X-ray excited fluorescence and phosphorescence of CaSO₄: Sm phosphors

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Abstract. Calcium sulphate phosphors activated with samarium as an impurity with various percentage composition have been prepared and their fluorescence rise and phosphorescence decay behaviours have been studied. The growth curve is investigated to study the density of traps. The process of filling of traps during x-ray excitation is revealed. The decay curves are analysed to study the distribution of traps, the nature of decay and kinetics involved in the luminescence process. The concentration dependence of fluorescence emission of the phosphors is also discussed.

Keywords. Fluorescence; phosphorescence; traps; calcium sulphate phosphors; samarium.

1. Introduction

There is renewed interest in alkaline earth sulphate phosphors in view of their use in thermoluminescence dosimetry. These phosphors doped with various impurity elements have been extensively studied by many workers (Nambi *et al* 1974; Bapat 1977; Yamashita and Takenaga 1977; Tomita 1978). Most of these investigations are, however, confined to their thermoluminescence (TL) behaviour and spectral studies, and very little attention has been paid to their fluorescence rise and phosphorescence decay, although such studies form an important aspect of luminescent materials. The phenomenon of fluorescence, where the luminescence intensity gradually increases with time and reaches to an equilibrium value, is mainly governed by the traps present in the phosphor. The process of filling of traps during excitation is not clearly known. In the present investigation, the nature of growth curve is investigated to reveal the process of filling of traps during excitation.

The phosphorescence decay curves are analysed to understand the nature of decay and kinetics involved in the luminescence process of CaSO₄ phosphors.

2. Experimental

Calcium sulphate phosphors doped with Sm as an activator were prepared from gypsum by the method reported earlier (Sabnis and Pawar 1977). Ten grams of purified gypsum, 1 g of Na₂SO₄ and appropriate quantity of Sm₂O₃ were dissolved in concentrated H₂SO₄ of AR grade and the mixture was heated to 300°C for about 8 hr. The heat-treated residue was washed repeatedly with hot distilled water to remove the

excess unused traces of Na_2SO_4 and then dried at 60°C. Final heat treatment of 2 hr at 600°C was given to the phosphors which was then quenched to room temperature. The concentration of Sm was varied from 0 to 0·3750 wt %. Some phosphors were prepared without the addition of Na_2SO_4. The excitation source used was an x-ray tube with molybdenum target operated at 30 kV and 11 mA. The sample was mounted on the sample holder by applying silicon vacuum grease on a glass substrates. The powder was spread over a glass substrate in a uniform layer containing about 0·01 g/sq cm. The fluorescence rise and phosphorescence decay have been recorded at room temperature (300 K) by using an IP 21 photomultiplier tube coupled with an Omniscribe strip chart recorder.

3. Results and discussion

3.1. *Fluorescence as a function of time*

The fluorescence intensity was recorded as a function of time. It was found that it increases with time and reaches an equilibrium value (I_0). It is noted that initially there is a fast rise of fluorescence intensity for almost all the samples studied. There are several possible considerations which might contribute to the observed effects. One possibility is that during excitation process some electrons may reach excitation levels of luminescence centres and return to the ground state without passing into the conduction band, and these electrons would give rise to an almost instantaneous fluorescence. Another possibility is that there may be empty luminescence centres in the phosphor before excitation begins; thus allowing electrons ejected into the conduction band to return almost immediately to ground state giving instantaneous fluorescence. Further, the instantaneous rise may also result if there are no effective traps at the excitation temperature of the phosphor. The first two possibilities are very unlikely in our phosphor system, as our phosphors exhibit TSC and change in conductivity after x-ray excitation. The third possibility seems to be more likely which may be supported with the result of TL studies (Sabnis and Pawar 1979).

From the nature of growth curve, it is possible to reveal the process of filling of the traps during excitation. If there are no traps, one expects the instantaneous rise in fluorescence intensity. The existence of traps, however, decreases the number of electrons combining with the luminescence centre due to filling of traps. The rate of filling of the electrons in the traps is a function of time and this influences the nature of growth curves. In order to study the nature of filling of traps, the values of $(I_0 - I)$ at time t which gives the density of unfilled traps at that time were noted. The rate of decrease of unfilled traps $(d/dt)\,(I_0 - I)$ at various times is evaluated and the graphs of $\log\,(d/dt)\,(I_0 - I)$ are plotted against t for both with and without Na_2SO_4 added phosphors and are presented in figure 1. The plots show almost linearity indicating the possibility of power law rise for the phosphors system studied.

