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Thermoluminescence and isothermal decay of Sr_2SiO_4: Dy

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The thermoluminescence (TL) of strontium silicate activated by dysprosium is reported. It gave two groups of TL peaks. The peak at 57° C showed anomalous behaviour with the dose of excitation. It was found that the higher-temperature TL group (140 to 250° C) was affected by the concentration of dysprosium and also by the dose of excitation. On the basis of various observations, it is concluded that the TL behaviour of the phosphor Sr_2SiO_4: Dy(0.05 mol %) is associated with some structural defect. It was also found that the filling rate of trapping groups depends on the degree of transfer to these groups from the host lattice. This communication reports isothermal decay from Sr_2SiO_4: Dy at different temperatures and the process of electron tunnelling.

1. Introduction

Isothermal decay monitored at different temperatures has been studied by many workers [1–3] to determine the kinetics involved in the luminescence emission. Isothermal decay at two temperatures within the range of a thermoluminescence (TL) group also give an approximation to the frequency factor [4] involved in the luminescence kinetics.

Silicate phosphors, especially alkaline earth silicate phosphors doped with rare earths, have long been used for cathode screens [5, 6]. The silicate series shows a continuous shift in the emission band when the cation of the host is changed from calcium to strontium [7]. We have studied a mixed silicate system with different activators. It was observed that Dy^{3+}-activated strontium silicate behaved somewhat differently from the other members of the series. This work reports the behaviour of Sr_2SiO_4: Dy in its thermoluminescence as well as isothermal decay properties. A comparison is made with other samples in the series and a possible mechanism is discussed.

2. Experimental procedure

Starting materials were used in powder form of analytical grade. The material was in the form of carbonates. Weighed quantities of carbonate together with SiO_2 and NH_4Cl (5% as flux) were mixed with appropriate quantities of activator. The mixture was ground thoroughly. The ingredients were placed in a platinum crucible and heated slowly up to 1060° C in one hour. Phosphors were prepared by solid-state reaction of the ingredients at 1060° C in a tubular furnace for a further two hours. It was observed that strontium silicate phosphor was susceptible to temperature conditions. Even a slight variation in the temperature of insertion of the material gave an indication of colour-centre formation.

The spectral distribution curves for the phosphors were recorded by a Bellingham and Stanley spectrometer in conjunction with an IP21 photomultiplier tube. The excitation source was 30 kV, 10 mA X-rays with a copper target.

Thermoluminescence curves were obtained by heating the phosphor at a linear heating rate of 70° C min^{-1}.

The decay of phosphorescence was recorded after giving a fixed initial dose of X-ray to the samples. Different ambient temperatures were maintained (± 2° C) by a temperature controller unit.

3. Results

3.1. Emission spectra

The spectrum of Sr_2SiO_4: Dy showed two narrow bands characteristic of dysprosium activation. The first band consisted of two narrow peaks at 478 and 491 nm and the other band was at 572 nm. The ratio of the two peaks in different systems was as follows:

Sr_2SiO_4: Dy(0.05)	491 nm : 572 nm :: 1 : 2.25
Ba_2SiO_4: Dy(0.05)	490 nm : 576 nm :: 1 : 3.32

The ratio remained constant in Sr_2SiO_4: Dy for different concentrations (mol %) of the activator.

3.2. Thermoluminescence

The glow curve for Sr_2SiO_4: Dy(0.05) gave one peak at 57° C and three closely spaced peaks in the range 140 to 250° C.

The peak at 57° C increased with excitation dose up to 1 min. At 2 min excitation the peak decreased in magnitude. To check this, the experiment was performed with doses differing by 15 sec. For a dose of 75 sec the TL peak height was less than for 1 min. Table I summarizes the variation of this TL peak with dose. After 90 sec dose, however, the peak continued to increase continuously. Between 5 and 8 min the change in height was larger than would be expected from the initial growth rate, as shown in Fig. 1.

