-I, I-SmC$_A$ transitions and (b) SmC-SmC$_A$, SmC$_A$- SmC transitions in enlarged view. (Figure appears in color online.)

The phase sequences obtained from DSC and PLM studies in the heating and cooling cycles of the pure material are as follows:

$$\text{Cr.} - (57.0^\circ\text{C}) \rightarrow \text{SmC}_A - (96.2^\circ\text{C}) \rightarrow \text{SmC} - (99.2^\circ\text{C}) \rightarrow \text{I}$$
$$\text{I} - (98.0^\circ\text{C}) \rightarrow \text{SmC} - (88.3^\circ\text{C}) \rightarrow \text{SmC}_A - (8.0^\circ\text{C}) \rightarrow \text{Cr.}$$

The phase sequences obtained from the dielectric studies of the pure and irradiated materials are given as:

$$\text{Pure Material: I} - (98.0^\circ\text{C}) \rightarrow \text{SmC} - (86.7^\circ\text{C}) \rightarrow \text{SmC}_A - (39.0^\circ\text{C}) \rightarrow \text{Cr.}$$
$$\text{Irradiated Material: I} - (111.8^\circ\text{C}) \rightarrow \text{SmC} - (101.3^\circ\text{C}) \rightarrow \text{SmC}_A - (31.0^\circ\text{C}) \rightarrow \text{Cr.}$$

The transition temperatures obtained from the dielectric studies of the pure material are slightly different with those obtained from DSC and PLM studies. Such differences have also been reported earlier and are not surprising because appearance of the different phases and transition temperatures sensitively depends on sample history, surface condition and also on the thickness of the sample [19]. Mode of temperature change during the different experiments may also be responsible for the observed difference in transition temperatures. From the analysis of the PLM and dielectric studies of the pure and irradiated material, we find that the range of the SmC$_A$ phase is increased by 20.6°C with marginal decrease in the SmC range.

Figure 3 shows the variation of the transverse component of the relative dielectric permittivity ($\varepsilon'_\perp$) (henceforth we will call it only 'dielectric permittivity' for the purpose of brevity) of the pure and irradiated materials with temperature at various frequencies. Values of $\varepsilon'_\perp$ in the SmC phase is comparatively small as observed in other materials possessing SmC* phase [19]. From Figure 3, we find that $\varepsilon'_\perp$ of the irradiated sample is higher than that of the pure sample in all the phases.

From the dielectric investigations of the different mesophases of the pure and irradiated materials, we find one relaxation mechanism in SmC phase (named M1) and two relaxation modes in SmC$_A$ phase in the low (named M2) and high frequency region (named M3) in both the cases. The different characteristic parameters of the modes M1, M2 and M3 of the pure and irradiated materials are listed in Table 1.

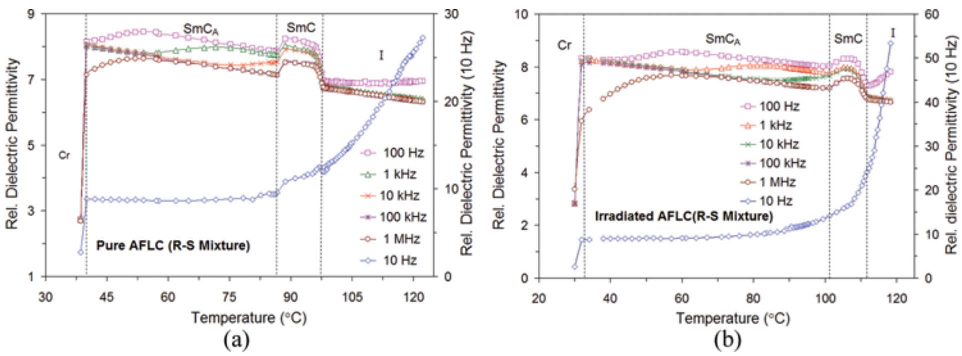

Figure 3. Variation of the transverse component of the dielectric permittivity with temperature (°C) at various frequencies: (a) pure material and (b) irradiated material.

Frequency dependence of the transverse component of the dielectric permittivity ($\varepsilon'_{\perp}$) and dielectric loss ($\varepsilon''_{\perp}$) in the SmC phase are shown in Figures 4a and 4b respectively for pure and irradiated materials. Figures 5a and 5b show frequency dependence of $\varepsilon''_{\perp}$ in the SmC$_A$ (for modes M2 and M3) for pure and irradiated materials respectively. Figure 6 shows the variation of the relaxation frequencies of the different modes (M1, M2 and M3) observed in the SmC and SmC$_A$ phases of the pure and irradiated material with temperature.

