JOURNAL OF MATERIALS SCIENCE 27 (1992) 4184–4188

Anomalous Poole–Frenkel effect observed in some polyenes in sandwich cell configuration

D. GHOSH, S. HAZRA, P. PAL, T. N. MISRA
Department of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032, India

Both the dark- and photo-current–voltage characteristics of zeaxanthin and lutein is ohmic in the lower field regime followed by non-ohmic behaviour in the higher voltage regime, which has been satisfactorily explained by the anomalous Poole–Frenkel effect. A single dominant donor level is the major contributor to the dark-current while a single dominant trap level is the major contributor to the photo-current, both levels have been identified from Arrhenius type plots. Photo-action spectra suggest that the predominant mechanism of charge carrier generation is the same both in dark and illuminated conditions.

1. Introduction

Highly conjugated π-electronic structure of polyene molecules results in their semi- and photo-conductive properties in the solid state. Photo-conduction in polyenes is thought to be involved in photo-biological processes like photosynthesis [1–4]. Polyenes like lutein and zeaxanthin were detected in the macular region of the retina. Macular degeneration is one of the leading causes of blindness. The possible role of a light induced sensitized reaction in the degeneration process [5] has been suggested. These polyenes may act as a scavenger of radicals or a quencher of singlet oxygen generated in the photo-sensitization process. The generation of photo-carriers and their transport in these materials, is, therefore of considerable interest. In this paper we report the results of our investigation on zeaxanthin and lutein.

2. Experimental procedure

High quality polyenes used in this investigation were obtained as a gift from Hoffmann–La Roche Switzerland. The purity of the samples was checked by absorption spectra and they were used without further purification. The powdered samples were used in a sandwich cell with a stainless steel and tin oxide coated glass electrode. The cell was placed in a suitably designed conductivity chamber [6] with a quartz window through which light can pass and illuminate the sample. For current measurements Keithley's programmable electrometer model 617 was utilized. The electrometer has a built-in isolated d.c. voltage source which can be adjusted between − 100 to + 100 V. Voltages up to + 100 V were applied across the electrodes from this source and for higher voltages, a high voltage regulated power supply (model 7333 APLAB, India) was used. Temperature measurements were made by a copper-constant thermocouple and a panel meter (HIL 2301, India). A 100 W Xenon lamp was used to illuminate the sample for the steady state photo-conductivity study. A Shimadzu spectrophotometer (model 210A) was used to run the absorption spectra. For photo-conductivity action spectra measurements a monochromator (Jobin Yvon H20 UV 1673, France) was used. The sandwich cell thickness and area were maintained at 0.0025 cm and 0.25 cm^2, respectively. After each voltage application sufficient time was allowed to attain equilibrium current values. Several measurements were made in order to ensure reproducibility of results both in vacuum and in a dry nitrogen atmosphere.

3. Results and discussion

The observed current–voltage characteristics of zeaxanthin and lutein are ohmic at the low voltage regime followed by non-ohmic behaviour at higher voltages both in the dark and in the illuminated condition. The non-ohmic region does not satisfy the space-charge limited conduction relation. The data yielded a straight line when plotted as log I versus $V^{1/2}$. Such plots for zeaxanthin and lutein are shown in Figs 1 and 2, respectively. In the low voltage regime, the experimental points fall below the straight line drawn with the points in the higher voltage regime. Such a linear plot is attributed either to the Schottky effect or to the Poole–Frenkel effect [7–10]. But the temperature dependence measurements of dark- and photo-currents at various voltages and excitation wavelength measurements suggest the Poole–Frenkel effect to be operative. Moreover, different parameters evaluated lie in an acceptable range only when the Poole–Frenkel effect is assumed to be operative. A photo-conductivity study of Poole–Frenkel effect is rather rare. The Poole–Frenkel effect operating simultaneously in dark- and photo-conduction was reported by Ieda *et al.* [11] and Jonscher and Ansari [12].