The same experiment performed on Sr_2SiO_4: Dy(0.01) and Sr_2SiO_4: Dy(1.0) did not show the anomalous variation in TL output with the dose of

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TABLE I Variation in thermoluminescence intensity of the peak at 57° C with the dose of X-ray excitation

Sample No.	Dose of excitation (sec)	TL intensity (arbitrary units)
1	15.0	270.0
2	30.0	290.0
3	45.0	440.0
4	60.0	500.0
5	75.0	420.0
6	90.0	280.0
7	120.0	490.0
8	300.0	700.0
9	480.0	1450.0

excitation. It was found, however, that the phosphor Sr_2SiO_4 : Dy(0.05) : Eu(0.001) also showed this type of anomaly. The peak intensity for different doses had the values 240 at 15 sec, 450 at 60 sec, 250 at 120 sec. 390 at 300 sec and 520 at 480 sec.

Again, other europium-doped samples did not show such a behaviour. The samples, in general, gave a higher TL output at higher doses.

The TL output was also investigated for different dysprosium concentrations in Sr_2SiO_4. Table II gives the TL intensities of the 57° C peak for different activator concentrations. This table also suggests an increase in the TL peak at 57° C with dysprosium concentration. At the same time higher-temperature peaks lose their identity. Fig. 2 brings out this feature clearly.

TABLE II TL peak intensities of Sr_2SiO_4 : Dy for 5 min dose of X-ray excitation

Dysprosium concentration (mol %)	Peak location (° C)*			
	57	~140	~180	~220
0.001	155	–	–	290
0.001	185	–	–	470
0.01	200	91	–	440
0.05	700	220	280	200
0.1	850	220	270	–
0.5	1250	–	–	–
1.0	1250	–	–	–

*Missing values indicate disappearance of the peak.

3.3. Decay of phosphorescence

Fig. 3 shows the decay curves for a Sr_2SiO_4 : Dy(0.05) sample at room temperature. These curves were recorded after fixed excitation doses. When the dose of excitation was increased the decay became slower. The times required for 90% reduction in the initial intensities are given in Table III.

When the ambient temperature of measurement was increased the decay became faster (Fig. 4). It was observed that when the ambient temperature was 150° C the decay showed an anomalous behaviour. The emission intensity first decreased up to 22 sec and then, instead of decreasing further, it showed an increase. The increase in intensities, akin to a time reversal, continued up to 45 sec and then again showed a decrease, but this decrease was slower than

