

Electrical and optical properties of sublimed films of heavy-fraction rare-earth-element bisphthalocyanines

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Steady-state electrical measurements and optical-absorption experiments were performed on 50 nm thick samples of sublimed heavy-fraction rare-earth-element bisphthalocyanines films. From the Arrhenius plot of $\ln \sigma(T)$ (where $\sigma(T)$ is the conductivity at temperature T) it was found that two conduction regimes existed. The activation energy of 0.18 eV at high temperatures ($T > 162$ K) relates to the distance of singlet states below the conduction band. The low-temperature activation energy of 4 meV indicates hopping conduction between localized states close to the Fermi level. Visible optical spectra in both absorption and transmission modes were obtained for the sample. The absorption data were analysed in terms of a well-known power law, and a value of 2.3 eV was found for the optical gap, E_0 . Estimates of the refractive indices and the dielectric constants were made over the visible spectrum.

1. Introduction

The spectroelectrochemical properties of rare-earth-element bisphthalocyanine complexes have been extensively studied because of their potential applications in multicolour electrochromic devices [1-5]. Electrochromism is observed when samples of bisphthalocyanine derivatives are subjected to reduction or oxidation processes through a series of voltage cycling. The neutral compounds are generally green but they turn red on oxidization in which the loss of one electron per molecule takes place. When the compounds are reduced, they become blue on the addition of one electron per molecule. Further addition of an electron per molecule induces a change in colour to purple. The samples are generally prepared by depositing sublimed [6, 7] or Langmuir-Blodgett [8, 9] films of bisphthalocyanines onto transparent conducting electrodes such as indium tin oxide (ITO) glass substrates.

The purpose of this paper is to report on the results for electrical measurements of, and optical absorption in, heavy-fraction rare-earth bisphthalocyanine, [HF(pc)(pc*)] (where pc is a phthalocyanato dianion, pc* is a phthalocyanato monoradical cation, HF is a mixture of heavy-fraction rare-earth elements as found in partially refined heavy fractions or as in previously reported compounds [10]). This paper is divided into four sections. Section 2 is devoted to a description of the experimental techniques employed. The results from the measurements are presented in Section 3. Since the colour change is due to the occurrence of

optical absorption at different frequencies, knowledge of the dispersion of optical constants such as the complex refractive index, N , and the dielectric constant, ϵ^* , is basic to an understanding of electrochromic behaviour. Using the one-electron theory, electrical and optical properties are then evaluated from the experimental data, and a full discussion is given in Section 4. Finally, Section 5 deals with the conclusions reached from treatments of the experimental results.

2. Experimental details

Heavy-fraction bisphthalocyanine [HF(pc)(pc*)] molecules were vacuum sublimed in an Edwards coater onto the surfaces of glass substrates. Using a Rank Taylor Hobson Form Talysurf instrument, the thickness of the deposited film was determined by obtaining the surface profile of the sample over the interface region between the film/glass substrate. A correction factor was introduced in order to compensate for the slight deviation of the sample surface from the horizontal.

For electrical characterizations, insulating substrates were used. A pattern of electrodes was generated by the vacuum deposition of copper through an all-steel mask onto the [HF(pc)(pc*)] film surface. The electrodes were approximately 1 mm in diameter. During the electrode deposition, the substrate was kept cooled at liquid-nitrogen temperature. Direct current (d.c.) measurements were made on the samples

in planar configurations in a vacuum of the order of 10^{-4} Pa inside an Oxford Instruments liquid-nitrogen cryostat. Leads were attached to the sample electrodes by means of silver paint. With the help of a Keithley 617 digital electrometer in a microprocessor-controlled instrumentation system, the in-plane circulating current, I , was monitored as a function of the d.c. bias potential, V , at various temperatures from 77 to 300 K. The sample was maintained under an environment of nitrogen gas throughout the investigation, so as to avoid the formation of ice on the sample and to prevent any possible influence of adsorbed oxygen on the material properties. Using a Phillips PU8720 ultraviolet/visible spectrophotometer, optical absorption and transmission spectra were obtained for [HF(pc)(pc*)] compounds at room temperature in air between 1.4 and 4 eV. For these investigations, these films were prepared on ITO glass substrates. An uncoated substrate was used as a reference in the single-beam spectrophotometer, so that the output was solely in terms of the transmission characteristics of the films.