From Figure 4 and Table 1, we find that the dielectric strength of the mode M1 of the irradiated material increases as compared to that of the pure material. Distribution parameter of the irradiated material varies with temperature unlike in the case of pure material. Relaxation frequencies of the mode M1 of the irradiated sample also increases as compared to that of the pure material. We conclude that observed low values of the $\varepsilon'_{\perp}$ in the SmC phase of the pure and irradiated materials are due to the complete destruction of the helix, so that the compound is behaving as an achiral material. This is because of the fact that the R and S enantiomers are

Table 1. Dielectric strength ($\Delta\varepsilon'_{\perp}$), relaxation frequencies (f_R) and distribution parameter (h) of the modes M1, M2 and M3 in the SmC and SmC$_A$ phases of the pure and irradiated material. The temperatures are shown in brackets. The various parameters are obtained from the fitting of dielectric data on generalized Cole-Cole equation [16–18] with the help of origin software

	Max $\Delta\varepsilon'_{\perp}$	f_R (Hz) (at higher temperature end)	f_R (Hz) (at lower temperature end)	h
Pure material				
Mode M1	0.5	10.0 kHz (98.0°C)	16.5 kHz (88.7°C)	0.1
Mode M2	0.9	13.0 kHz (86.7°C)	39.0 Hz (40.0°C)	0.11–0.13
Mode M3	3.2	5.0 MHz (57.0°C)	1.8 MHz (40.0°C)	0.1
Irradiated material				
Mode M1	0.6	33.0 kHz (110.8°C)	18.5 kHz (103.3°C)	0.22–0.022
Mode M2	1.0	15.0 kHz (101.3°C)	27.0 Hz (40.0°C)	0.04–0.10
Mode M3	3.6	11.0 MHz (57.0°C)	1.5 MHz (40.0°C)	0.1

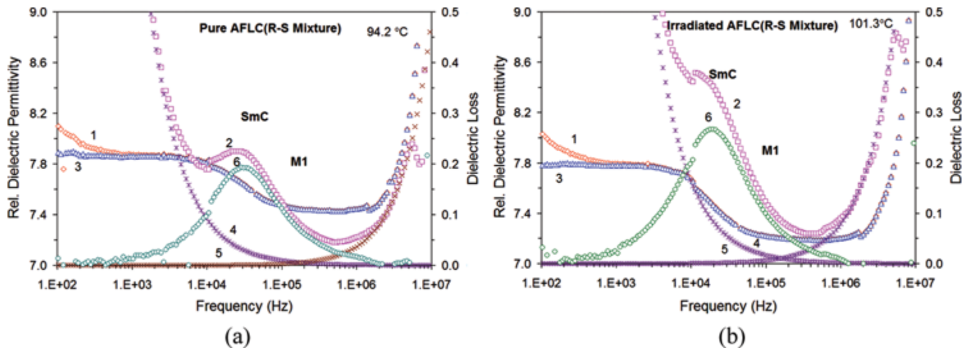

Figure 4. Frequency dependence of the transverse component of the dielectric permittivity and loss in the SmC phase. Curves 1 and 2 show the measured values of the dielectric permittivity and loss respectively. Curve 3 shows the corrected value of the dielectric permittivity after removing low and high frequency parasitic effects. Curves 4 and 5 show the low and high frequency parasitic terms of the dielectric loss respectively. Curve 6 shows the corrected value of the dielectric loss. Curves 1 and 3 are on the left vertical axis while 2 and 4-6 are on the right vertical axis.

mixed in the ratio 1:1 for making a recemic mixture. On the basis of the temperature dependence of the relaxation frequencies (f_R is increasing) and dielectric strength of mode M1, we can not identify it as the Goldstone mode. Rather, we correlate this mode as a domain mode [20]. It is important to recall that because of the achiral nature of the sample, possibility of the Goldstone mode is ruled out.