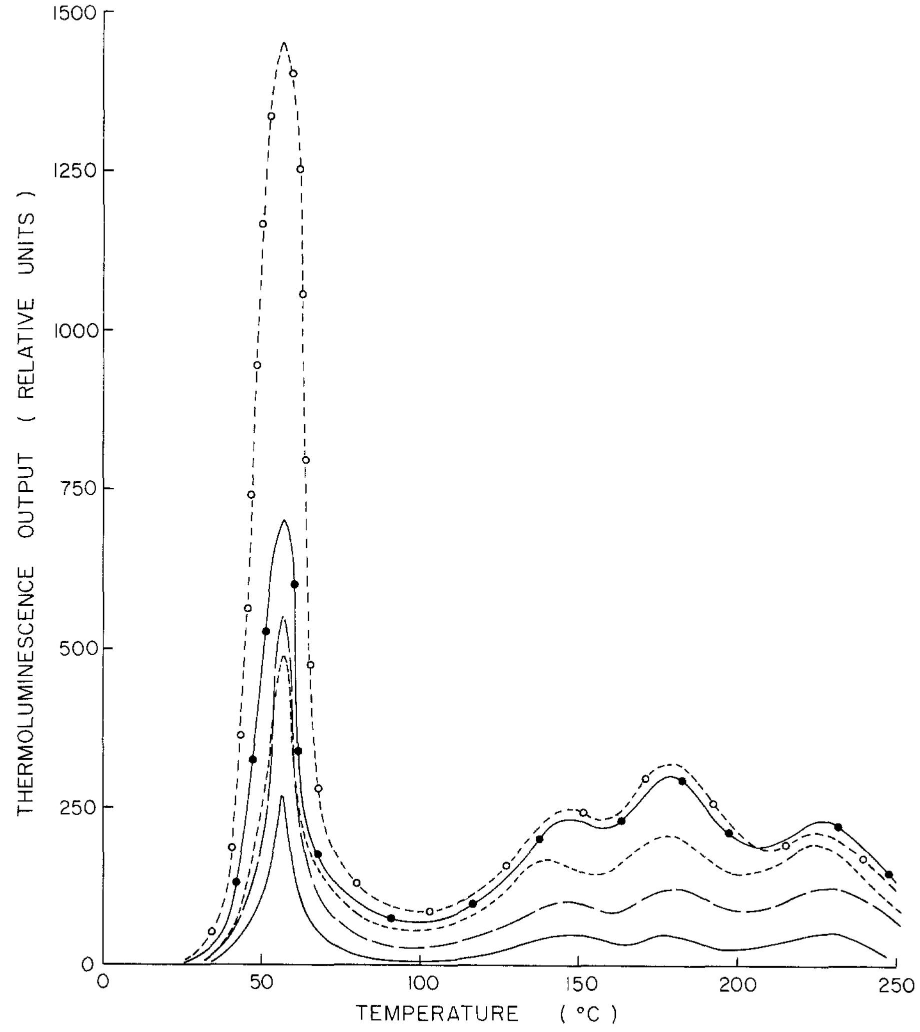

Figure 1 Thermoluminescence glow curves for Sr_2SiO_4 : Dy(0.05) for different doses of excitation: (—) 15 sec, (——) 1 min, (– –) 2 min, (●) 5 min, (○) 8 min.