In the Poole–Frenkel effect, electrons are thermally emitted from the randomly distributed traps to the conduction band of the insulator by the lowering of

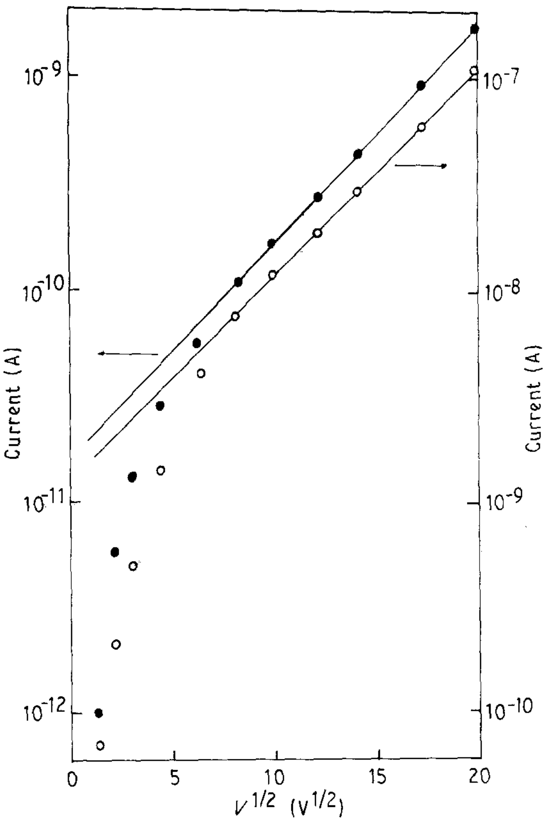

Figure 1 Log I versus $V^{1/2}$ plots of the current–voltage characteristics of zeaxanthin in a sandwich cell configuration: (—●—) dark-current; (—○—) photo-current.

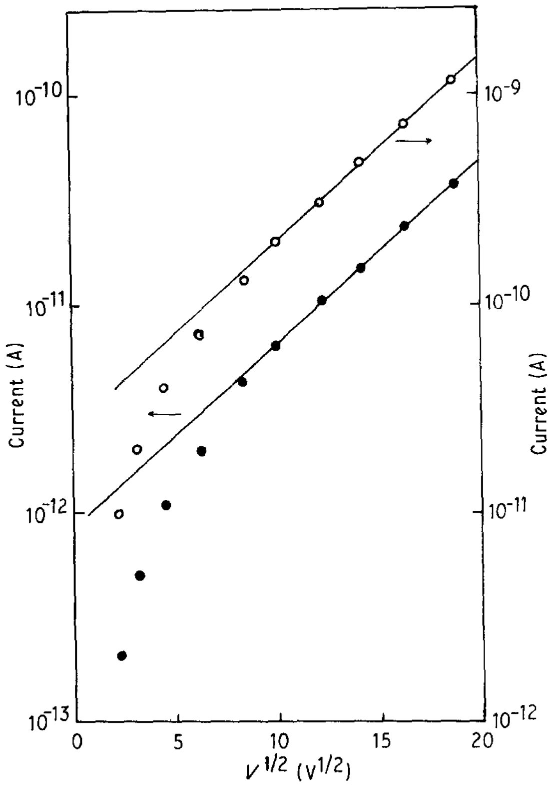

Figure 2 Log I versus $V^{1/2}$ plots of the current–voltage characteristics of lutein in a sandwich cell configuration: (—●—) dark-current; (—○—) photo-current.

the Coulombic potential barrier by an external electric field. The current density in thin insulators containing shallow traps is given by [13]

$$J = J_0 \exp(\beta_{PF} F^{1/2}/kT) \qquad (1)$$

where F is the applied electric field, k is Boltzmann constant, T the absolute temperature and β_{PF} is the Poole–Frenkel field lowering coefficient and is given by

$$\beta_{PF} = (e^3/\pi \varepsilon_0 \varepsilon_r)^{1/2} \qquad (2)$$

where e is the electronic charge, ε_0 is the permittivity of the free space and ε_r is the relative dielectric constant of the insulator.

