Thermochimica Acta, 141 (1989) 19–26
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

PREPARATION OF NOVEL NON-SYMMETRICAL SCHIFF BASES USING SOLID STATE REACTIONS

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(Received 5 April 1988)

ABSTRACT

The Schiff bases **I**, **II** and **III** were prepared using a solid state reaction technique. Their structures were studied using elemental analysis, IR and electronic spectra. The solid state reactions of preparation were also studied by differential thermal analysis (DTA), X-ray diffraction and IR spectroscopy. The energies of activation and the orders of the reactions were determined.

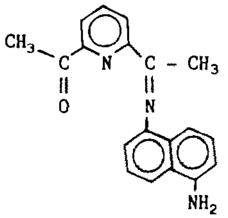
INTRODUCTION

Metal complexes of Schiff bases have contributed widely to the inorganic chemistry of chelate systems. In the complexes containing π-conjugated macrocyclic ligands the reactivity and the redox potential of the central metal are very sensitive to the nature of the chelate ring. However, few studies have been devoted to complexes involving non-symmetrical bases. In general, the known non-symmetrical diimines have been obtained by a template synthesis and have not been isolated in the free (non-coordinated) state [1–4]. Recently, Costes et al. [5] have reported a reliable procedure in solution for obtaining non-symmetrical diimines involving ethylenediamine, acetylacetone, salicylaldehyde and 2-hydroxyacetophenone. The redox potential $E_{1/2}$ related to the reaction $Co^{III} \rightarrow Co^{II}$ in the non-symmetrical complexes obtained was measured [5]. The data emphasize the usefulness of non-symmetrical ligands in affording a convenient way of varying the properties of complexes. Because of our interest in solid reactions, in this work, a reliable, simple and economic method for obtaining non-symmetrical diimines is reported using a solid state reaction. The thermal behaviour of the reaction and the products obtained are investigated.

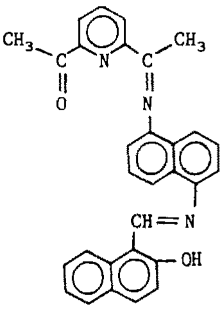
EXPERIMENTAL

Preparation of ligands

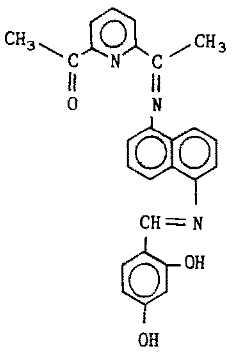
The Schiff bases **I**, **II** and **III** were prepared using a solid state reaction technique as follows.



I



II



III

Ligand **I** was prepared by mixing equimolar ratios (1 : 1) of 1,5-diaminonaphthalene and 2,6-diacetylpyridine. The mixture was heated to 90 °C for 15 min in a drying oven. A green compound was obtained. Analysis gave: C, 75.5%; H, 5.4%; N, 13.6%. Calculated for $C_{19}H_{17}N_3O$: C, 75.2%; H, 5.6%; N, 13.9%. Ligands **II** and **III** were prepared by mixing equimolar ratios (1 : 1) of ligand **I** with 2-hydroxy-1-napthaldehyde and 2,4-dihydroxybenzaldehyde respectively. The mixtures were heated to 90 °C for ligand **II** and to 110 °C for ligand **III** for 30 min. Red and orange compounds were obtained respectively. Analysis of ligand **II** gave: C, 79.4%; H, 5.1%; N, 8.9%. Calculated for $C_{30}H_{23}N_3O_2$: C, 78.7%; H, 5.0%; N, 9.2%. Analysis of ligand **III** gave: C, 72.9%; H, 5.0%; N, 9.6%. Calculated for $C_{26}H_{21}N_3O_3$: C, 73.7%; H, 5.0%; N, 9.9%.

The elemental analyses were carried out at National Research Centre Dokki, Cairo, Egypt. IR spectra were measured as KBr discs using a Perkin–Elmer 598 (4000–200 cm^{-1}) spectrophotometer. Electronic spectra were recorded in $CHCl_3$ using a Unicam SP 100 spectrophotometer. Thermal analysis was carried out using a Shimadzu XD-30 thermal analyser. X-ray powder diffraction was recorded with a Shimadzu XD-3 diffractometer using the Cu $K\alpha$ line.