3. Results

Electrical measurements were performed on untreated [HF(pc)(pc*)] biphthalocyanine film in planar configurations, and a characteristic material parameter, such as the d.c. activation energy, was deduced. The optical data were analysed in order to obtain information regarding the dispersion of the refractive index, the tails of localized states and the optical gaps. The film thickness was found to be 50 nm.

3.1. Electrical measurements

The circulating current, I , was measured for [HF(pc)(pc*)] films as the applied bias potential, V , was varied up to 100 V, both in the forward and the reverse directions. Fig. 1 displays a family of curves showing the typical variation of the current as a

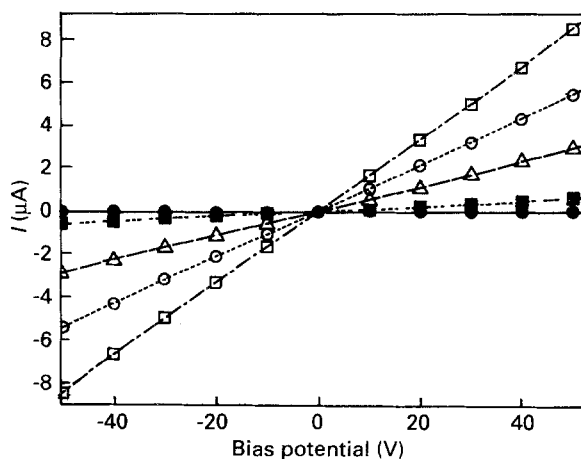


Figure 1 A set of five curves showing the variation of the circulating current through a 50 nm thick heavy-fraction biphthalocyanine [HF(pc)(pc*)] film as a function of the applied bias potential up to ± 50 V, at different temperatures: (\square) 297 K, (\circ) 267 K, (\triangle) 247 K, (\blacksquare) 207 K, and (\bullet) 77 K. The device structure was planar; aluminium electrodes were used.

function of the applied d.c. voltage at five different temperatures from 77 to 297 K. The $I(V)$ characteristics were reproducible and symmetrical in both the forward and the reverse directions. This implies that the field due to the applied potential is symmetrically distributed in the bulk of the film. This conduction is not strictly ohmic, but at a given temperature, T , the current was found to have a power-law dependence on the potential, V , of the form

$$I = \rho V^s \quad (1)$$

where the coefficient ρ and the index s are both temperature-dependent quantities. The value of s varied from 0.7 at 77 K to 1.1 at room temperature. ρ , on the other hand, had the values $7.2 \text{ k}\Omega^{-1} \text{ V}^{0.3}$ and $21 \text{ }\Omega^{-1} \text{ V}^{-0.1}$ at corresponding temperatures. The temperature of transition from the dependence with $s < 1$ to that with $s > 1$ is believed to be 162 K in which the $I(V)$ characteristic is found to be truly ohmic. As expected, the conduction generally increased with the rise in temperature, but the rate of the rise in conductivity was not as large at temperatures below 127 K as at temperatures above 127 K.

3.2. Optical measurements

Fig. 2 displays the absorption and transmittance spectra within the visible optical frequency range. The reflectivity, R , is also shown as a function of photon energy, $h\nu$. As expected, $R + T + A = 1$, where the absorption, A , and the transmittance, T , are given in terms of I_0 and I_t , the input and output optical intensities, respectively. Values of $[\ln(I_0/I)/t]$ are calculated for α as a function of the photon energy, $h\nu$, since the absorption coefficient, α , for [HF(pc)(pc*)] films of thickness t is defined by the condition that the energy in the wave falls to a value of $\exp(-1)$ in a distance α^{-1} . Like monophthalocyanines, [HF(pc)(pc*)] films are found to be strongly absorbing materials, with α of the order of 10^7 m^{-1} . Fig. 3 shows typical features of absorption in biphthalocyanine molecules in the visible region; the absorption rising to the Q-band peak at about 1.9 eV is probably due to $a_{1u}-e_g$ type transitions [9]. There is also a noticeable

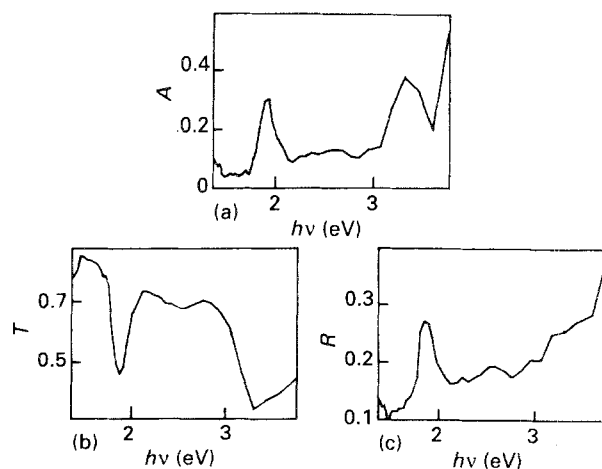


Figure 2 (a) The visible absorption spectra, (b) transmission, and (c) the reflectivity spectra.

