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Phenomena of fluorescence and phosphorescence

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Abstract
The present paper introduces the basic concepts of luminescence via defining, classifying and enumerating the applications of various types of luminescence. Two key aspects of luminescence- fluorescence and phosphorescence - have been dealt with theoretically for monomolecular and bimolecular materials. The rate equations of these materials have been derived and discussed. The rise and decay of luminescence intensities for both monomolecular and bimolecular materials have been discussed.

Keywords: Fluorescence, phosphorescence, bimolecular materials

INTRODUCTION

There are two types of light sources, namely, the hot light sources and cold light sources. The sun, hot iron, burning piece of coal, tungsten filament, etc. are examples of hot light sources. Oscilloscope screen, television screen, light emitting diodes, fluorescent tubes, self-luminous watch dial etc. are examples of cold light sources. The phenomenon of cold emission of light is known as luminescence. In other words, any type of emission except incandescent is called luminescence. Scientifically, 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 [1-5].

TYPES OF LUMINESCENC

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 in the following ways:

(I) **Photoluminescence:** It is produced by absorption of photons with energy ranging from a few electron volts to several electron volts, for example, form infrared to ultraviolet radiation.

(II) **Electroluminescence:** It is produced by the AC or DC voltage applied to the luminescence substance.

(III) **Cathodoluminescence:** It is produced by high energy electrons or cathode rays.

(IV) **Chemiluminescence:** It is produced by the application of energy released by chemical reaction.

(V) **Bioluminescence:**It is produced by the application of energy released by bio-chemical reaction.

(VI) **Thermoluminescence:** It is produced when a previously irradiated substance is warmed to a moderate temperature, which releases the trapped charge carriers, which form radiative transition by recombination at luminescence centre.

(VII) **Mechanoluminescence:** It is produces due to mechanical deformation of solids, for example grinding, stretching, cleaving, scratching, bending etc. Here the mechanical energy induces the emission of light.

(VIII) **Sonoluminescence:** It is produced by ultrasonic waves.

(IX) **Lyoluminescence:** It is produced during dissolution of certain previously irradiated crystals (By high energy radiation in aqueous solutions).

(X) **Crystalloluminescence:**It is produced during the growth of crystals from solutions.

FLUORESCENCE AND PHOSPHORESCENCE

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 then 10^{-8} after excitation, whereas latter deals with the emission of light from material till long time that is more than 10^{-8} second after the excitation. Fig.1 shows the different steps involved in the occurrence of fluorescence and phosphorescence in luminescent materials.

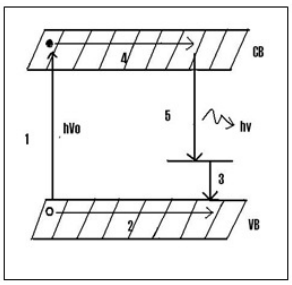

Fig.1(a) Fluorescence

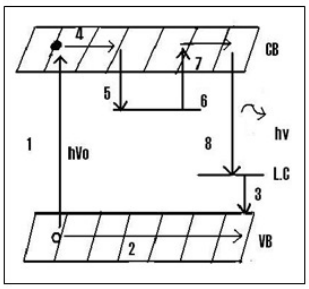

Fig.1 (b) Phosphorescence

RISE AND DECAY OF FLUORESCENC AND PHOSPHORESCENCE

Monomolecular Fluorescence

In monomolecular fluorescence only one type of carrier either electron or holes are responsible .The process can be understood

involving generation and recombination of carriers. The rate of generation g of carriers may be express as

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

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 of electrons in the conduction band or holes in the valance band or singlet excitons, then the rate equation may be written as

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

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

$$n=\frac{g}{\alpha}[1 - e^{-\alpha t}] \quad (3)$$

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

$n = n_o = \frac{g}{\alpha}$ or $g = \alpha n_o$

Thus the fluorescence quantum efficiency η may be expressed as

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

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

Rise of monomolecular fluorescence intensity

Using equation (3) the rising portion of the fluorescence intensity may be expressed as

$$I_F{}^r = \alpha_1 n = \alpha_1 g/ (\alpha_1+\alpha_2)\left[1 - e^{(-\alpha t)}\right] \quad (5)$$

