

Decay characteristics of SrS :Nd phosphors

M G PATIL and R D LAWANGAR*

Department of Physics, Rajaram College, Kolhapur 416 004, India

*Department of Physics, Shivaji University, Kolhapur 416 004, India

MS received 3 December 1979; revised 18 April 1980

Abstract. The phosphorescence decay of a series of strontium sulphide microcrystalline phosphors prepared with varying amounts of neodymium as an activator has been studied at room temperature. The decay obeys the relation $I=I_0 t^{-b}$ with b lying between 0.35 and 0.98. The trap depths have been evaluated by peeling off $\log I-t$ curves. The results show that the distribution of trap levels is likely to be quasi-uniform and the process of retrapping during luminescence is negligible.

Keywords. SrS:Nd phosphors; decay characteristics.

1. Introduction

The phenomenon of phosphorescence decay and thermoluminescence are used to investigate the presence of trapping levels in a phosphor due to their experimental simplicity and the method involved. These studies also provide information about the type of kinetics and hence about the process of retrapping during luminescence. Recently, such studies have been reported by Lawangar and Narlikar (1975a) on CaS:Bi:Pd phosphors and by Sharma and Singh (1968) on SrS:Zr phosphors. In this paper we report the phosphorescence decay measurements carried on SrS:Nd phosphors. The object of the investigation was to understand the type of kinetics involved in the phosphorescence decay and to obtain information about the distribution of trapping levels. The effect of incorporation of activator on trapping levels is also discussed.

2. Experimental

The SrS:Nd phosphors containing varying concentrations of neodymium were prepared by the method of thermal reduction of strontium sulphate (Paliwal and Sinha 1976). Na_2SO_4 (AR grade) was used as a flux. The samples studied are listed in table 1.

The samples were excited to saturation using an ultraviolet source which emitted predominantly the 3650 Å Hg doublet. The decay intensity was measured using a photomultiplier tube RCA 931 A. The output of the photomultiplier was fed to a sensitive automatic plotter on which the decay curve was recorded. The decay measurements were carried out at room temperature (301°K).

Table 1. Decay constant, correlation coefficient, trap depth as calculated from decay curves for SrS:Nd phosphors.

Sample No.	Concentration of Nd --- gm. atom per mole SrS	Decay constant ($-b$)	Correlation coefficient ($-r$)	Trap depth from peeling off of decay curves (eV)		
				Slowest exponential E_1	Middle exponential E_2	Fastest exponential E_3
S_{11}	—	0.45	0.84	0.69	0.62	0.58
S_3	0.75×10^{-3}	0.71	1.00	0.67	0.61	0.57
S_4	1.0×10^{-3}	0.72	0.99	0.68	0.62	0.58
S_5	2.5×10^{-3}	0.66	1.00	0.69	0.62	0.58
S_6	5.0×10^{-3}	0.48	0.98	0.65	0.61	0.58
S_7	7.5×10^{-3}	0.89	0.99	0.65	0.61 <td 0.57	
S_8	1×10^{-2}	0.35	0.98	0.71	0.62	0.57
S_9	2×10^{-2}	0.98	0.99	0.68	0.61	0.58
S_{10}	3×10^{-2}	0.67	0.98	0.69	0.61	0.58

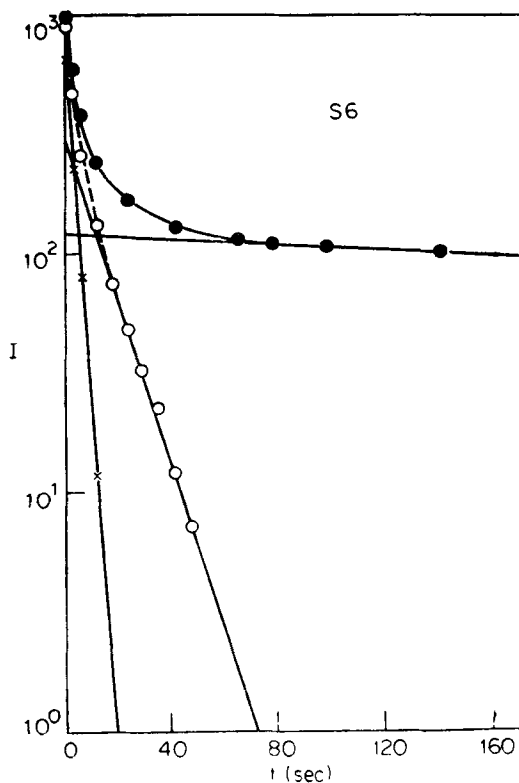


Figure 1. Plot of log of intensity of phosphorescence decay versus time—peeling off decay curve.