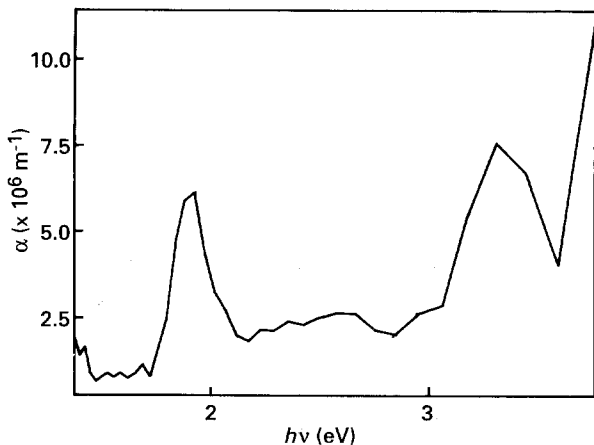


Figure 3 The variation of the absorption coefficient with the incident photon energy for a 50 nm thick [HF(pc)(pc*)] film.

broadening of the Q-band, which may be due to the interaction of molecules in the solid phase. In vapour spectra of these materials, it is normally possible to identify five bands Q, B, N, L and C; these are characteristic of the phthalocyanine ring. The B-band is seen to be located at approximately 3.0 eV. The N-, L- and C-bands have been noted to occur between 4 and 6 eV; and they were therefore outside the scope of our measurements. In sublimed films of monophthalocyanine complexes, the minimum of the transparent band usually occurs at $h\nu \approx 2.4$ eV [11]. For [HF(pc)(pc*)] films, an extra peak is observed within the energy window 2.2–2.4 eV. This peak is referred to as a radical band and has been shown to be present only in neutral and oxidized [M(pc)(pc*)] materials [12].

4. Discussion

In order to understand the conduction processes involved, values of $\ln I_c$ are plotted in Fig. 4 against the inverse of temperature, T^{-1} , where I_c is the circulating current at a bias potential of 50 V. For a given geometry of the device, the circulating current at a constant potential may be taken as a measure of the

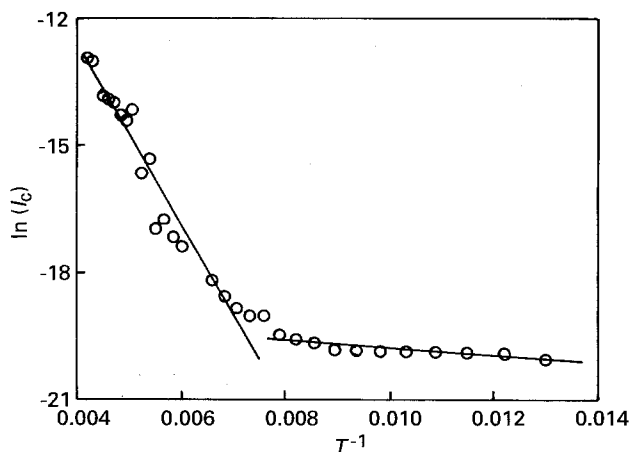


Figure 4 An Arrhenius plot showing the variation of $\ln I_c$ as a function of the inverse of temperature, T^{-1} , where I_c is the current (measured in μA) at a bias potential of 50 V.

conductivity, σ , therefore, the resulting curve may be regarded as being an Arrhenius variation of the conductivity with temperature in the usual form:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (2)$$

The symbol E_a represents the activation energy. σ_0 is the value of the conductivity, σ , as $T \rightarrow \infty$. It can be observed from Fig. 3 that the activation energy, E_a , is a temperature-dependent quantity. For the high-temperature regime (that is, $T \geq 162$ K), the activation energy is estimated to be 0.18 eV. The activation energy for the low-temperature region was found to be very small, of the order of 7 meV. A tentative band diagram for electronic transport is given for phthalocyanines in [13]. The intrinsic band gap is normally believed to be 2.0 eV. Although this value is likely to vary, depending upon the nature of the central metal atom, the two values obtained for E_a are considered too small to excite carriers from the valence band to the conduction band. Singlet states, S_1 , which lie in the energy-band gap of a phthalocyanine film are believed to be involved with the conduction at high temperatures, since the activation energy of 0.18 eV in this temperature regime compares well with the value of 0.21 eV for the approximate distance of the singlet state from the conduction-band edge. The low-temperature activation energy, on the other hand, is thought to be associated with hopping of carriers between localized states close to the Fermi level. The existence of these states is consistent with the non-crystalline nature of sublimed films.