For insulators containing both trapping and donor centres in a manner shown in Fig. 3, the current density is given by [14]

$$J = J_0 \exp(\beta_{PF} F^{1/2}/2kT) \qquad (3)$$

where J_0 is given by

$$J_0 = e\mu N_c (N_d/N_t)^{1/2} F \exp[-(E_d + E_t)/2kT] \qquad (4)$$

where μ is the free electron mobility, N_c is the effective density of states in the conduction band, N_d/N_t is the ratio of concentrations of the donor centres to the trapping centres, E_d and E_t are the energy levels of the donor and trap centres from the bottom of the conduction band as shown in Fig. 3, F is the applied electric field, k the Boltzmann constant and T the absolute temperature.

Equation 3 is called the anomalous Poole–Frenkel effect and it is valid even if there exists a range of trap and donor levels and one of the trap levels is distinctly more predominant than the others [15].

Now β_{PF} can be calculated theoretically according to Equation 2, for which the relative dielectric constant ε_r of the material is to be known. We do not know the ε_r values of the materials used in this investigation. Misra *et al.* [16] determined the dielectric constant of β-carotene as 2.5. We expect similar value of ε_r for these polyenes belonging to the same group of β-carotene. Taking $\varepsilon_r = 2.5$ the theoretical value of β_{PF} becomes 4.50×10^{-4} eV $V^{-1/2}$ cm$^{1/2}$. The experimental value of β_{PF} can be found from the slope of log I versus $V^{1/2}$ plots. The values of β_{PF} (theoretical) and β_{PF} (experimental) are listed in Table I for easy comparison. They are in good agreement.

It is apparent from Equation 3 that a plot of log I against $1/T$ at a constant voltage should yield a straight line of slope $[\beta_{PF} F^{1/2} - (E_d + E_t)]/2k$. The values of $(E_d + E_t)$ can be determined from this slope since β_{PF} is known from the isothermal plot of log I versus $V^{1/2}$. We have shown log I versus $10^3/T$ plots for dark- and photo-currents at different voltages in the range 20–100 V for zeaxanthin and lutein in Figs 4 and 5, respectively. The experimental data fit well to a straight line for both the polyenes. It is observed that

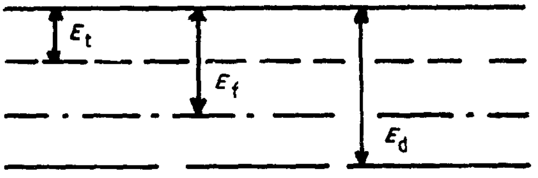

Figure 3 Energy level diagram of insulators containing both donor and trap level of the model used to develop Equation 3 [12].

TABLE I Comparison of β_{PF}(exp) with β_{PF}(theo)

Polyene	β_{PF}(exp) dark ($eV\,V^{-1/2}\,cm^{1/2}$)	β_{PF}(exp) photo ($eV\,V^{-1/2}\,cm^{1/2}$)	[β_{PF}(theo)/β_{PF}(exp)] dark	[β_{PF}(theo)/β_{PF}(exp)] photo
Zeaxanthin	5.85×10^{-4}	5.62×10^{-4}	0.77	0.80
Lutein	4.98×10^{-4}	5.04×10^{-4}	0.90	0.89