RESULTS AND DISCUSSION

IR spectra

Table 1 shows the IR spectra and their assignment for ligands **I**, **II** and **III**. For ligand **I** the well-defined bands at about 3200–3410 cm^{-1}, 1690 cm^{-1} and 1635 cm^{-1} are assigned to $\nu(NH_2)$, $\nu(C{=}O)$ and $\delta(NH_2)$ respectively [6]. This indicates the formation of a "half unit" of Schiff base with a free NH_2 group (see structure above). The spectra of ligands **II** and **III** show characteristic bands at 3400 cm^{-1}, 1690 cm^{-1} and 1610 cm^{-1}. These are

TABLE 1

IR spectra of Schiff bases (cm^{-1})

Assignment	I	II	III
$\nu(NH_2)$	3410 m 3310 m 3200 m	–	–
$\nu(OH)$	–	3400 br	3400 br
$\nu(=CH)$	3060 w	3060 w	3060 vw
$\nu(C=O)$	1690 s	1690 s	1690 s
$\delta(NH_2)$	1635 vs	–	–
$\nu(C=N)$	covered by $\delta(NH_2)$	1610 vs	1610 vs
Aromatic rings	1580 m	1580 w	1580 sh
$\delta_{as}(CH_3)$	1420 m	1420 sh	1430 w
$\delta_s(CH_3)$	1350 s	1350 m	1350 m

m, medium; w, weak; s, strong; vs, very strong; sh, shoulder.

assigned to $\nu(OH)$, $\nu(C=O)$ and $\nu(C=N)$ respectively [6,7]. The disappearance of the NH_2 from the spectra of **II** and **III** (Table 1) confirms the formation of the "half unit" of the Schiff base (**I**), while the appearance of OH and C=O in their spectra confirm the formation of non-symmetric Schiff bases **II** and **III** (see structures above).

Electronic spectra

The electronic spectra of the ligands show two bands (Table 2, Fig. 1) around 315–320 nm and 365–390 nm. These are assigned to $n-\pi^*$ [6] and charge transfer (CT) [8,9]. The appearance of a new band at 365–395 nm (CT band) in the spectra of the ligands in comparison with the bands in the spectra of the reactants emphasizes the formation of ligands. Elemental analysis, IR and electronic spectra measurements confirm the structures given in the experimental section.

Thermal studies

The solid state reactions for the preparation of ligands **I**, **II** and **III** were studied using a differential thermal analyser. Figure 2 shows the thermo-

TABLE 2

The electronic spectra of the Schiff bases in $CHCl_3$ (nm)

Assignment	I	II	III
$n-\pi^*$	320 s	315 m	315 sh
CT	365 sh	390 m 475 sh	365 sh

amined, and numerical methods derived for calculating these using trap depth data. Chen suggested that, even if S was temperature dependent, i.e., $S \propto T^{-a}$ where $-2 < a < +2$, the error would not be greater than ±10%.

A second method devised by Chen is a "general-order" method [24], i.e., no assumptions are made about the reaction order. The method combines the work of several authors and a mathematical analysis. A method for calculating trap depths using T_m and the low-temperature half-width was found by linear interpolation between known formulae for the first- and second-order kinetics. A correction factor is also introduced for temperature-dependent frequency factors as in the modified Keating model.

The general equation for E introduced is

$$E = C_\alpha(2kT_m/\alpha) - b_\alpha(2kT_m)$$

where b_α, c_α are constants, and α is τ, δ or ω

$$C_\tau = 1.51 + 3(\mu'_g - 0.42);\; b_\tau = 1.58 + 4.2(\mu'_g - 0.42) \quad \text{(low } T \text{ profile)}$$

$$C_\delta = 0.976 + 7.3(\mu'_g - 0.42);\; b_\delta = 0 \quad \text{(high } T \text{ profile)}$$

$$C_\omega = 2.52 + 10.2\,(\mu'_g - 0.42);\; b_\omega = 1.0 \quad \text{(overall shape)}$$

μ'_g is the geometry or shape factor for the peak, and is equal to δ/ω, where $\delta = T_2 - T_m$, $\omega = T_2 - T_1$, $\tau = T_m - T_1$. μ'_g is a good approximation to the factor $\mu_g = n_0/n_m$ (see earlier).

Characteristic values of μ'_g were found for first-order peaks ($\mu'_g = 0.42$) and second-order peaks ($\mu'_g = 0.52$). The method using τ appears to be the most accurate due to the slight dependence of this term on kinetic order (see multiplier term on front of bracket). However, problems arise with overlapping peaks which make the determination of μ'_g difficult.