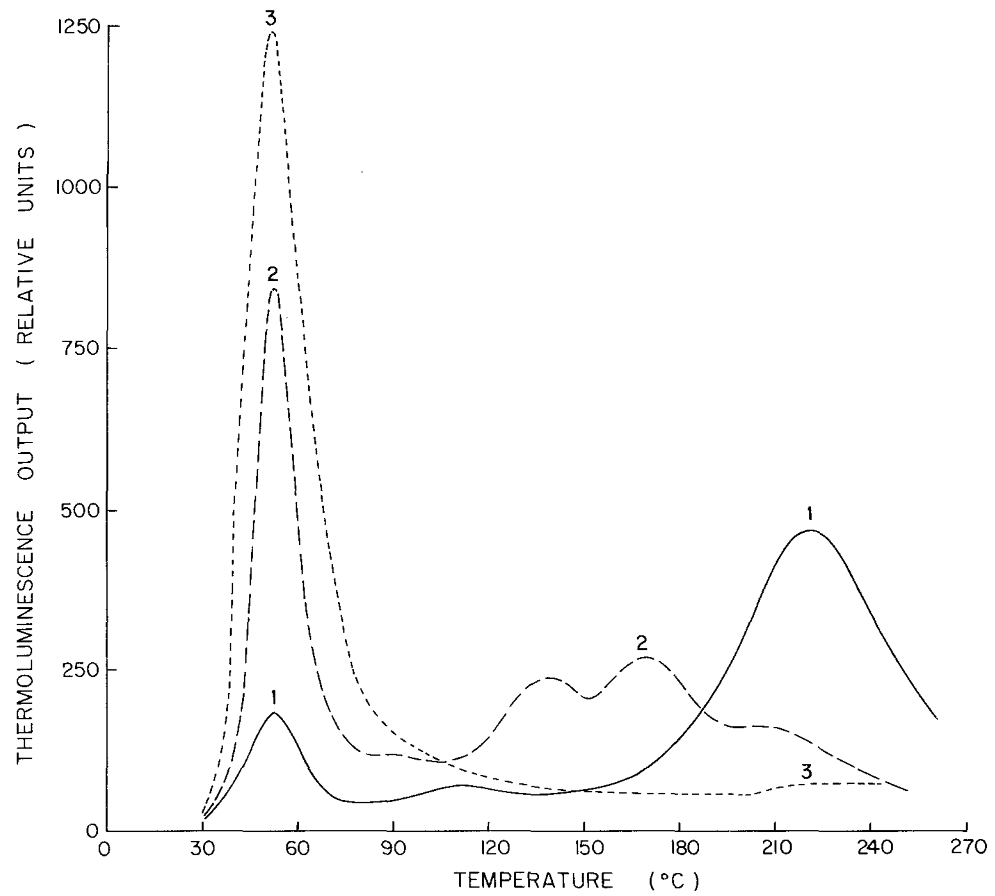

Figure 2 Thermoluminescence curves for Sr_2SiO_4 : Dy samples: dysprosium concentration (mol %) (—) 0.001, (– – –) 0.1, (- - -) 1.0.

before. Similarly, the decay curve obtained at 180° C showed a systematic decrease in emission intensity up to 92 sec. The intensity then improved and gave a peak at 145 sec. When the temperature was raised to 210° C the first decay portion continued up to 80 sec and the peak was observed at 126 sec.

The above results obtained in the sample were further confirmed by changing a variety of parameters as given below.

3.3.1. Dose of excitation

Fig. 5 shows the decay curves obtained at 180° C for different excitation doses. When the dose of excitation was 1 min the decay continued up to 120 sec and gave a peak at 173 sec. The intensity of this peak was 37 units. The 4 min and 8 min excitation doses showed peaks at 120 and 57 sec with intensity values of 42 and 48 units, respectively. These values indicate that as the dose of excitation is increased the normal decay period decreases; the peak occurs at an earlier time and the peak intensity increases.

The peak locations for different excitation doses at 210° C are shown in Figs 6 and 7. As in the earlier case the peak in this case also shifted to an earlier time with increase in initial excitation. The curve for 8 min excitation dose had a peak at 42 sec and then showed a continuous decrease in brightness before giving a second peak at 215 sec. Different excitation doses were tried to check the phenomenon thoroughly. Further, the phosphorescence decay of Sr_2SiO_4 : Dy for different dysprosium concentrations also showed increased decay when the activator concentration was increased.

4. Discussion

When an activator enters into the lattice, host energy levels and metastable states are slightly modified. When it is present in small proportions the perturbation may be small and only deep traps are affected. As the concentration increases, increased perturbation causes an abundance of shallower trapping levels. Our observation on the variation of TL with activator concentration (Fig. 2) is consistent with this view. For Dy(0.001) the TL group at 222° C is the prominent one. With increase in concentration the 57° C TL group also becomes pronounced (Curve 2 of Fig. 2). For Dy(1.0) only the 57° C TL group is observed (Curve 3). Further phosphorescence decay of Sr_2SiO_4 : Dy for different concentrations also shows an increased decay time when the concentration is increased.

The increase in TL output with the dose of excitation is in agreement with existing theories [8]. However, the behaviour of the phosphor Sr_2SiO_4 : Dy(0.05) at doses in the vicinity of 1 min led us to investigate its other property, namely the absorbance. It was found