The above equation shows that initially the fluorescence intensity rise linearly with time and then it attain a saturation value given by

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

Decay of monomolecular fluorescence intensity

When the source of excitation is turned off at $t = t_C$ then g will become zero and thus equation (2) may be written as

$$\frac{dn}{dt} = - \alpha n \quad (7)$$

Integrating equation (7) and taking $n=\frac{g}{\alpha}$, equation (3) at $t = t_C$, we get

$$n=\frac{g}{\alpha}\left[-e^{-\alpha(t-t_c)}\right] \quad (8)$$

Thus the decay of fluorescence intensity may be given by

$$I_F{}^d=\alpha_1 n=\frac{\alpha_1}{\alpha} g\left[-e^{-\alpha(t-t_c)}\right] \text{ Or } I_F{}^d= \eta g\left[-e^{-\left(\frac{t-t_c}{\tau}\right)}\right] \quad (9)$$

where $\tau = \frac{1}{\alpha}$ is the lifetime of carriers in the respective band.

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

Equation (9) indicates the exponential decrease of fluorescence intensity with decay time τ. It is to be noted that the decay time of fluorescence depends on the lifetime of carriers in the respective band.

MONOMOLECULAR PHOSPHORESCENCE

When a phosphorescent material is exposed to light, free electrons are generated in conduction band and holes are generated in valance band. If electrons or holes are trapped in a metastable state then their subsequent thermal release and recombination may give rise to delayed luminescence that is phosphorescence. If α_3 is the rate constant for the transfer of carriers to the metastable states or traps, then we can write the rate equation for the change in number of carriers in the respective band may be written as

$$\frac{dn_1}{dt} = g - \alpha_1 n_1 - \alpha_2 n_1 - \alpha_3 n_1$$

$$\text{Or } \frac{dn_1}{dt} = g - \alpha n_1 - \alpha_3 n_1 = g - \beta n_1 \quad (10)$$

where $\beta = (\alpha_1+\alpha_2+\alpha_3)$ and n_1 is the number of carriers in the respective band at any time t.

Integrating equation (10) and taking $n_1 = 0$, at t = 0, we get

$$n_1 = g \left[1 - e^{(-\beta t)}\right] \quad (11)$$

If γ is the rate constant for the release of carriers from the traps, then we can write the following rate equation

$$\frac{dn_2}{dt} = \alpha_3 n_1 - \gamma n_2 = \alpha_3 n_1 - n_2/\tau_t \quad (12)$$

where $\tau_t = 1/\gamma$ is the lifetime of carriers in traps, and n_2 is the number of electron in the traps at any time t.

From equations (11) and (12), we get

$$\frac{dn_2}{dt} = \frac{\alpha_3}{\beta} g\left[1 - e^{(-\beta t)}\right] - \gamma n_2 \quad (13)$$

Integrating equation (13) and taking $n_2 = 0$, at t = 0, we get

$$n_2 = \frac{\alpha_3}{\beta\gamma} g\left[1 - e^{(-\gamma t)}\right] + \frac{\alpha_3}{\beta(\beta-\gamma)} g\left[1 - e^{(-\beta t)} - e^{(-\gamma t)}\right] \quad (14)$$

For $\beta \gg \gamma$, equation (14) may be expressed as

$$n_2 = \frac{\alpha_3}{\beta\gamma} g\left[1 - e^{(-\gamma t)}\right] \quad (15)$$

Rise of monomolecular phosphorescence intensity

The rise of monomolecular phosphorescence intensity may be given by

$I_{P^r} = \eta\gamma\, n_2 = (\alpha_1\gamma\alpha_3\, g/(\alpha_1+\alpha_2+\alpha_3)\beta\gamma)\left[1 - e^{(-\gamma t)}\right]$

Or

$$I_{P^r} = (\alpha_1\alpha_3\, g/\beta^2)\left[1 - e^{(-\gamma t)}\right] \quad (16)$$