The optical absorption data were analysed within the framework of the one-electron theory for molecular solids in order to obtain information on the density of localized states and the optical band gap. It was observed that, for the range of incident photon energies between 1.66 and 1.9 eV, there was a sharp increase in the values of the absorption, α . From the linear variation of the logarithm of α with the photon energy, $h\nu$, given in Fig. 5, this increase is found to be exponential and in the form of the Urbach relation

$$\alpha(\nu) = \alpha_0 \exp[(h\nu/\Delta) - b] \quad (3)$$

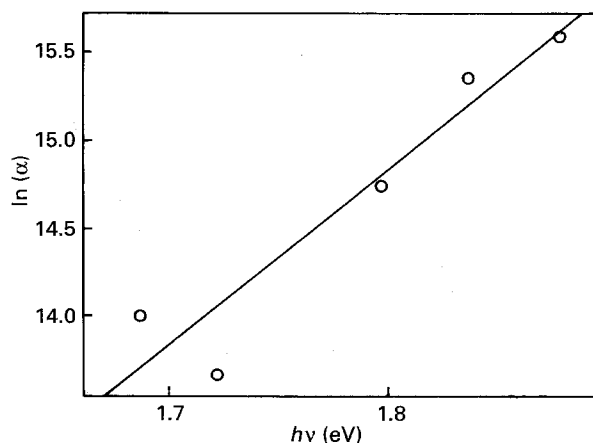


Figure 5 The exponential dependence of the absorption coefficient, α , on the incident photon energy, $h\nu$, for the energy range $1.66 \text{ eV} \leq h\nu \leq 1.90 \text{ eV}$.

where α_0 and b are constants at a given temperature [14]. The value of Δ is estimated to be 0.10 eV from the gradient of the graph. Although several amorphous semiconductors are known to exhibit a similar law for $\alpha \approx 10^6 \text{ m}^{-1}$, very little information is available for Urbach tails in molecular-solid-type materials. Our value for Δ agrees well with a value recently obtained for Langmuir-Blodgett films of substituted copper amphiphilic phthalocyanine molecules [15]. In some analyses, the quantity Δ can be interpreted as the tail widths of localized states in the band gaps, the densities of which are assumed to fall off exponentially with energy [16]. Davis and Mott [17], however, have pointed out that electronic transitions between the states in the band tail are not a plausible proposition in the light of the extremely small variation in the value of Δ between 0.05 and 0.06 eV. X-ray studies show that the molecular structure consists of two nearly parallel phthalocyanine ligands with the metal atom at the centre [18]. It is believed that the van der Waals force between the chemiphores gives rise to the Gaussian distribution of random fields yielding an exponential absorption edge.

At the lower energy range ($h\nu \leq 2.2 \text{ eV}$), the absorption coefficient α decreases sharply with increasing photon energy. The absorption edge at the higher energy end ($h\nu \geq 2.8 \text{ eV}$) is believed to be related to an interband transition. For direct band-to-band transitions, the absorption coefficient, α , is given in the form

$$\alpha(\nu) = (B/h\nu)[h\nu - E_0]^x \quad (4)$$

where E_0 is the optical gap. The coefficient B can be determined from the conductivity of the film. The index x takes on a value of 1/2 for allowed transitions [13]. For the energy range $2.84 \text{ eV} \leq h\nu \leq 3.4 \text{ eV}$, Fig. 6 gives a plot of $(\alpha h\nu)^2$ as a function of the photon energy, $h\nu$. Using the least-squares technique, the best straight line was drawn. From the ratio of intercepts on the ordinate to their respective slopes, the value 2.3 eV was determined for the optical gap, E_0 . For a similar energy range, a modified form of Equation 4 was recently used to analyse the optical absorption edge for sublimed films of lead phthalocyanine [11], and a value of 2.4 eV was obtained for E_0 .