TABLE III Time for 90% reduction in initial phosphorescence

Pre-excitation dose (min)	Lifetime (sec)
0.25	12
1.00	40
2.00	57
5.00	85
8.00	91

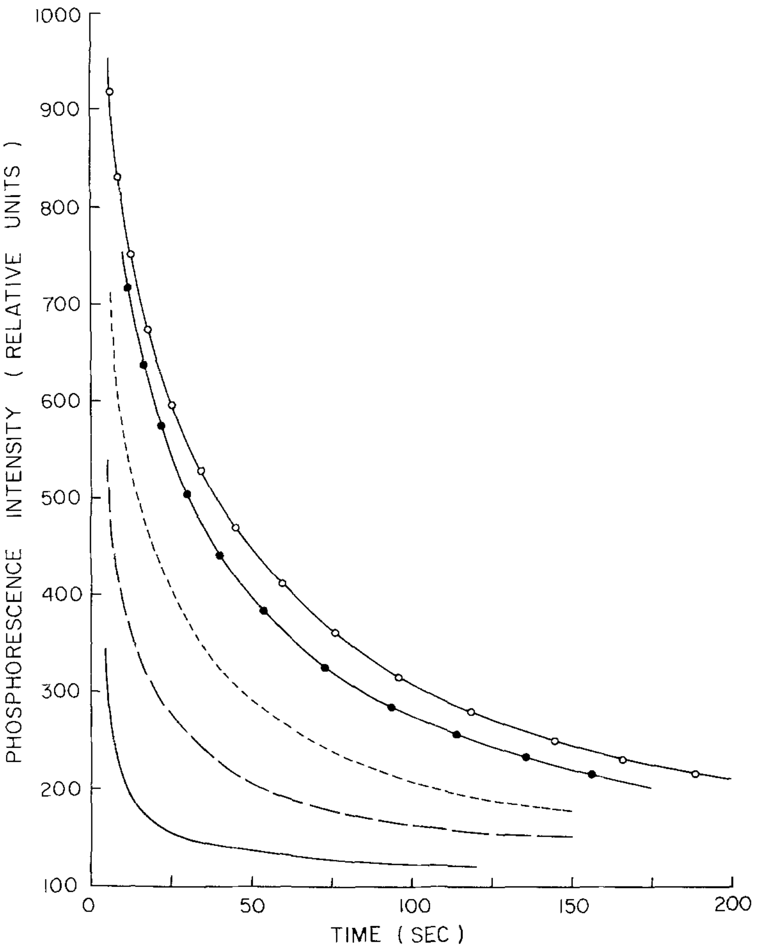

Figure 3 After-glow curves for Sr_2SiO_4 : Dy(0.05) at room temperature for different excitation doses: (—) 15 sec (I_0 = 2000), (——) 1 min (I_0 = 2300), (---) 2 min (I_0 = 2700), (●) 5 min (I_0 = 3000), (○) 8 min (I_0 = 3300).

that only Sr_2SiO_4 : Dy(0.05) showed a departure in absorption characteristics at 271 nm (Fig. 8).

The decrease in intensity of the 57° C TL peak beyond a dose of 1 min can only be understood on the basis of a transfer of charge carriers from this trap group to some deeper levels. In this event, the decrease in population of this trap group should be accompanied by a rapid increase in the TL intensity of a higher-temperature peak. In the range of temperature investigated, the peaks lying between 140 and 250° C do not show any sudden increase in their intensity after 1 min excitation. The transfer is apparently not to these groups.

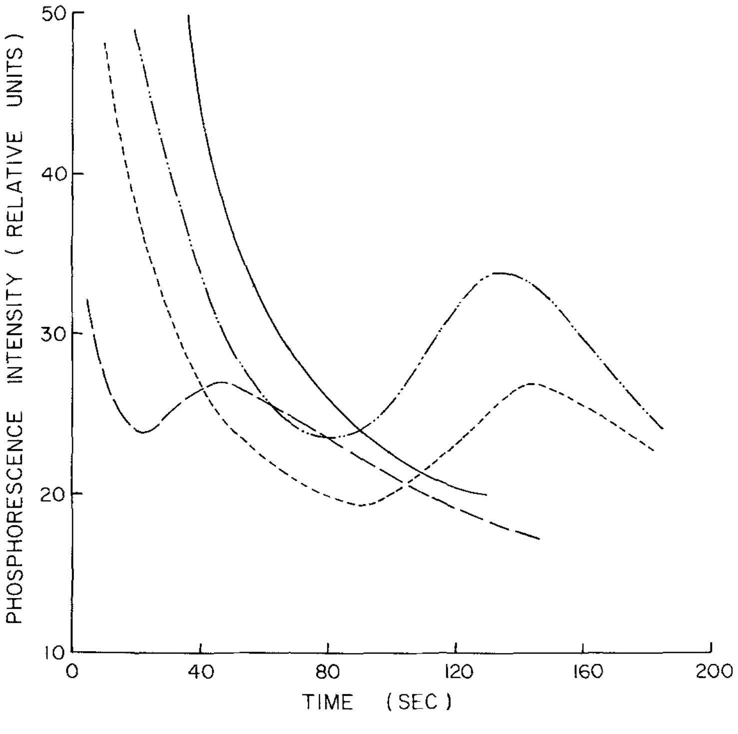

Figure 4 After-glow characteristics of Sr_2SiO_4 : Dy(0.05) (5 min X-ray dose) at different temperatures: (—) 60, (——) 150, (---) 180, (-·-·-) 210° C.

