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Enhancement in the thermal stability of the mesophases of 4-*n*-(decyloxy) benzoic acid due to Li ion beam irradiation

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ABSTRACT

Liquid crystalline compound 4-*n*-(decyloxy) benzoic acid has been irradiated by Li ion beam in its crystalline phase at room temperature by a pelletron beam using 3 nA current. Thermodynamic, dielectric and UV–Visible spectroscopic characterization of the pure and irradiated materials has been carried out. Thermodynamical studies of the pure and irradiated materials show that all the transition temperatures, enthalpies and hence entropies are increased due to the irradiation suggesting enhancement in the thermal stability of the mesophases. Dielectric results obtained on the irradiated vis-à-vis pure material suggest how the value of the transverse component of the dielectric permittivity of the irradiated material increases in the SmC phase whereas it decreases in the N phase as compared to that of the pure material. UV–Visible spectrum of the irradiated material shows an additional peak along with the peak of the pure material suggesting formation of new species in the irradiated materials.

1. Introduction

Study of the effect of different types of radiations is important not only for the basic study point of view but for the applications also. Energetic ion beam radiations, produced in accelerators have been widely used for the modification of materials [1,2]. Sometimes the properties of interest are improved and in other cases the materials are deteriorated [1–4]. Fink et al. [1,2] used ion beams for the deposition of localized high energy densities in solid materials. Effect of ion implantation has been studied on conducting polymers by bombarding them with low energy light weight ions such as hydrogen, boron, fluorine and argon [3,4]. Schiestel et al. observed an increase in resistivity by several orders when polypyrole (PPY) was bombarded with low energy noble gas ions [4].

Liquid crystalline materials have been widely used in every walk of life from calculators, computer monitors, vehicle and space shuttles' dash boards to wide screen television sets. In addition to the display applications, the liquid crystalline materials are also used in electro tunable lasers, optical fibers and lenses, liquid crystal colloids, organic charge transport devices, artificial muscles, drug delivery systems and many others. The devices made up of liquid crystalline materials are sometimes used in high radiation prone environments such as nuclear installation centers and space applications. When these devices are used in such environments for a long time, different types and doses of irradiation highly affect these devices and often cause their malfunctioning. Some of the earlier studies on the effect of different types and doses of irradiation suggest that generally the transition temperatures, enthalpies and entropies are lowered; ac and dc conductivities of the materials are increased [5–11]. On the other hand different types of radiations can be used to modify the various properties of different polymers (made up of long chain molecules same as LC molecules) [12–14]. In some of our earlier publications, it has been reported that electron beam irradiation can be used for the optimization of the various display parameters (viz. threshold voltage (V_{th}), switching voltage ($\Delta V = V_{90} - V_{10}$), steepness of transmission voltage curve (TVC, $\Delta I/\Delta V$, $\Delta I = I_{90} - I_{10}$), transverse component of the dielectric permittivity ($\varepsilon'_{\perp}$) etc.) of the twisted nematic (TN) display material viz. 5CB, 8CB and 6CHBT [15–18]. Therefore, it becomes important to study how and up to what extent different types and doses of radiations affect these materials. For this reason, we have irradiated 4-*n*-decyloxybenzoic acid (DOBA) by Li ion beam of different fluences (ions/cm^2) and studied the radiation induced transformations in the physical properties. In the present paper, we are reporting the effect of Li ion beam irradiation (of fluences 10^{11}, 10^{12} and 10^{13} ions/cm^2) on the thermodynamical and electrical properties of DOBA. DOBA is the 10th member of the alkyloxy benzoic acid series. Its molecular formula and weight are $C_{17}H_{26}O_3$ and 278.208 respectively. The material used for the present study is of 99% purity. The molecular structure of DOBA is given in Fig. 1.

2. Experimental techniques

The irradiation experiments were performed by Li ion beam from a 15UD pelletron beam setup at Inter University Accelerator Centre

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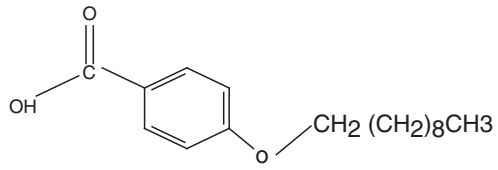

Fig. 1. Molecular structure of 4-(*n*-decyloxy) benzoic acid (DOBA).

(IUAC), New Delhi by using 3 nA current. For irradiation, the materials have been mounted on a target ladder of cuboidal shape having four faces. On each faces, a maximum of 7 materials of area 1 cm^2 could be mounted. Therefore, in one shift pelletron beam irradiation of a maximum of 28 materials was carried out. After mounting the materials on the ladder, the ladder is kept inside a chamber in which a very high vacuum (of the order of 5×10^{-6}) is created. The time of the beam bombardment for a desired fluence can be calculated by the following formula

$$\text{Time} = \frac{(\text{Fluence} \times \text{Area of beam scan})}{6.25 \times 10^9 \times \text{Current(pnA)}}$$

where pnA = nA/Charge State and it stands for particle nano ampere.