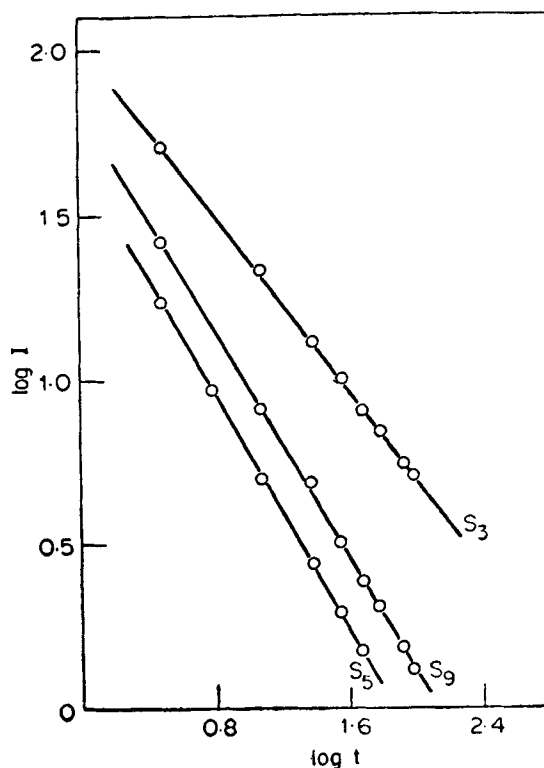


Figure 2. Log intensity versus log time plots for various samples.

3. Results and discussion

3.1. Mode of decay

To examine the nature of decay the logarithm of intensity (I) was plotted as a function of time (t). The curves show deviation from the straight line eliminating the possibility of exponential decay (figure 1). However the plots of $\log I$ versus $\log t$ are almost linear indicating the decay to be hyperbolic. Some of the typical plots obtained for samples containing different concentrations of Nd are shown in figure 2. To estimate the degree of linearity between $\log I$ and $\log t$, the correlation coefficient (r) was calculated by the method of least squares. The calculated value of r for all samples is close to unity with a negative sign indicating decrease of $\log I$ with increase of $\log t$. Moreover, this also indicates a fairly close linear relationship between $\log I$ and $\log t$.

The hyperbolic decay observed could be represented by the equation of the form (Randall and Wilkins 1945)

$$I = I_0 t^{-b}, \quad (1)$$

where I is the intensity at time t , I_0 is at the beginning of the decay. b , the decay constant indicates the decay rate and provides information about the relative popu-

lation of traps at various depths. This value was calculated by the method of least squares, using the relation

$$b = \frac{\Sigma x \Sigma y - n \Sigma xy}{(\Sigma x)^2 - n \Sigma x^2} \quad (2)$$

where $x = \log t$, $y = \log I$, and n is the number of observations. The values thus obtained are listed in table 1. The b values vary from 0.35 to 0.98 with added activator concentration. However the variation is not systematic. For all samples studied b is less than unity implying that the distribution of trapping levels is not uniform but likely to be quasi-uniform (Lawangar and Narlikar 1972).

3.2. Activation energies

The hyperbolic decay can be explained on the basis of the monomolecular superposition theory suggested by Randall and Wilkins (1945). Such a decay results due to superposition of various exponentials corresponding to different traps and is expressed by the equation.

$$\begin{aligned} I &= I_0 t^{-b}, \\ &= I_{01} \exp(-p_1 t) + I_{02} \exp(-p_2 t) + \dots \\ &\dots + I_{0n} \exp(-p_n t), \dots \end{aligned} \quad (3)$$

where I_{0n} is the phosphorescence intensity due to electrons in the traps of energy En , $p_n = S \exp(-En/kT)$ is the probability of an electron escaping from a trap, K the Boltzmann constant, and S is the escape frequency factor. It is possible then to split each decay curve into a set of exponentials by the 'peeling off' procedure as has been followed by Bube (1950). In the present case all the decay curves were split into three exponentials. An example of the procedure is illustrated in figure 1 where each straight line corresponds to each exponential and is a plot of $\log I$ versus t for the decay resulting from traps having single depth. Trap depths corresponding to these exponentials were calculated from slopes of straight lines. The E values thus obtained are summarised in table 1. The S values used in the above calculations were taken from the thermoluminescence studies carried on the same samples and were of the order of 10^9 sec^{-1} . (Patil and Lawangar 1980).

From table 1 it is seen that the trap depths corresponding to the slowest exponential vary from 0.65 to 0.71 eV, the middle exponential from 0.61 to 0.62 eV and the fastest exponential from 0.57 to 0.58 eV with the addition of an activator. The variation observed in E values is negligibly small and also unsystematic. This implies that the addition of the activator does not introduce new trapping levels but only modifies the relative importance of traps responsible for the phosphorescence decay. Thus the trapping levels in the present phosphor system may be attributed to defects in host lattice which are likely to be the sulphur vacancies (Lawangar and Narlikar 1975b). The contention is supported by the variation in b values with activator concentration.

3.3 Kinetics of luminescence

The kinetics of luminescence may be inferred from the nature of the decay. If the decay is exponential, the kinetics is monomolecular (first order) and a semilog plot between I and t gives a straight line. Power law decay results due to bimolecular process (second order) and a plot between $\log I$ and $\log t$ is linear with a slope equal to -2 (Curie 1963; Hoogenstraaten 1958). The decay observed in the present investigation is not of either form. However it could be explained on the basis of the monomolecular superposition theory suggesting that the kinetics of luminescence is monomolecular. The existence of the first order kinetics implies that the process of retrapping is negligible and traps are situated quite close to luminescence centres so that the two may be regarded as a single unit (Mor and Bhawalkar 1970).

Acknowledgements

The authors are grateful to the authorities of Shivaji University, Kolhapur for financing a research scheme under which the work is carried. They are also thankful to Dr C S Shalgaonkar for helpful discussions.

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