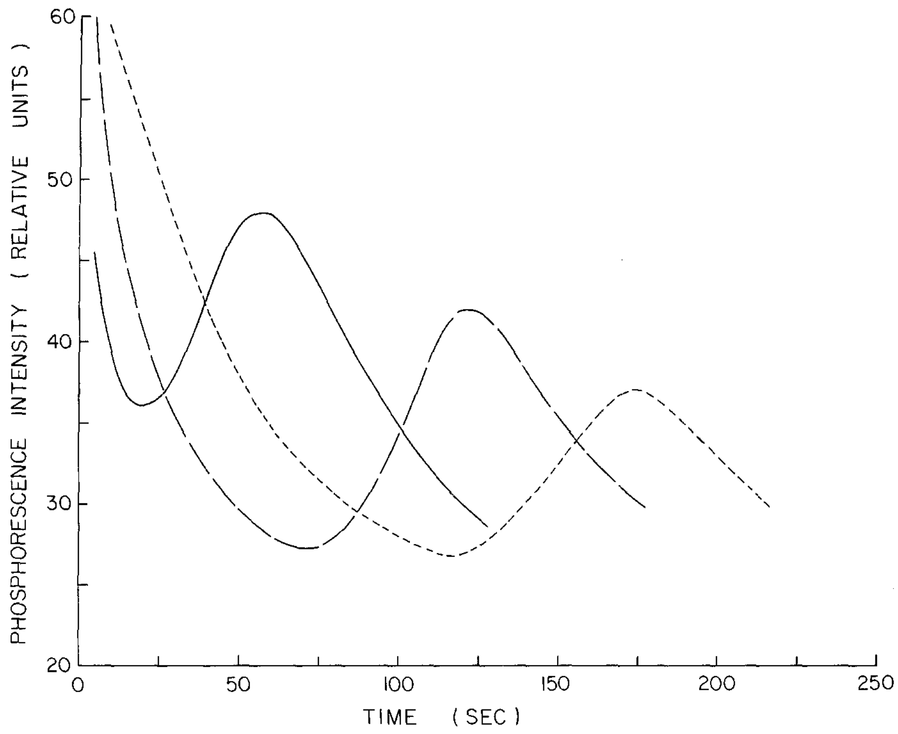

Figure 5 After-glow curves for Sr_2SiO_4: Dy(0.05) at 180° C for different excitation doses: (---) 1 min, (——) 4 min, (—) 8 min.

The phosphor was annealed at 500° C and excited for different doses, but the glow run was obtained only up to 60° C so that only the first peak is emptied, while all the deeper traps are practically unaffected and continue to remain populated. Table IV shows that the intensity of the TL peak consistently increased with the dose of excitation. Since the higher group of traps was not emptied each time, the anomaly at 1 min dose disappeared. Similarly, when different pre-excitation doses are given to the phosphor before the TL experiment, the time at which the first TL peak shows a decrease is altered. The above experiments appear to confirm the view that there is a transfer of charge carriers to deeper traps, the transfer depending on the relative populations of the trapping levels.

It is generally observed that the TL units in a phosphor are a property of the host [9]. Association of dysprosium with these units leads to a higher TL output. Tables I and II are in agreement with this view. A low concentration of europium (0.001) when simultaneously present in the sample does not alter the phosphor character, as was evidenced by the decay and absorption data (not given) of samples of Sr_2SiO_4: Dy(0.05) and Sr_2SiO_4: Dy(0.05) : Eu(0.001).

