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Characterization and Electrical Conductivity of Electron Beam Irradiated Metal Phthalocyanine Complexes

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Abstract

Variation of DC electrical conductivity with temperature from 273-473 K of electron beam irradiated Tetra-nitro zinc, and Cu-Pcs, were carried out. It shows semiconductor behavior and resistivity varies from 0.043×10^5 Ω-cm to 64.61×10^5 Ω-cm for all complexes. Variation of conductivity with temperature shows two straight lines of different slopes the first line (LT), resembles the α–phase, (Ea_1) = 0.226 eV while the second line at 362 K resembles the β- phase (Ea_2) = 0.460 eV (for Cu-Pcs). The β-phase shows higher activation energy than the α-phase, and the X-ray diffraction studies reveal that the crystals are monoclinic. The conductivity is explained on the basis of Davis and Mott model. The conduction mechanism at lower temperature is explained in terms of hoping through a band of localized states and at higher temperatures in terms of thermal excitation of carriers to the band edge.

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1. Introduction

Phthalocyanines (Pcs) are most studied compounds in supramolecular chemistry, it receive a great interest now a days due to their variety of applications such as gas sensors, organic thin film transistors, and various optoelectronic applications [1-3]. Metal phthalocyanines (MPcs) have been studied with many metal ions and different substituents on peripheral (β) and non-peripheral (α) position. Pcs are highly colored, p-type organic semiconducting compounds which exhibit high chemical and thermal stability and thus can be sublimed without decomposition to form high quality thin films and complexes by the thermal evaporation technique or by synthetic route. Physical properties of Pcs are strongly influenced by the growth parameters and the post deposition treatments such as annealing, etc. [4-10]. Irradiation with high energy radiations are expected to affect their physical properties. These irradiated samples show enhanced efficiency its applicability of a radiation environment and is also important in obtaining basic information on vacancies, defects and their interaction with impurities. In this paper we report detailed electrical studies on organic semiconductor Pcs prepared by synthetic route.

2. Experimental

The phthalocynine complexes were prepared by synthetic route. The electrical conductivity measurements of the above samples were performed using two probe method with disc shape pellets. The pellets were sandwiched between two silver electrodes which provide the ohmic contacts. DC conductivity measurements were carried out using programmable Keithley source meter (model 2400) in the temperature range of 300–473 K. The temperature was monitored using a chromel–alumel thermocouple. The irradiation measurements were carried out at microtron center Mangalore University. The samples were irradiated with electron beam (beam energy 4-8 MeV cavity type -1, beam current-15-20mA, pulse repetition rate = 5Hz, pulse width = 1.5-2μs, target to sample

distance is 30 cm, time of exposure = 1-4 h by lanthanum hexa fluorite source). The monochromatic beam is made to fall on sample kept at particular distance in air and the above beam parameters are maintained. Radiation doses were controlled through the exposure time. XRD analysis were carried out using X-ray diffractometer of model Philips X-pert with monochromatic Cu-Kα (λ = 1.5418 Å). The activation energy was measured by using Arrhenius plot by equation 1.

$$\sigma = \sigma_0 \exp (-\Delta E/KT) \quad (1)$$

3. Results and Discussion

Electrical conductivity follows the Arrhenius equation. The Arrhenius plot (log σ v/s 1000/T) yields a straight line with the slope corresponding to the value of thermal activation energy. Log σ v/s 1000/T is plotted for tetra-nitro zinc, and Cu-Pcs, Ni-Pcs and iodine doped Pcs before and after irradiation (Figures 1, 2, 3, 4). In this type of material, the conduction mechanism is different in various regions of the Arrhenius plot. There are two linear regions for each graph, which give two activation energies E_1 and E_2. The activation energy E_1 is related to the intrinsic generation charge carrier process and E_2 to the impurity scattering. The conduction mechanism at lower temperatures is explained in terms of hopping through a band of localized states and at higher temperatures in terms of thermal excitation of carriers to the band edges. The change in the slope, and hence the change in activation energy, reflects a change from intrinsic conduction to the extrinsic one. The activation energies determined for non-irradiated and irradiated samples are listed in Table 1. The activation energy increases with dosage of irradiation and then decreases. Activation energy is found to increase and then reduction in activation energy at 454 K for radiation dose of 60 K Gy for Cu-Pcs may be attributed to the instability of the material due to heavy vibrations of the atoms. The Presence of trap levels is attributed to defects generated which affects electrical conductivity, mobility and trap density. The irradiation of the samples with high-energy creates structural defects which act as trapping centers. This is indicated by the increase in activation energy and thus the reduction in the conductivity of Tetra-nitro zinc and Tetra nitro Cu.

The powder X-ray diffraction spectra of the above samples were studied in the range of 2θ from 20-80$^{0.}$ X-ray diffraction patterns shows many sharp peaks in the spectrum indicating the crystalline nature due doping. For irradiated sample, the X-ray diffraction spectra show semi crystalline nature due to more number of defects (Figures 5, 6, 7, 8).

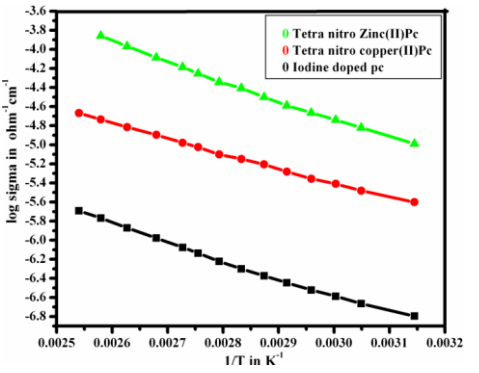

Fig 1. DC conductivity studies Cu-II, Ni, I PC before radiation.