The problem of peak overlap and complex spectra was discussed by Khare and Ranade [25] who used Chen's method [24] and Lushchick's [15] method of separating peaks. Two cases were discussed:

(1) in which the position of the peak maximum is unaffected by the neighbouring peaks;

(2) in which the peak maximum is affected by neighbouring peaks.

Khare and Ranade used the initial rise method [4] for the first peak; this method is roughly independent of kinetic order. They then used Halperin and Braner's formula [16] as modified by Chen [18], to calculate E for the first- and second-order kinetics. These values were compared with those obtained by the initial rise method for each peak in turn. The nearest value of E to the initial rise value indicated the kinetic order. The analysis was started on either the high- or low-temperature side of the peak, wherever interference from other peaks was negligible.

Methods involving area measurement

Muntoni et al. [26] devised an area measurement method which is similar to that of Urbach [27] and which is derived from the work of Lushchick [15] and Anatov-Romanovski [28].

$$\ln 1/S(T)^{\alpha} = E/kT + C$$

where $S(T)$ is the area under the curve from T to T_f (the latter being the temperature at the end of the glow curve), α is a number representing kinetic order. Values of E obtained are similar to those from Muntoni et al.'s method. The model and method are complex and require well-defined thermoluminescent processes.

Isothermal decay [29,30]

In this method, the decay of thermoluminescence is measured over a period of time with the sample held at constant temperature.

For first-order kinetics

$$I(T) = n_0 S \exp(E/kT) \exp[-St \exp(E/kT)]$$

where t is the time in seconds and the other terms have been previously defined.

$$\ln I(T) = \ln n_0 S - St \exp(-E/kT) - (E/kt)$$

If $\ln I$ is plotted vs. t, a straight line of slope $S \exp(-E/kt)$ should result. If the experiment is carried out at two different temperatures, T_1 and T_2, and slopes M_1 and M_2 are measured, then

$$\ln M_1/M_2 = (1/T_1 - 1/T_2)(-E/kT)$$

and E and S can be determined free of assumptions about the temperature dependence of S. It is also claimed that many of the problems associated with peak overlap are removed [30]. This may not be correct since it is possible that at longer times other processes may become important, giving rise to changes of slope.

ELECTRON RETRAPPING

Thermal excitation of a trapped electron causes it to pass over an energy barrier. In pure materials the positive hole left by the excitation step is often the only possible combination site for the now free electron. In most materials, however, other traps of differing depths exist, and the liberated electron may become associated with one of these. Such retrapping leads to delay in the thermoluminescence, since the total process becomes multistage rather than single stage.

One obvious effect of retrapping is that the intensity of luminescence will be reduced when compared with that expected in the absence of retrapping. These effects were used by Hoogenstraten [13], who compared "built-up" curves (i.e., those produced by exciting the material under study with insufficient quanta of radiation to reach saturation) with those from the fully excited curve. In the case of a single glow peak with traps of a single depth and following first-order kinetics, it is to be expected that the built-up curves should be fully conformable with the fully excited peak and also have the same T_m value. If the kinetics are not of first order, then the concentration of filled traps will also influence the shape and position of the peak.

Garlick and Gibson [4] examined the retrapping phenomenon by:

(i) curve-fitting methods;
(ii) isothermal decay;
(iii) the use of different intensities of exciting radiation; and
(iv) the proportionality of trap depth to T_m.

In (i) the area under the glow curve is proportional to the number of electrons trapped, but the curve shape is dependent on n_0 when retrapping is important. For (ii) when retrapping is negligible, the curve height at any point is proportional to n_0 which is in turn proportional to the area under the curve at that point. The latter point only applies for a single peak due to a single-valued trap depth; (iii) using the initial rise method [4], for no retrapping

$$I = n_0 S \exp(-E/kT)$$

while for retrapping

$$I = (n_0^2/n) S \exp(-E/kT)$$

i.e., intensity is proportional to the total concentration of two types of trap; (iv) when retrapping occurs then T_m is proportional to the trap depth for fixed values of S, n_0 and β.

Hoogenstraten [13] extended Garlick and Gibson's methods and suggested that a kinetic order might be deduced as follows

$$g = I_m/I_\infty \exp E/kT$$

where g is a factor lying between (C_m/C_0) and $(C_m/C_0)^2$, C_m = the concentration of filled traps at T_m, C_0 = concentration of filled traps at the start of the experiment, I_m = intensity of T_m, and I_∞ is the intercept on the ln I axis of the initial rise plot, (C_m/C_0) and $(C_m/C_0)^2$ are the limits for the mono-molecular and bimolecular cases, respectively. Since $C_m/C_0 = 0.5$, the value of g may give an indication of the kinetics. The method is claimed to be useful if the depth distribution is narrow.