Fig. 1 indicates that the TL groups around 140 to 250° C are populated linearly up to 5 min dose of excitation. Further dose, however, does not fill this trapping group. The hump at 230° C for 8 min dose even has a lower intensity value than for 5 min dose. This probably suggests that these trapping groups are saturated around an X-ray dose of 5 min. The peak at 57° C increases dramatically in the dose range 5 to

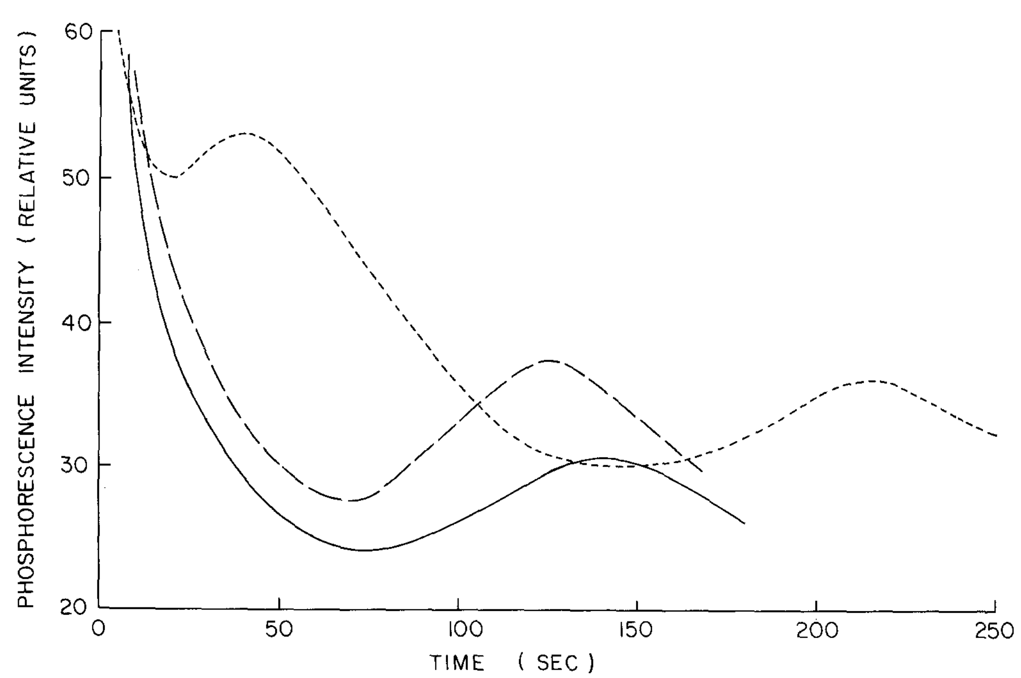

Figure 6 After-glow curves for Sr_2SiO_4: Dy(0.05) at 210° C for different excitation doses: (—) 30 sec, (——) 2 min, (---) 8 min.