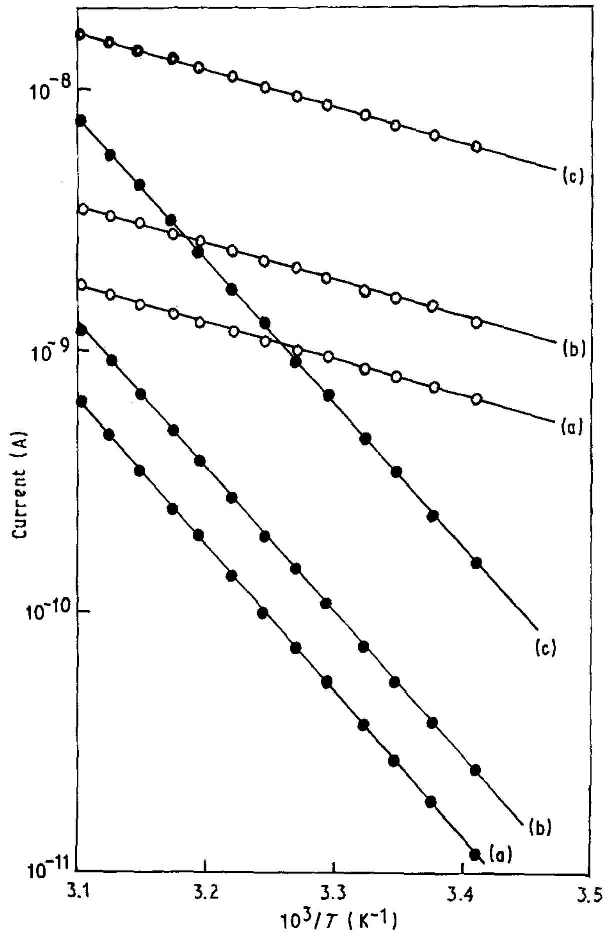

Figure 4 Plots of log I versus $10^3/T$ for zeaxanthin at various applied voltages: (a) 20; (b) 40; (c) 100 V. (—●—) dark; (—○—) photo-current.

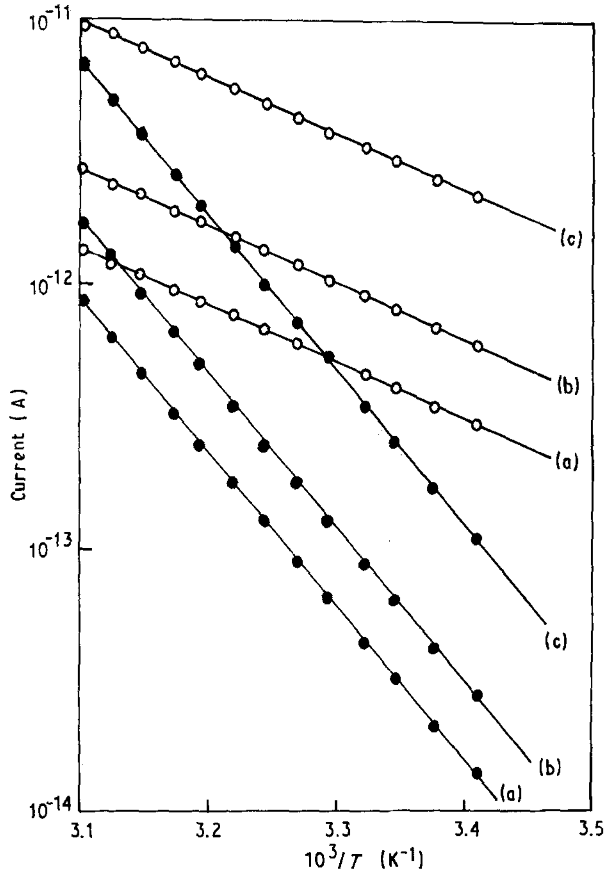

Figure 5 Plots of log I versus $10^3/T$ for lutein at various applied voltages: (a) 20; (b) 40; (c) 100 V. (—●—) dark; (—○—) photo-current.

the slope of the lines does not vary appreciably with voltage. In fact, taking β_{PF} as 4.5×10^{-4} (theoretical value of β_{PF}) the value of $\beta_{PF} F^{1/2}$ becomes 0.03 eV for 20 V and 0.06 eV for 100 V, the variation being 0.03 eV, which is negligible and within the experimental error limit. ($E_d + E_t$) values for all the polyenes are listed in Table II.

Once ($E_d + E_t$) is known, μ can be calculated from the intercept of log I versus $1/T$ plot i.e., at $1/T = 0$, provided the trap to donor ratio, N_t/N_d, is either known or can be estimated. For a wide band gap insulator the value of the effective density of states N_c in the conduction band can be taken as 10^{21}. For the insulators whose electronic state configuration resembles that shown in Fig. 3, the trap to donor density ratio is given by [17]

$$N_t/N_d = \exp - [(E_d + E_t) - 2E_F]/kT \quad (5)$$

where E_F is the position of the Fermi energy level. Assuming that the Fermi level is positioned [18] within $2kT$ of the dominant trap level E_t, Equation 5 can be written as

$$N_t/N_d = \exp - [E_d - E_t - 4kT]/kT \quad (6)$$

Further assuming that the majority of the contribution to the photo-current comes from the trapped charge carriers, the slope of log I_{ph} versus $1/T$ plot should give E_t instead of ($E_d + E_t$). Thus the trap to