The above equation indicates that initially the phosphorescence intensity should rise linearly with time and then it should attain a saturation value given by

$$I_{P^s} = (\alpha_1\alpha_3\, g/\beta^2) \quad (17)$$

Decay of monomolecular phosphorescence intensity

when the light source turned off at t = t_C then g = 0 and equation (10) becomes

$$\frac{dn_1}{dt} = -\beta\, n_1 \quad (18)$$

Integrating equation (18) and taking $n_1 = g/\beta$ [from equation (11)] at t = t_C , we get

$$n_1 = (g/\beta)\left[-e^{-\beta(t-t_C)}\right] \quad (19)$$

Now we can write the following rate equation

$$\frac{dn_2}{dt} = \frac{\alpha_3}{\beta} g\left[e^{(-\beta(t-t_C)}\right] - \gamma n_2 \quad (20)$$

Integrating equation (20) taking $n_2 = \frac{\alpha_3}{\beta\gamma} g$ [from equation (15)], we get

$$n_2 = -\frac{\alpha_3}{\beta(\beta-\gamma)} g\left[e^{\{-\beta(t-t_C)\}}\right] + \frac{\alpha_3}{\beta\gamma} g\left[e^{\{-\gamma(t-t_C)\}}\right] + \frac{\alpha_3}{\beta(\beta-\gamma)} g\left[e^{\{-\gamma(t-t_C)\}}\right] \quad (21)$$

For $\beta \gg \gamma$ equation (21) may be written as

$$n_2 = \frac{\alpha_3}{\beta\gamma} g\left[e^{\{-\gamma(t-t_C)\}}\right] \quad (22)$$

Thus the decay of phosphorescence intensity may be express as

$I_{P^d} = \eta\gamma\, n_2 = (\alpha_1\gamma\alpha_3\, g/(\alpha_1+\alpha_2+\alpha_3)\beta\gamma)\left[1 - e^{\{-\gamma(t-t_C)\}}\right]$

$$I_{P^d} = (\alpha_1\alpha_3\, g/\beta^2)\left[e^{\frac{-(t-t_C)}{\tau}}\right] \quad (23)$$

Equation (23) indicates the exponential decrease of phosphorescence intensity with decay time $\tau_t = 1/\gamma$. As the lifetime of carrier in the traps is given by $\tau_t = \tau_0 e^{\left(\frac{E_a}{KT}\right)}$, (where E_a is the trap depth, K is the Boltzmann constant and T is the temperature), by changing E_a using different types of dopants, by the phosphorescent materials having any decay time can be tailored.

BIMOLECULAR LUMINESCENCE

In this case, luminescence is produced during the radiative recombination of electrons and holes; here the recombination rate is proportional to n^2. If γ is the bimolecular recombination coefficient, then we can write the following rate equation

$$\frac{dn}{dt} = g - \gamma n^2 \quad (24)$$

Equation (24) may be written as

$$\frac{dn}{g-\alpha n^2} = dt = \frac{dn}{\alpha\left(\frac{g}{\alpha}\right)-n^2} = dt \quad (25)$$

Integrating equation (25) and taking n = 0, at t = 0, we get

$$n = \sqrt{\frac{g}{\gamma}} \tanh\sqrt{g\gamma t} \quad (26)$$

Rise of bimolecular luminescence intensity

If η is the efficiency of the radiative electron-hole recombination, then the rise of luminescence intensity may be expressed as

$$I_{F^r} = \frac{dn}{dt} = \eta\gamma(g/\gamma)\ \tanh^2\sqrt{g\gamma t} \quad (27)$$

The above equation shows that when a luminescent material is exposed to light, initially the luminescence intensity should increase quadratically with time and finally it should attain a saturation value given by the expression

$$I_{F^s} = \eta\, g \quad (28)$$

Decay of bimolecular luminescence intensity

When the light source will be switched off at t = t_C , the rate of generation of carriers g will become zero and equation (24) may be expressed as

$$\frac{dn}{dt} = -\gamma n^2 \quad (29)$$

The integration of equation (29) for $n = \sqrt{\frac{g}{\gamma}}$ [equation (26)] , at t = t_C , gives

$$n = \frac{\sqrt{\frac{g}{\gamma}}}{[\sqrt{g\gamma}(t-t_C)+1]} \quad (30)$$

Thus the luminescence intensity may be given by

$$I_{F^d} = \eta\gamma\, n^2 = \frac{\eta g}{[\sqrt{g\gamma}(t-t_C)+1]^2} \quad (31)$$