THE COMPARISON

The numerical data used in the comparison were derived from the spectrum shown in Fig. 3, which is from a sample of tricalcium aluminate, $Ca_3Al_2O_6$; this was produced as part of a TL and ESR study of various synthetic cement minerals [32]. Table 1 gives, for peak 1, the calculated trap depths, frequency factors, etc., grouped according to the method of calculation (initial rise, T_m, etc.) and also according to the "order" assumed by the equations. The Halperin and Braner calculation has been limited to the case where $\rho = 1$. The Table shows the predominance of first-order kinetics used throughout the equations. Most of these are derived in some way from Randall and Wilkins' equation. Only 30% of the equations attempt to derive second-order kinetic parameters. However, since all of the equations use the same numbers (T_m, T_1, T_2), there is no way to distinguish properly between the two mechanisms on the basis of the numbers themselves. Only Chen's general-order method and the isothermal method are capable of analysing curve shape to determine kinetic order separately from the determination of E and S. For the curve in Fig. 3, this analysis gives a μ'_g value of 0.42, which strongly suggests a first-order process. This being the case, all of the second-order values can be neglected.

Examination of the first-order values indicates a considerable range of trap depths (0.83–1.55 eV). Those methods using T_m give a range of values whereas those using peak shape give a remarkably uniform value in the middle of the range. These latter methods, therefore, have a double ad-

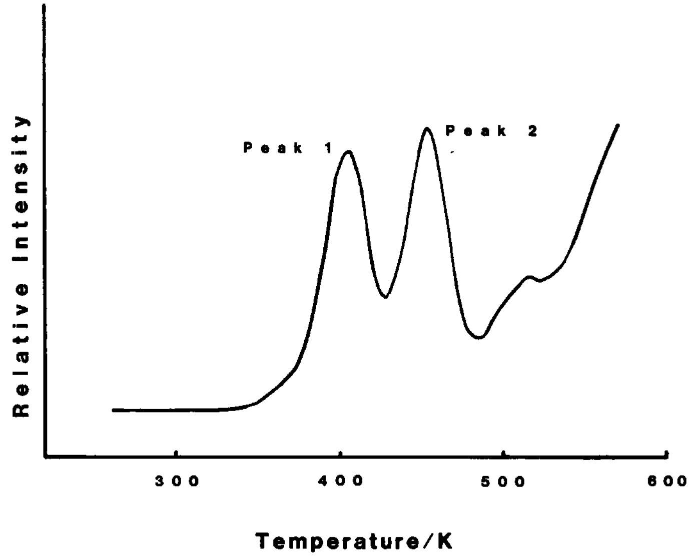


Fig. 3. Experimental glow curve for synthetic tricalcium aluminate.

TABLE 1

Kinetic parameters derived from the spectrum of tricalcium aluminate

Peak 1	$E(1)$	$S(1)$	$E(2)$	$S(2)$	E General	S	μ'_g
Initial rise [4]	0.83						
Peak maximum							
Randall and Wilkins [8]	1.55	10*E*13	assumed				
Booth [9], Bohun [12]	1.02	10*E*11					
Schon [11]	0.96						
Hoogenstraten [13]	1.44	10*E*17					
Peak shape							
Lushchick [15]	1.07		1.87				
Halperin and Braner [16]	1.12		2.29				
Chen [18]	1.11	10*E*12	1.59	10*E*14			0.40
Grossweiner [19]	1.13	10*E*12					
Keating [21]	1.15						
E_τ					1.14		
E_δ					1.11	10*E*12	0.42
E_ω					1.09		
Khare and Ranade [25]	1.12	10*E*12	1.33				
Peak area [26]	0.91		1.76				
Isothermal [29,30]	0.97	10*E*15					

vantage, in that some indication of "order" is given and, as a group, they give consistent values from a single set of numbers. They also use a number of ways to arrive at a result, i.e., T_m, high- and low-temperature profiles, and, therefore, the consistency is double encouraging. If the consistency of these analyses is good, what of the accuracy of the trap depth they indicate?