3.2. *Concentration dependence of fluorescence intensity*

The maximum intensity of fluorescence emission (I_0) was measured for $CaSO_4$: Sm phosphors (with and without Na_2SO_4) of various activator concentrations and I_0 is plotted against logarithm of concentration of samarium in $CaSO_4$ (figure 2). It
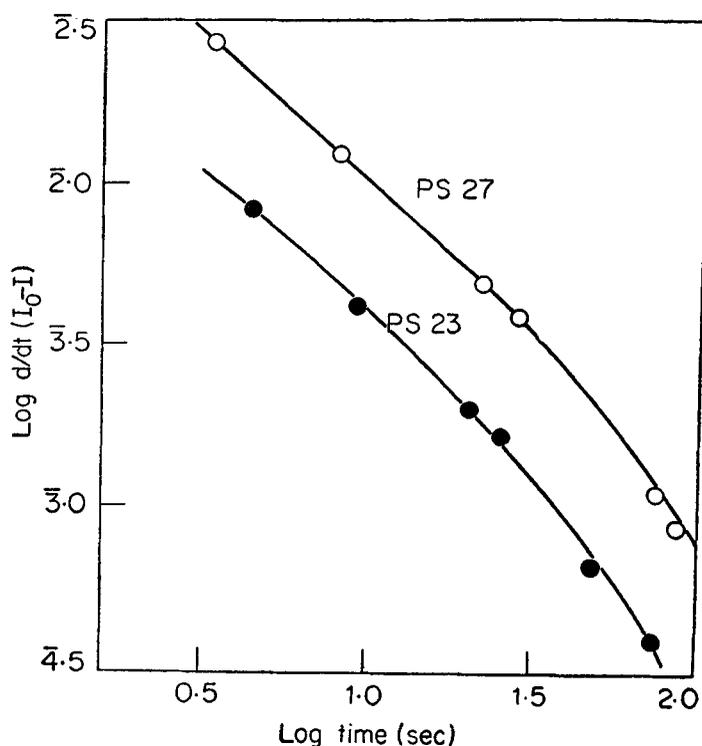
Figure 1. Plots of log (d/dt) $(I_0 - I)$ versus time for with (PS27) and without (PS23) Na_2SO_4 added $CaSO_4$: Sm phosphors. The concentration of Sm is 0.0375 wt. %.

can be noted from figure 2 that I_0 increases with increase of activator concentration, reaching a maximum at concentration level at about 0.0875 wt. % of Sm after which the intensity falls off for any further increase in activator concentration. This is the well-known concentration quenching effect observed for $CaSO_4$:Sm phosphors with and without Na_2SO_4. The phenomenon of concentration quenching in TL emission has also been observed by Nambi *et al* (1974) and Mulla and Pawar (1978). The mechanism of concentration quenching of fluorescence may not be the same for all the fluorescent solids. However, in all the cases the excitation energy, which is not emitted as fluorescent radiation, is finally absorbed by the centres in which internal conversion of this energy may occur (Dekker 1969).

3.3. *Analysis of decay curves*

The decay curves are recorded for $CaSO_4$:Sm phosphors with and without charge compensator at room temperature. The decay curves are analysed to understand the nature of decay and kinetics involved in the luminescence process. As evidenced by TL studies and predicted by the theory of phosphorescence, the decay observed in the present phosphors is due to the existence of electron traps in the phosphors.