From Figure 5 and Table 1, it is evident that $\Delta\varepsilon'_{\perp}$ of mode M2 of the irradiated material is higher as compared to that of the pure material. M2 shifts to low frequency side for the irradiated material i.e., f_R of M2 decreases for the irradiated material as compared to that of the pure material. This low frequency mode M2 in the SmC_A phase is a phase fluctuation around the cone. In the antiferroelectric state this motion takes place having the anti-tilt pairs moving in phase around the tilt cones, i.e., with the phase variable φ changing in the same sense [21,22]. For the mode M3, $\Delta\varepsilon'_{\perp}$ increases for the irradiated material as compared to that of the

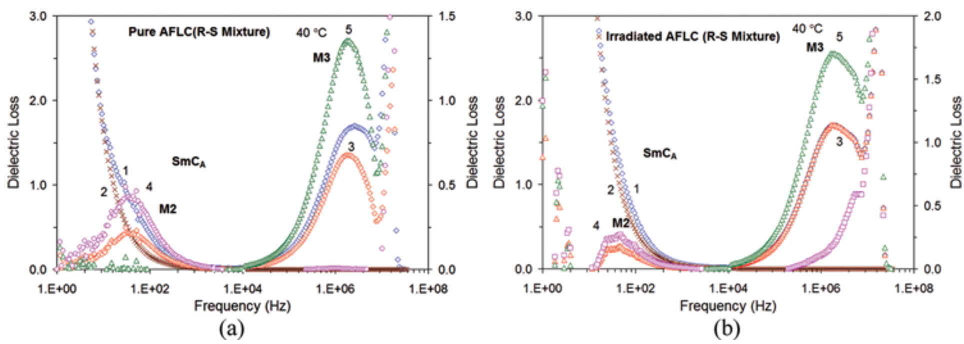

Figure 5. Frequency dependence of the dielectric loss ($\varepsilon''_{\perp}$) in the SmC_A phase at 40°C. Curve 1 shows the measured dielectric loss. Curves 2 represent the low frequency parasitic term. Curve 3 shows the corrected value of the dielectric loss. Curves 4 and 5 show the corrected loss separately for two modes and shown on right vertical axes.

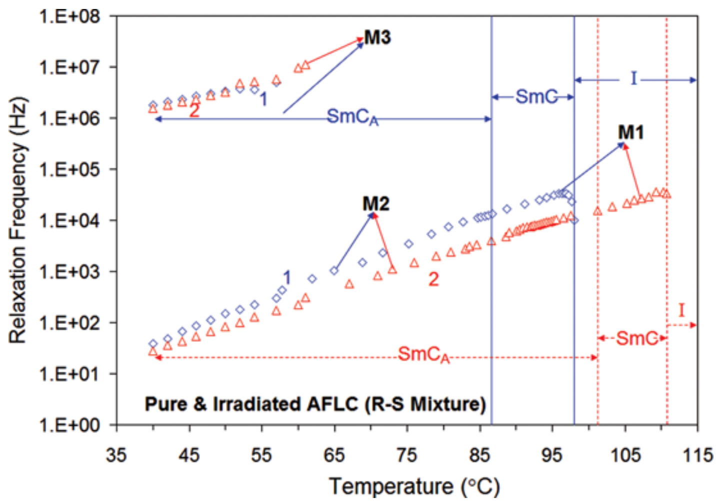

Figure 6. Temperature dependence of the relaxation frequencies of various modes for the pure and irradiated samples. Curves 1 (rhombus) and 2 (triangle) are respectively used for the pure and irradiated materials. The solid and broken vertical lines respectively show the range of the SmC phase for the pure and irradiated samples.

pure material whereas f_R is almost unchanged. This high frequency absorption can be related to the antiferroelectric order and only exists as long as this order persists. In this case molecules rotate against each other in their anti-tilt position, i.e., with φ changing in opposite sense around the cones [21,22].

4. Conclusions and Perspectives

The values of dielectric permittivity and strength of the observed mode in the SmC phase are small due to the destruction of the helix which confirms achiral nature of the material. Due to achiral nature of the material, Goldstone mode of the SmC phase could not be observed. From the behavior of relaxation frequency and dielectric strength, we correlate the observed mode of the SmC phase as the domain mode.

It has been observed that due to the electron beam irradiation all the transition temperatures (except that of SmC$_A$-Cr.) are surprisingly increased. Dielectric strengths of all the observed collective relaxation modes (M1 in SmC and M2 and M3 in SmC$_A$ phase) also increase whereas the relaxation frequencies decrease due to the irradiation.

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