The high values are produced from Hoogenstraten's [13] and Randall and Wilkins' models [8]. The former is generally assumed to be almost independent of mechanistic assumptions, while the latter is dependent on an assumed value for S. The value assumed in this case is 10^{13}. If these high values are correct then lower values can be accounted for by postulating a range of trap depths, rather than a single value. However, closer analysis using Garlick and Gibsons's method [4], suggests that if such a range exists, it is narrow. It is therefore unlikely that this is the correct reason for the lower values. Hoogenstraten's analysis requires absolute intensity values which were not used in this case. Both of these trap depth values were calculated by using different heating rates which should produce a shift in T_m (see Appendix). The variation in T_m was small and this may cause a large error in the trap depth.

The initial rise method produced a low value (0.83 eV). The shortcomings of this method have already been pointed out. Repeated runs at higher photomultiplier sensitivities gave a wide range of trap depths, down to 0.02 eV, which does not argue well for the accuracy of the value given here. The peak area method is known to be inaccurate when overlapping peaks are present, while the isothermal method suggested an order slightly greater than unity overall. At low levels of recombination the order was close to unity, but increased to about 1.5 at 50% recombination. This method is also known to be inaccurate when overlapping peaks are present. If the degree of overlap present in the glow curve shown in Fig. 3 does contribute to the error in the derived trap depths, this is an indication of the limits in the methods used. It is possible, therefore, to suggest reasons for rejecting the high and low values of trap depth, but these are not overwhelmingly convincing.

A similar analysis on peak 2 in Fig. 3 indicates a first-order process with a trap depth of 1.2 eV. This value is subject to the same arguments and difficulties as is peak 1, except that the initial rise method produces a very high value of 2.2 eV, due to peak overlap on the leading edge.

CONCLUSIONS

It can be seen that, for the relatively simple glow curve shown in Fig. 3, to decide on an order for the thermoluminescence process is straightforward, but it is much more difficult to decide on the numerical value of the trap depth. Obviously, part of this difficulty lies in the relatively large number of models considered here. Most published work on TL and trap depth studies seems to use only a single model [32]. As with much thermal methods work, there is a trade-off between time spent on analysis and the number of assumptions made. If a single method is to be used in thermoluminescence, then the Chen general-order method is probably the most useful, in that reaction order, trap depth and frequency factor can be determined. However, as is the case for most of the models in the literature, a single order of reaction is assumed to operate throughout the whole process. This may not be the case (as is suggested here), and the isothermal method will generate all of the parameters required, and will also give information on fractional order processes, but only at the expense of time taken to follow several runs at constant temperature.

APPENDIX

To account for a single TL peak, Halperin and Braner [16] devised a set of three simultaneous equations

(a) $I = -\mathrm{d}m/\mathrm{d}t = A_{\mathrm{m}}Mn_{\mathrm{c}}$

i.e., intensity of radiation is equal to the decay of holes, which is again proportional to the recombination of holes and free electrons.

(b) $-\mathrm{d}n/\mathrm{d}t = Sn \exp(-E/kT) - An(N-n)n_\mathrm{c}$

i.e., decay of electrons in traps equals rate of ejection of trapped electrons less those electrons being retrapped.

(c) $\mathrm{d}n_\mathrm{c}/\mathrm{d}t = \mathrm{d}m/\mathrm{d}t - \mathrm{d}n/\mathrm{d}t$

i.e., change of concentration of free electrons = change in number of holes less the change in the number of trapped electrons, where N = concentration of traps (cm^{-3}); n = concentration of electrons in traps (cm^{-3}); n_c = concentration of free electrons in the conduction band (cm^{-3}); A_m and A_n are the recombination and retrapping probabilities (cm^3 sec^{-1}), and m is the concentration of holes in luminescent centres.

Assuming that the number of free electrons is low ($n_\mathrm{c} \ll n$) but reasonably constant ($\mathrm{d}n_\mathrm{c}/\mathrm{d}t \ll \mathrm{d}n/\mathrm{d}t$) then

$$I = -\mathrm{d}m/\mathrm{d}t = Sn \exp(-E/kt) A_m m/[A_\mathrm{m}M + A_\mathrm{n}(N-n)]$$

If $A_\mathrm{m}M \ll A_\mathrm{n}(N-n)$, i.e., retrapping is negligible, this equation reduces to

$$I = -\mathrm{d}m/\mathrm{d}t = Sn \exp(-E/kT) \tag{1}$$

which is Randall and Wilkins' equation for first-order kinetics.

It follows, also, that if retrapping is dominant, then

$$A_\mathrm{n}(N-n) \gg A_\mathrm{m}M; \; N \gg n$$

then

$$I = -\mathrm{d}n/\mathrm{d}t = (SA_\mathrm{m}/NA_\mathrm{n})n^2 \exp(-E/kT)$$

which is the equation for second order kinetics with

$$S = (SA_\mathrm{m}/NA_\mathrm{n})$$

It follows, therefore, that the appearance of first- or second-order kinetics is only in special, limiting cases and that other intermediate "orders" may be observed.