For $\sqrt{g\gamma}(t-t_c) \gg 1$, equation (31) may be written as

$$I_{F^d} = \frac{\eta}{[\gamma(t-t_C)]^2} \quad (32)$$

The above equation shows that in the case of bimolecular luminescence, the decay of luminescence intensity should follow the power law.

From equation (28) and (31), we get

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

Or $(I_F^r/I_F^d)^{1/2} = \left[\sqrt{g\gamma}(t-t_c)+1\right]$ (33)

The above equation shows that plot of $(I_F^r/I_F^d)^{1/2}$ versus $(t - t_c)$, should be a straight line with a positive slope $\sqrt{g\gamma}$ and intercept 1 on the y-axis. Thus if g is known, γ can be determined from the slope.

APPLICATIONS OF LUMINESCENCE

Phosphors are used in fluorescent tubes, energy saving lamps, etc. Semiconductor luminescent materials capable of exhibiting recombination luminescence are used to fabricate LED's and semiconductor lasers. Luminescent material are used in fabricating the detectors for ultraviolet rays, x-rays, infrared rays etc. Light emitting diodes and thin film electroluminescence are used for numeric and alphanumeric displays. Using LED's and thin film EL displays flat panel televisions have been designed whose shape is similar so that of a picture frame. Phosphors are used in the fabrication of x-ray intensifying screens. X-ray fluorescence is used in non-destructive testing of rocket and ship materials. Bioluminescence in used in the detection of bacterial infection and in the dose determination for the treatment of cancer tumor. Mechanoluminescence is used in the design of fuse-system for war-head and also in damage sensors. Luminescent materials are used in the design of several type of sensors.

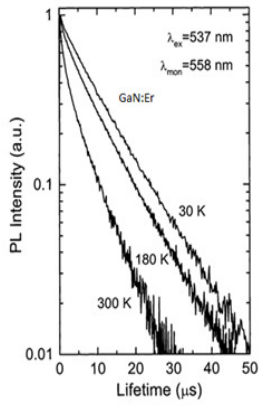

Fig. 1-Luminescence lifetime curves at 30, 180, and 300 K.

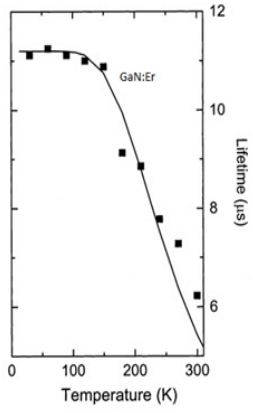

Fig 2-Temperature dependence of the luminescence lifetime from 15 to 300 K.

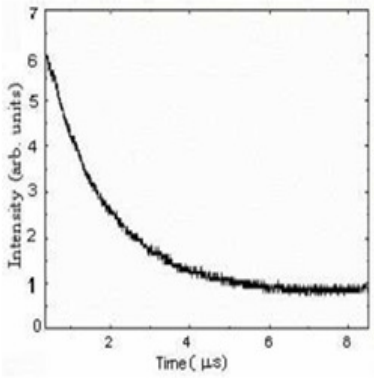

Figure 3. Hyperbolic type of luminescence decay curve for ZnS:Mn (0.05%): Co (0.05%) at room temperature showing three overlapping exponentials.

CONCLUSIONS

Fluorescence and Phosphorescence are two special aspects of luminescence. These two phenomenon find several applications in domestic appliances, industrial , technological and scientific devices. For the development of fluorescent and phosphorescent materials, the basic knowledge of fluorescence and phosphorescence are essential. In the present study theories of monomolecular fluorescence and monomolecular phosphorescence and bimolecular luminescence are discussed, which are capable to explain satisfactory the rise and decay of luminescence of a wide variety of materials.

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