In the present investigation the plots of log I versus t for all the phosphors studied are nonlinear and not presented here. This rules out the possibility of exponential
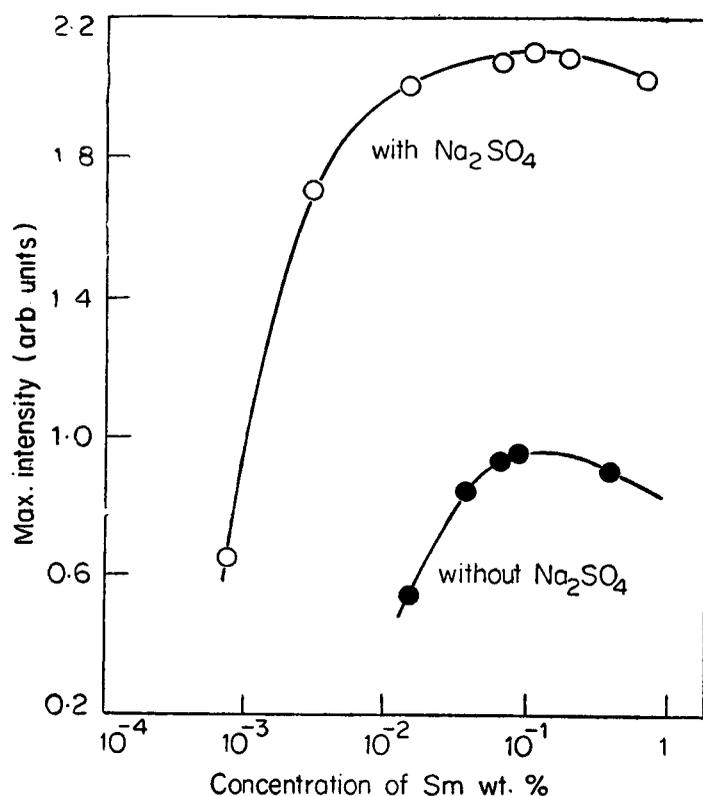
Figure 2. Concentration dependence of fluorescence intensity for $CaSO_4$: Sm phosphors (with and without Na_2SO_4)

decay of monomolecular kinetics. For bimolecular kinetics, the plot of $1/\sqrt{I}$ versus t should be linear in accordance with the relation (Mott *et al* 1964)

$$1/(I)^{1/2} = 1/(I_0)^{1/2} \cdot (1 + A\, n_0 t)$$

where A is a constant and n_0 the number of recombining electrons at $t = 0$. In the present investigation the plots of $(1/\sqrt{I})$ versus t (figure 3) are closely linear indicating second order kinetics.

3.4. *Role of Na_2SO_4*

The phosphors prepared with Na_2SO_4 have different properties than those without the addition of Na_2SO_4. Addition of Na_2SO_4 predominantly increased the fluorescence intensity and decreased the number of electron traps. These observations may be understood on the basis of charge compensation theory of Kroger and Hellingmann (1949). In $CaSO_4$ phosphors, Sm^{3+} ions are incorporated at the place of Ca^{++} sites with the generation of Ca^{2+} vacancies for the charge balancing to occur (3 Ca^{2+} → 2 Sm^{3+}). A good deal of energy is required to create the vacancy which restricts the large entry of Sm^{3+} ions in $CaSO_4$. The simultaneous addition of Na^+ ions from
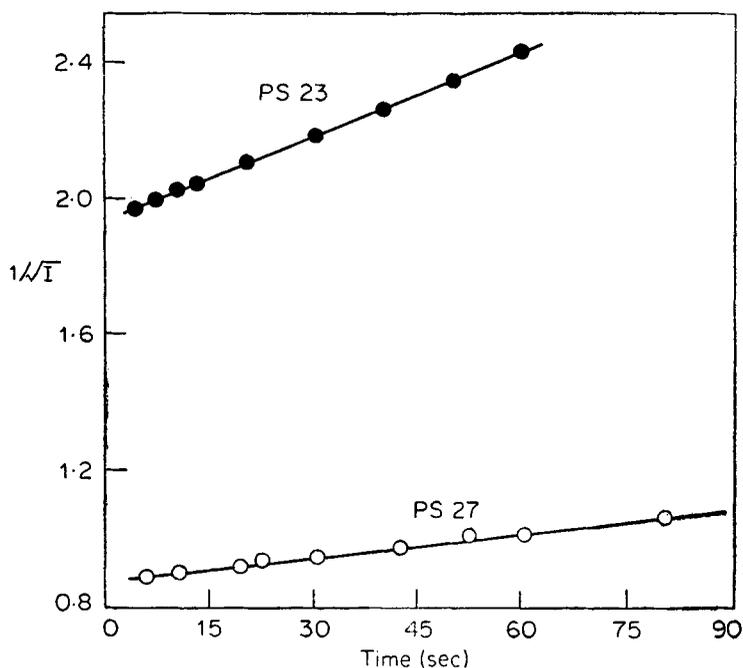
Figure 3. Plots of $(1/\sqrt{I})$ versus t for with (PS 27) and without (PS 23) Na_2SO_4 added $CaSO_4$: Sm phosphors.

Na_2SO_4 makes an easy entry of Sm^{3+} ions without creating vacancies (2 $Ca^{2+} \rightarrow Sm^{3+} + Na^+$). This reduces the number of traps and encourages the entry of large number of Sm^{3+} ions in $CaSO_4$, giving rise to high fluorescence intensity.

Acknowledgements

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