In TL, a rising-temperature programme is commonly used: $T(t) = T_0 + \beta t$, where β = heating rate (K s^{-1}). It is possible to integrate eqn. (1) between the temperature limits T_i and T_f and the results represent the TL curve

$$I(T) = n_0 S \exp(-EkT) \exp\left[-\int_{T_\mathrm{i}}^{T_\mathrm{f}} (S/\beta) \exp(-EkT')\mathrm{d}T'\right] \tag{2}$$

Solution of this equation is laborious and the equations given here represent other approaches to its solution, e.g., at T_m: $\mathrm{d}I/\mathrm{d}T = 0$. This gives

$$\beta E/(kT_\mathrm{m}^2) = S \exp(-E/kT_\mathrm{m}) \tag{3}$$

which, when rearranged, is Randall and Wilkins' equation. Rearrangement of eqn. (3) gives

$$\beta E/Sk = T_m^2 \exp(-E/kT_m)$$

which indicates that as β varies T_m must also vary; and this forms the basis of the methods which use variation in heating rate, β, to determine E without the requirement of S.

REFERENCES

1 A.B. Carel and D.K. Cabbiness, Lab. Pract., 33 (1984) 88.
2 See D.J. McDougall (Ed.), Thermoluminescence of Geological Materials, Academic Press, New York, 1968.
3 D. Curie, Luminescence in Crystals (Translated by G.F.J. Garlick), Wiley, New York, 1973.
4 G.F.J. Garlick and A.F. Gibson, Proc. Phys. Soc., 60 (1948) 574.
5 M.C. Ball and C.M. Marsh, unpublished results.
6 See P. Braunlich, J. Appl. Phys., 38 (1967) 2516, and refs. therein; C. Heake, J. Opt. Soc. Am., 47 (1957) 694.
7 P.L. Land, J. Phys. Chem. Solids, 27 (166) 509.
8 J.T. Randall and M.H.F. Wilkins, Proc. R. Soc. London, Ser. A, 184 (1945) 366.
9 A.H. Booth, Can. J. Chem., 32 (1954) 214.
10 A. Wrezeskinska, Acta Phys. Pol., 15 (1956) 151.
11 M. Schon, Tech.-Wiss. Abh. Osram-Ges., 7 (1958) 175.
12 A. Bohun, Czech J. Phys., 4 (1954) 91.
13 W. Hoogenstraten, Philips Res. Rep., 13 (1958) 515.
14 P. Kivits, J. Lumin, 16 (1978) 119.
15 C.B., Lushchick, Dokl. Akad. Nauk. SSSR., 101 (1955) 641.
16 A. Halperin and A.A. Braner, Phys. Rev., 117 (1960) 408.
17 P.J. Kelly and M.J. Laubitz, Can. J. Phys., 45 (1967) 311.
18 R. Chen, J. Appl. Phys., 40 (1969) 570.
19 L.I. Grossweiner, J. Appl. Phys., 24 (1953) 1306.
20 G.A. Dussell and R.H. Bube, Phys. Rev., 155 (1967) 764.
21 P.N. Keating, Proc. Phys. Soc., 78 (1961) 1408.
22 G. Bemski, Phys. Rev., 111 (1958) 1515.
23 M. Lax, J. Phys. Chem. Solids, 8 (1959) 66.
24 R. Chen, J. Electrochem. Soc., Solid State Sci., 116 (1969) 1254.
25 R.P. Khare and J.D. Ranade, Phys. Status Solidi, A, 32 (1975) 221.
26 C. Muntoni, A. Rucci and A. Sepi, Ric. Sci., 38 (1968) 762.
27 F. Urbach, Ber. Akad. Wiss. Wien, Abt. IIa, 139 (1930) 363.
28 V.V. Anatov-Romanovski, Izv. Akad. Nauk. SSSR. Fiz. Ser., 10 (1946) 477.
29 G.F.J. Garlick, Luminescent Materials, Oxford University Press, Oxford, 1949.
30 P.D. Townsend, C.D. Clark and P.W. Levy, Phys. Rev., 155 (1967) 908.
31 C.E. May and J.A. Partridge, J. Chem. Phys., 40 (1964) 1401.
32 C.M. Marsh, Ph.D. Thesis, Loughborough University of Technology, 1980.