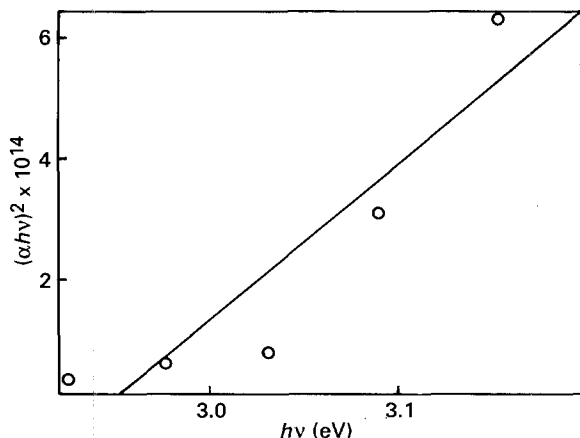


Figure 6 The power-law dependence of the absorption coefficient, α , (measured in units of m^{-1}), on the incident photon energy, $h\nu$, for the energy range of $2.84 \text{ eV} \leq h\nu \leq 3.4 \text{ eV}$.

The optical properties of a bisphthalocyanine film are characterized by its complex refractive index, $N (= n - j\kappa)$, and its complex dielectric constant $\epsilon^* (= \epsilon_1 - j\epsilon_2)$.

The extinction constant, κ , is given in the form

$$\kappa = \frac{\alpha\lambda}{4\pi} \quad (5)$$

where λ is the wavelength. On the other hand, the real part, n , of the refractive index, N , represents the propagation constant and it may be found from the reflectivity, R , of an absorbing medium in air for normal incidence using the expression [19]

$$R = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2} \quad (6)$$

The two components, ϵ_1 and ϵ_2 , of the dielectric constant ϵ^* are related to n and κ by the following equations

$$\epsilon_1 = n^2 - \kappa^2, \quad \epsilon_2 = 2n\kappa \quad (7)$$

Using values of the absorption coefficient, α , and the reflectivity, R , from Fig. 2, the components n and κ of the complex refractive index, N , are plotted in Fig. 7 as a function of the photon energy. The variations of the dielectric constant ϵ^* are shown in Fig. 8. The variation of κ is found to be symbatic with the absorption spectrum. Overall, n increases as the photon energy, $h\nu$, decreases, and it appears to follow the properties indicated by the simple oscillator dispersion model. Peaks in n are observed in the vicinity of the peak absorbance values for the material. The propagation constant, n , falls from the peak value as the photon energy decreases further; it is to be expected that this fall in n on the low-energy side of the peak would be characterized by the Cauchy dispersion formula

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (8)$$

where A , B and C are constants peculiar to the

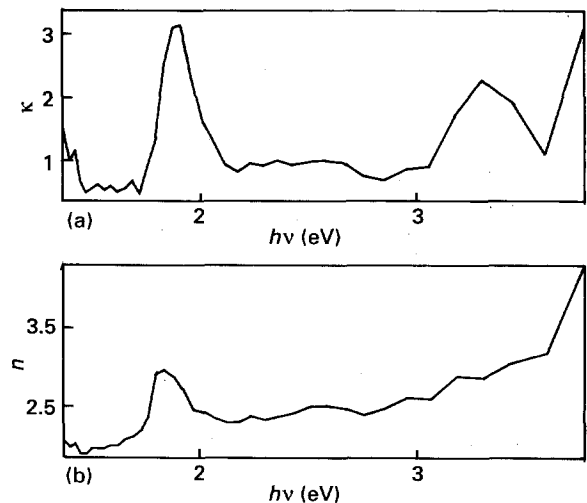


Figure 7 The variations of (a) the extinction coefficient, κ , and (b) the optical propagation constant, n (the real component of the refractive index) with respect to the incident photon energy for the 50 nm [HF(pc)(pc*)] sample.