TABLE II Evaluated μ values of polyenes

Polyene	$E_d + E_t$ (eV)	E_t (eV)	N_t/N_d (dark)	μ_{dark}($cm^2\,V^{-1}\,s^{-1}$)	N_t/N_d (photo)	μ_{photo} ($cm^2\,V^{-1}\,s^{-1}$)
Zeaxanthin	2.18	0.55	9.45×10^{-18}	4.13×10^{-7}	5.11×10^{11}	3.63×10^{-5}
Lutein	2.19	0.90	9.16×10^{-6}	4.03×10^{-4}	2.35×10^{17}	7.96×10^{-3}

donor density ratio under illuminated conditions becomes

$$(N_t/N_d)_{\text{photo}} = \exp[E_t + 4kT]/kT \quad (7)$$

Thus E_d and E_t being known, we can estimate the value of the ratio N_t/N_d both for dark and illuminated conditions following Equations 6 and 7, respectively and hence the corresponding μ values can be evaluated. The μ values for zeaxanthin and lutein for both dark and photo are listed in Table II. μ_d and μ_{ph} values obtained are reasonable but the difference between them cannot be rationalized at this stage.

We have also studied the photo-conduction action spectra of these materials. We show the photo-conduction action spectra of zeaxanthin and lutein in Figs 6 and 7, respectively, along with their optical absorption spectrum in thin films. The intense electronic absorption peak around the 400–550 nm region is known as the trans peak and the weak band in the 200–350 nm region is known as cis peak of polyenes. The photo-conduction action spectrum has two distinct bands: a strong band around the 550–750 nm region and a broad weaker band around the 300–500 nm region. In some polyenes like β-carotene [2] the photo-conduction action spectrum is reported to be in coincidence with the trans absorption peak. But in the present case, the intense photo-conduction peak is red shifted from trans absorption peak for both the polyenes. Not only the energetic position but also the structural feature of the photo-conduction action spectra are different from optical absorption spectra and there is no correlation.

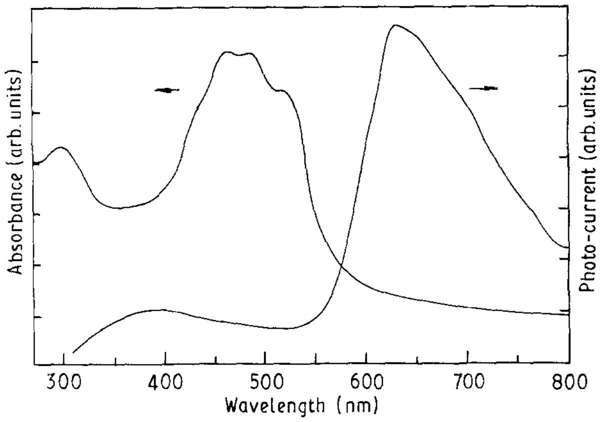

Figure 6 Absorption spectrum and photo-conduction action spectrum of zeaxanthin.

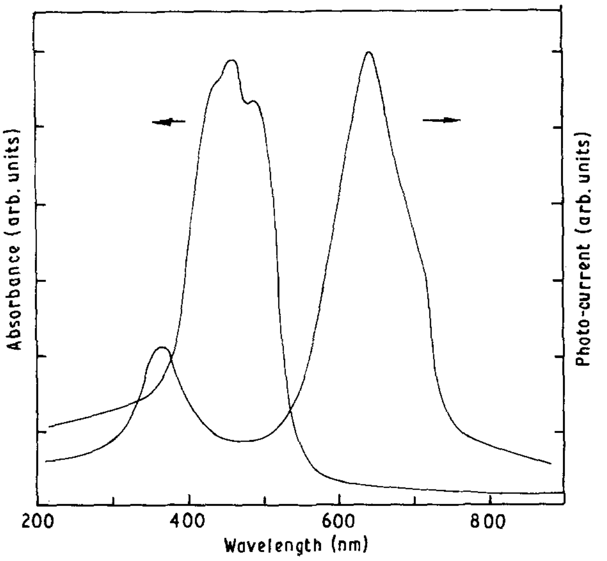

Figure 7 Absorption spectrum and photo-conduction action spectrum of lutein.