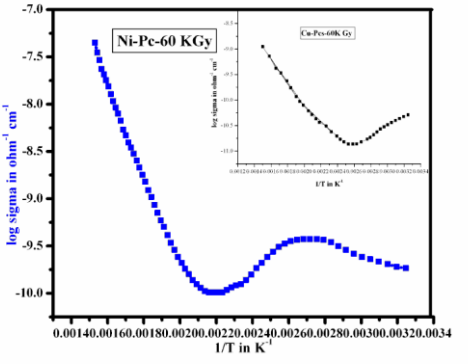

Fig 2. DC conductivity of of Cu-II, Ni, after irradiation.

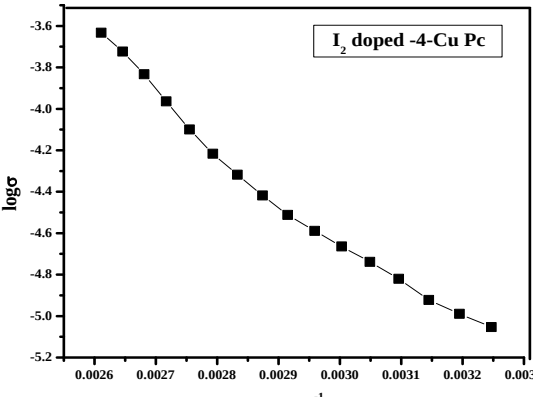

Fig 3. DC conductivity studies before radiation I doped PC

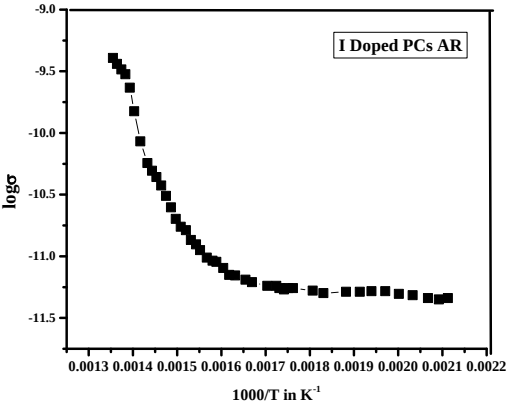

Fig 4. DC conductivity studies I doped PC after radiation.

Table1. Activation energy of the Pcs samples before and after irradiation

No	Compound	Activation Energy at high temperature E_1 (eV)	Activation Energy at low temperature E_2 (eV)
Pc-1	Tetra Nitro Copper (II) Phthalocyanine	0.4324 (BR)	0.1062 (BR)
		0.896 (AR)	0.177 (AR)
Pc-2	Tetra Nitro Zinc(II) Phthalocyanine	0.2596(BR)	0.1503(BR)
		0.745 (AR)	0.312(AR)
Pc-3	Iodine Doped 4-copper Phthalocyanine	0.212(BR) 0.858 (AR)(40KGy)	0.017(BR) 0.092 (AR)(40KGy)
		0.195(AR)(80KGy)	0.1109(AR)(80KGy)

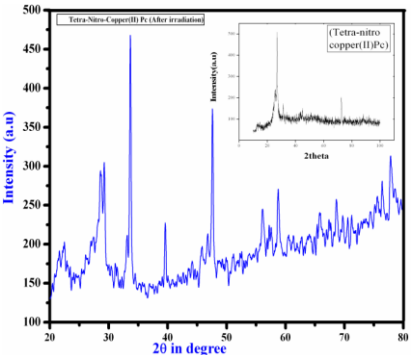

Fig 5. XRD Tetra nitro copper (BF and AF irradiation).

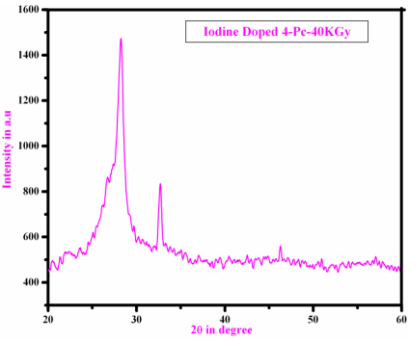

Fig 6. X-ray iodine doped Pc with **40KGy.**

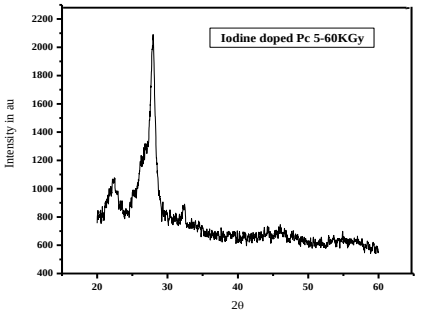

Fig 7. X-ray iodine doped Pc with 60KGy

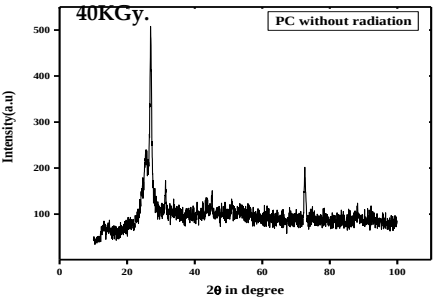

Fig 8. X-ray iodine doped Pc without Radiation

4. Conclusion

X-ray diffraction studies reveal that due to the irradiation samples shows semi crystalline nature. The variation of electrical conductivity explained due to drain of oxygen molecules out of the sample during heating. A partial phase transformation from α to β phase in the samples was identified with the change in the thermal activation energy ΔE. The mechanism of the charge carrier were discussed as a short lived charge transfer between impurity and the complex at high temperature and as an intrinsic generation process at low temperature shows semiconductor nature of the sample.

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