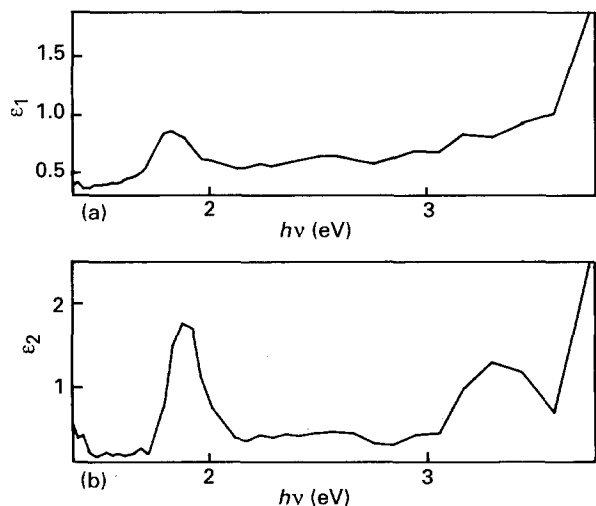


Figure 8 The dependence of both (a) the real component ϵ_1 , and (b) the imaginary component, ϵ_2 , of the dielectric constant, ϵ , for the 50 nm [HF(pc)(pc*)] sample.

material. λ is the wavelength at a given photon energy. The values of A , B and C are estimated to be 10.3 , $-1.05 \times 10^{-11} \text{ m}^2$ and $3.35 \times 10^{-24} \text{ m}^4$.

5. Conclusion

Nearly linear $I(V)$ characteristics were obtained for 50 nm thick samples of rare-earth-element bisphthalocyanine complexes in planar configurations with aluminium electrodes. The activation energy was found to be 0.18 eV and 7 meV at high and low temperatures, respectively; and the excitation to a singlet state below the conduction edge was associated with the conduction process at high temperatures, while the carrier transport between localized states was the dominant mechanism at a low temperature. The increase in the values of the absorption, α , for the range of incident photon energies between 1.66 and 1.9 eV was found to be exponential in the form of an Urbach relation, giving a value of 0.10 eV for the tail width, Δ , of localized states in the band gap. Optical absorption in the range of $2.84 \text{ eV} \leq hv \leq 3.4 \text{ eV}$ was, on the other hand, attributed to the allowed band-to-band transitions.

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References

1. P. N. MOSKALEV and I. S. KIRIN, *Opt. Spectrosc.* **29** (1970) 220.
2. M. PETTY, D. R. LOVETT and J. M. O'CONNOR, *Thin Solid Films* **179** (1989) 387.
3. Y. LIU, K. SHIGEHARA, M. HARA and A. YAMADA, *J. Amer. Chem. Soc.* **113** (1991) 440.
4. B. LUKAS, D. R. LOVETT and J. SILVER, *Thin Solid Films* **210/211** (1992) 213.
5. J. SILVER, P. LUKES, P. HEY and M. T. AHMET, *J. Mater. Chem.* **2** (1992) 841.
6. J. SILVER, P. LUKES, A. HOULTON, S. HOWE, P. HEY and M. T. AHMET, *ibid.* **2** (1992) 849.
7. Y. LIU, K. SHIGEHARA and A. YAMADA, *Thin Solid Films* **179** (1989) 220.
8. M. L. RODERIGUEZ-MENDEZ, R. AROCA and J. A. DeSAJA, *Chem. Mater.* **4** (1992) 1017.
9. M. J. STILLMAN and T. NYOKONG, in "Phthalocyanines - properties and applications", edited by C. C. Lenzenoff and A. P. B. Lever (VCH Publishers, New York, 1989) p. 133.
10. C. S. FRAMPTON, J. N. O'CONNOR, J. PETERSON and J. SILVER, *Displays Tech. Appl.* **9** (1988) 174.
11. R. A. COLLINS, A. KRIER and A. K. ABASS, *Thin Solid Films* **229** (1993) 113.
12. J. SILVER, P. LUKES, S. D. HOWE and B. HOWLIN, *J. Mater. Chem.* **1** (1991) 29.
13. J. SIMON and J. J. ANDRE, "Molecular semiconductors" (Springer Verlag, Berlin, 1984) p. 124.
14. N. F. MOTT and E. A. DAVIS, "Electronic processes in non-crystalline materials" (Clarendon Press, Oxford, 1979) p. 291.
15. A. K. RAY, S. MUKHOPADHYAY and M. J. COOK, *Phys. Status. Solidi (a)*, **134** (1992) k73.
16. J. TAUC, in "The optical properties of solids", edited by F. Abeles (North-Holland, Amsterdam, 1970) p. 277.
17. E. A. DAVIS and N. F. MOTT, *Phil. Mag.* **22** (1970) 903.
18. A. GIEREN and W. HOPPE, *J. Chem. Soc. Chem. Comm.* **8** (1971) 413.
19. T. S. MOSS, G. J. BURRELL and B. ELLIS, "Semiconductor opto-electronics" (Butterworth, London, 1973) p. 10.

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