TABLE III Comparison of E_d with photo-conductivity threshold energy

Polyene	$E_d + E_t$ (eV)	E_t (eV)	E_d (eV)	Long wavelength photo-conductivity threshold energy (eV)
Zeaxanthin	2.18	0.55	1.63	1.59
Lutein	2.19	0.90	1.29	1.53

The short wavelength photo-conduction band (300–450 nm) has been observed in some other polyenes [19, 20] and has been attributed to photo-injection of charge carriers from an illuminated electrode, which is very weak in the present systems. The most intense peak in the photo-action spectra observed in zeaxanthin and lutein are in the longer wavelength region (550–750 nm). If we extrapolate the long wavelength tail of this band it intersects the abscissa at an energy which corresponds to the photon energy at which the compound displays photo-conductivity. This value is in good agreement (Table III) with the distance of the conduction band edge from the donor level which is the major contributor to dark-conduction. These results suggest that the predominant mechanism of carrier generation is the same in both dark and illuminated conditions.

4. Conclusion

1. Current–voltage characteristics is ohmic in the low voltage regime followed by non-ohmic behaviour in the higher voltage regime which can be satisfactorily explained by the anomalous Poole–Frenkel effect.
2. A single dominant donor level is the major contributor to the dark-current while a single dominant trap level is the major contributor to the photo-current.
3. The predominant mechanism of carrier generation is the same in both the dark and illuminated conditions.

Acknowledgement

A generous gift of the polyenes used in the present investigation by M/S Hoffmann–La Roche. Ltd., Switzerland is gratefully acknowledged.

References

1. B. ROSENBERG, *J. Opt. Soc. Amer.* **51** (1961) 238.
2. *Idem*, in "Advances in Radiation Biology" Vol. 2 (Academic Press, New York, 1966) p. 193.
3. R. J. CHERRY and D. CHAPMAN, *Mol. Cryst.* **3** (1967) 251.
4. G. FALK and P. FATT, *J. Physiol.* **167** (1966) 36.
5. B. CHAKRABARTI, Private communication.

6. B. MALLIK, A. GHOSH and T. N. MISRA, *Bull. Chem. Soc. Jpn.* **52** (1979) 2091.
7. M. IEDA and G. SAWA, *J. Appl. Phys.* **42** (1971) 3737.
8. T. E. HARTMANN, J. C. BLAIR and R. BAUER, *ibid.* **37** (1966) 2468.
9. T. HIRAI, *ibid.* **7** (1968) 112.
10. A. C. LILLY and J. R. McDOWELL, *ibid.* **39** (1968) 141.
11. M. IEDA, T. MIZUTAMI and Y. JAKAI in Proceedings of the International Micro-symposium on Polarisation and Conduction in Insulating Polymers (Bratislava, 1972).
12. A. K. JONSCHER and A. A. ANSARI, *Phil. Mag.* **23** (1971) 205.
13. C. A. MEAD, *Phys. Rev.* **128** (1962) 2088.
14. J. G. SIMMONS, *ibid.* **155** (1967) 657.
15. J. G. SIMMONS, *J. Phys. D: Appl. Phys.* **4** (1971) 613.
16. T. N. MISRA, B. ROSENBERG and R. SWITZER, *J. Chem. Phys.* **48** (1968) 2096.
17. J. G. SIMMONS, *Phys. Rev. Lett.* **15** (1965) 967.
18. C. A. HOGARTH and M. ZOR, *Phys. Stat. Sol. (a)* **98** (1986) 611.
19. P. PAL and T. N. MISRA, *J. Phys. D: Appl. Phys.* **22** (1989) 1358.
20. Y. HOSHINO and K. TATEISHI, *J. Phys. Soc. Jpn* **46** (1979) 72.

Received 9 April
and accepted 30 July 1991