KINETICS OF FLUORESCENCE AND PHOSPHORESCENCE OF SOLIDS

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Luminescence is the non equilibrium phenomenon of excess emission over and above the thermal emission of a body, in which emission has a duration considerably exceeding the period of light oscillations [1,2]. In luminescence system, the output is light energy and input may be any form of energy like photon energy, electrical energy, chemical energy, etc. Thus, according to the mode of excitation the luminescence has been classified into different types such as photoluminescence, electroluminescence, cathodoluminescence, chemiluminescence, bioluminescence, thermoluminescence, mechanoluminescence, sonoluminescence, lyoluminescence, crystalloluminescence, etc. Fluorescence and phosphorescence are two special aspects of luminescence. The former deals with the emission of light from the materials spontaneously in time ranging less than 10^{-8} second after excitation, whereas latter deals with the emission of light from material till long time, that is, more than 10^{-8} second after the, cessation of excitation.

The present paper reports the theoretical approach made on the kinetics of t he fluorescence and phosphorescence and makes the comparison between the theoretical and experimental results.

Kinetics of Fluorescence and Phosphorescence

(i)   Monomolecular fluorescence

In monomolecular fluorescence only one type of carrier either electrons or holes are responsible .The process can be understood involving generation and recombination of carriers. The rate of generation g of carriers may be expressed as

$$g = \varepsilon_L(\lambda)\, I_L \qquad\qquad (1)$$

where $\varepsilon_L(\lambda)$ is the absorption coefficient of the phosphor and I_L is the intensity of incident light.

If α_1 and α_2 are the radiative and non-radiative transition rate-constants for the monomolecular recombination of electrons in the conduction band or holes in the valence band or singlet excitons, then the rate equation can be written as

$$\frac{dn}{dt} = g - \alpha_1 n - \alpha_2 n = g - \alpha n \qquad\qquad (2)$$

where $\alpha = (\alpha_1 + \alpha_2)$ and n is the number of carriers in the respective band at any time t.

Integrating equation (2) and taking n=0 at t=0, we get

$$n = \frac{g}{\alpha}[1 - \exp(-\alpha\, t)] \qquad\qquad (3)$$

For $\alpha t \gg 1$, that is in equilibrium we get,

$$n = n_o = \frac{g}{\alpha} \qquad\qquad \text{or} \qquad g = \alpha\, n_o$$

Thus, the fluorescence quantum efficiency η may be expressed as

$$\eta = \frac{\text{Rate of radiative recombination of carriers}}{\text{Rate of total recombination of carriers}}$$

or, $\eta = \alpha_1 n / (\alpha_1 + \alpha_2)$ n $= \alpha_1 / (\alpha_1 + \alpha_2)$ (4)

Using Eqs.(3), the rising portion of the fluorescence intensity, saturation value of the fluorescence intensity and the decay of monomolecular fluorescence intensity can be expressed as

$$I_F^r = \alpha_1 n = \alpha_1 g / (\alpha_1 + \alpha_2) [1 - \exp(-\alpha\, t)] \tag{5}$$

$$I_F^s = \alpha_1 g / (\alpha_1 + \alpha_2) = \eta g \tag{6}$$

And, $\quad I_F^d = \eta g \exp\left[-\frac{(t - t_c)}{\tau}\right]$ (7)

where $\tau = \dfrac{1}{\alpha}$, is the lifetime of carriers in the respective band and τ_c is the time at which the light source is turned off.

As $\alpha = 10^8 \text{ s}^{-1}$, $\tau = 10^{-8}$ s

(ii) Monomolecular phosphorescence

In this case, the rise, saturation and decay of monomolecular phosphorescence intensity are be given by

$$I_P^r = (\alpha_1 \alpha_3 g / \beta^2)[1 - \exp(-\gamma\, t)] \tag{8}$$

$$I_P^s = (\alpha_1 \alpha_3 g / \beta^2) \tag{9}$$

and, $\quad I_P^d = (\alpha_1 \alpha_3 g / \beta^2) \exp\left[-\frac{(t - t_c)}{\tau}\right]$ (10)

where $\beta = (\alpha_1 + \alpha_2 + \alpha')$, α' is the rate constant for the transfer of charge carriers to the traps $\tau_t = 1/\gamma$, is the lifetime of charge carriers in traps, and

(iii)   Bimolecular luminescence

In this case, the rise, saturation and decay of bimolecular luminescence intensity are given by

$$I_F^r = \frac{dn}{dt} = \eta\gamma(g/\gamma)\tan h^2 \sqrt{g\gamma t} \tag{11}$$

$$I_F^s = \eta g \tag{12}$$

and, $\quad (I_F^r / I_F^d)^{1/2} = \left[\sqrt{g\gamma}(t - t_c) + 1\right]$ (13)

A comparison is made between the theoretical and experimental results, whereby a good agreement is found.

References

1] D. R. Vij(Ed.) Luminescence of Solids, Plenum Press, New York(1998).

[2] H.S. Nalwa and L.S. Rohwer, Handbook of Luminescence Display Materials and Devices, American Scientific Publishers, CA, USA (2003).