Pure and irradiated materials are characterized by differential scanning calorimeter (DSC) and UV–Visible spectroscopy. The thermodynamical study of the pure and irradiated materials has been carried out on a DSC of NETZSCH model DSC-200-F3-Maia. DSC is allowed to run initially for the first five cycles at the scan rate of 5 °C/min in the range 20–160 °C in order to stabilize the transition temperatures and enthalpy of the transitions. Transition temperatures have been determined with the accuracy of 0.1 °C whereas transition enthalpies (ΔH) have been determined with the accuracy better than 2% for fully-grown peaks. However, for very weak peaks, uncertainties are large due to the uncertainty in the localization of start and end point of the peaks. Different phases of the pure and irradiated materials have been identified from the texture study with the help of a CENSICO made polarized light microscope (PLM). Optical absorption spectra were recorded at room temperature for both pure and irradiated materials using a UV–Visible spectrophotometer (Ocean Optics) of model DH-2000 coupled with a detector of model HR-4000-CG-UV–NIR in the wavelength range 300–1100 nm. For acquiring the spectra, pure and the irradiated materials were dissolved in chloroform ($CHCl_3$) and then placed in a quartz spectrocell of path length 1 mm. For confirming the peak in UV–Vis spectra different scans were acquired repeatedly.

For the dielectric measurements electrical cells in the form of parallel plate capacitor were prepared using ITO and gold coated glass plates having sheet resistance less than 25 Ω/□, as electrodes, using 10 μm and 40 μm thick spacers. For planar and homeotropic alignment of the samples a thin layer of polyimide nylon and lecithin was deposited on the glass plates respectively. The active capacitance (C_L) was determined by using organic liquid of known dielectric permittivity, in this case cyclohexane, into the cell. Capacitance (C) and conductance (G) of the cell filled with material were determined in the frequency range 1 Hz to 35 MHz using N4L's phase sensitive multimeter model PSM-1735 coupled with impedance analysis interface model IAI-1257. A measuring electric field of 0.5 V_{rms} has been applied across the material. Acquired data of C and G were used to determine the frequency dependent dielectric permittivity ($\varepsilon'_\perp$) and dielectric loss ($\varepsilon''_\perp$) as follows:

$$\varepsilon'_\perp = \left(\frac{(C(m)-C(a))}{C_L}\right) + 1 \quad (1)$$

$$C_L = \left(\frac{(C(l)-C(a))}{(\varepsilon'(l)-1)}\right) \quad (2)$$

$$\varepsilon''_\perp = \left(\frac{\sigma}{\varepsilon_0\omega}\right) = \left(\frac{G(m)-G(a)}{\omega C_L}\right) \quad (3)$$

where C(m) and G(m) are the measured capacitance and conductance of the cell filled with material, C(a) and G(a) are the measured capacitance and conductance of the cell without any material i.e. with air, C(l) is the measured capacitance with standard liquid (in this case cyclohexane) in the cell and $\varepsilon'(1)$ is the dielectric permittivity of the standard liquid filled in the cell. C and G were determined with a basic accuracy of 0.2%, and hence the maximum uncertainty in the determination of $\varepsilon'_\perp$ and $\varepsilon''_\perp$ is not more than 1%. Temperature of the sample for dielectric and optical texture studies has been controlled with the help of a hot stage of Instec (model HS-1) having accuracy of ±0.1 °C and a resolution limit ±0.003 °C. Temperature near the sample has been determined by measuring thermo e.m.f. of a copper–constantan thermocouple with the help of a six and half digit multi-meter with the accuracy of ±0.1 °C.

3. Results and discussion

The DSC thermograms displaying the variation of the heat flow with temperature for the pure and 10^{13} ions/cm^2 fluence irradiated DOBA are shown in Fig. 2. From the figure, it is clear that, in the heating cycle Cr–Cr′, Cr′–SmC, SmC–N and N–I and in the cooling cycle Cr′–Cr, SmC–Cr′, N–SmC and I–N transitions are observed. The transition temperatures of the various phases of the pure material in the heating and cooling cycles are in good agreement with the literature data [19].

For the thermodynamical study of the pure and the irradiated materials, the heating and cooling scans of the material are allowed for the first five cycles so that the transition temperatures and the heat of transitions are stabilized. After stabilization, the DSC data are acquired with different scan rates ranging from 2.5 to 15.0 °C/min at an interval of 2.5. The variations of the transition temperatures with the different scan rates for the pure and irradiated materials are shown in Fig. 3. From the thermodynamical study, it has been observed that the transition temperatures vary linearly with the scan rate [20–25]. From the variation of the transition temperatures with scan rate using the least square fit (LSF), the true transition temperatures which are the intercepts of the straight lines on the temperature axis at the extrapolated scan rate of 0 °C/min have been obtained. The phase sequence of the pure and Li ion beam irradiated DOBA in the heating and cooling cycles at the virtual scan rate of 0 °C/min are given as follows:

Pure DOBA:

Heating cycle: Cr — (85.1 °C) → Cr′ — (90.3 °C) → SmC — (114.5 °C) → N — (137.7 °C) → I

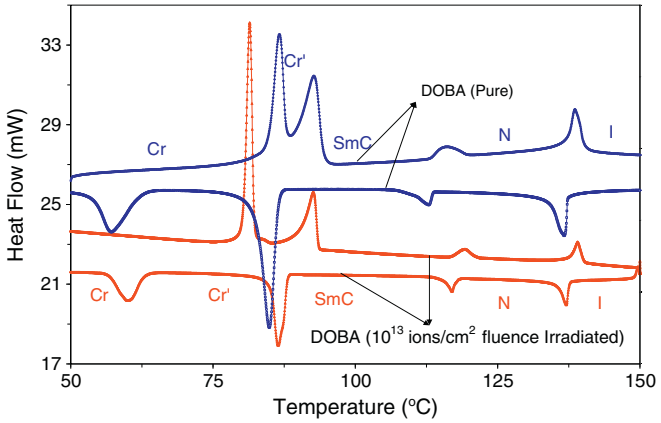

Fig. 2. DSC thermograms for the pure and irradiated (10^{13} ions/cm^2 of Li ion beam) DOBA at the scan rate of 5 °C/min.