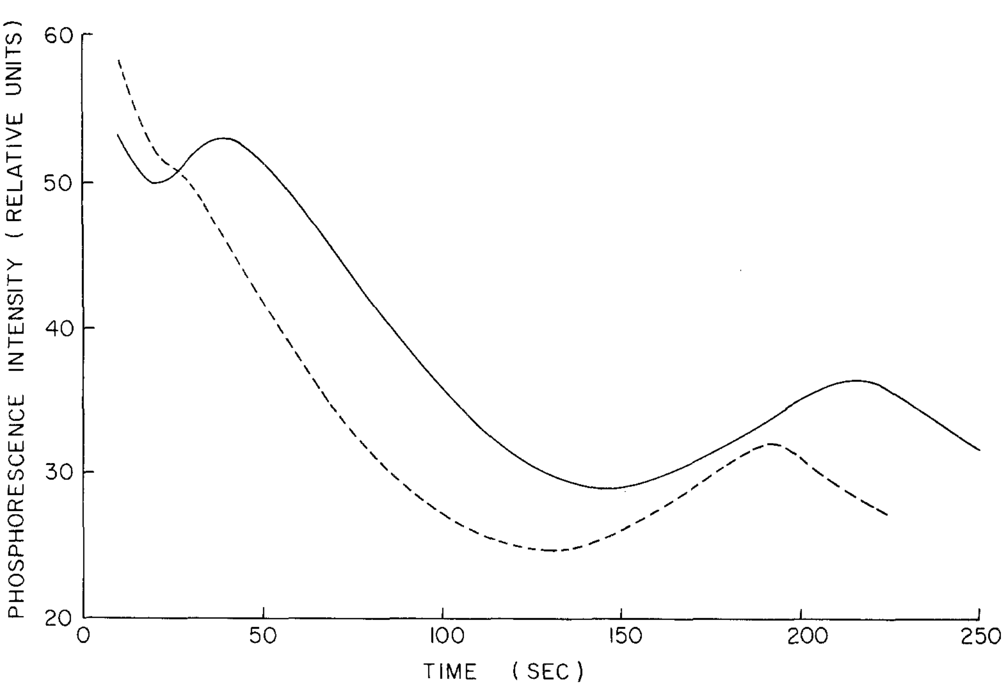

Figure 7 After-glow curves for Sr_2SiO_4: Dy(0.05) at 210° C for different excitation doses: (---) 1 min, (—) 8 min.

8 min. If we assume a better degree of transfer [10] to the TL units responsible for 140 to 250° C TL peaks up to saturation, the abrupt rise in the 57° C peak can follow, as soon as the higher-temperature group of traps is filled.

The longer duration of the decay of phosphorescence with increased excitation dose is related essentially to a bimolecular kinetics operating in the sample. An increase in excitation time gives a higher initial intensity (I_0) as shown in Fig. 3. If the decay were monomolecular the time required for reaching half of the maximum intensity should be the same.

The decay rate increases with the operating temperature. This is consistent with the theory where it is assumed that the rate of detrapping of the electrons is increased [11]. When the temperature was 150° C this sample showed a peak in the decay curve. Since the peak in the decay was reproducible there should be a source of electrons which would tunnel into the traps emptying at 150° C. The tunnelling electrons should have a source in the form of a higher-temperature trapping group, and there should be a sequence of events which follow that described by Bapat and Sivaraman [12]. The basics are as follows:

1. The rate of tunnelling of electrons is proportional to their population in the higher-temperature group.
2. The tunnelling electrons can rush into the shallower traps if there are ample sites available.
3. The tunnelling should also depend on the degree of wave-function overlap between the emptying group and the source group.

TABLE IV Variation in height of 57° C TL peak for Sr_2SiO_4: Dy(0.05) with dose of excitation when the glow run was stopped at 60° C

Dose of excitation (sec)	Peak intensity (arbitrary units)
30.0	175.0
60.0	370.0
90.0	470.0
120.0	530.0
300.0	570.0
480.0	1000.0

The curves shown in Fig. 5 show a shift in the peak to an earlier time as the dose of excitation is increased. Since the population of electrons in the source group is altered with the dose of excitation, the first hypothesis is consistent with the observation. When the ambient temperature of decay is increased, the rate of emptying is increased whereby the electrons can tunnel into the emptying sites at an earlier time (Figs 5 and 6). When different TL groups are sufficiently populated they have every chance to tunnel into the shallow traps if they are vacant. Since, as we have stated earlier, the tunnelling rates for different TL peaks can be different, one can observe as many peaks in the decay curve as the number of TL groups available. Figs 6 and 7 indicate this tunnelling from other TL groups, and we observe a second rise.

We have found that the phosphor had TL peaks at 57, 143, 178, 221 and 260° C. The trapping group which may be expected to empty at 150° C is at ~ 143° C. The emptying group at ~210° C will have two higher groups at 220 and 260° C which can form the source of electrons.

Interestingly, an experiment on the short-term fading of a LiF TL peak reported by Spurny and Kvasnicka [13] shows a small build-up after a normal initial decay. This "abnormal" effect has been attributed to a combination of the usual thermal decay along with a tunnelling transfer among traps.

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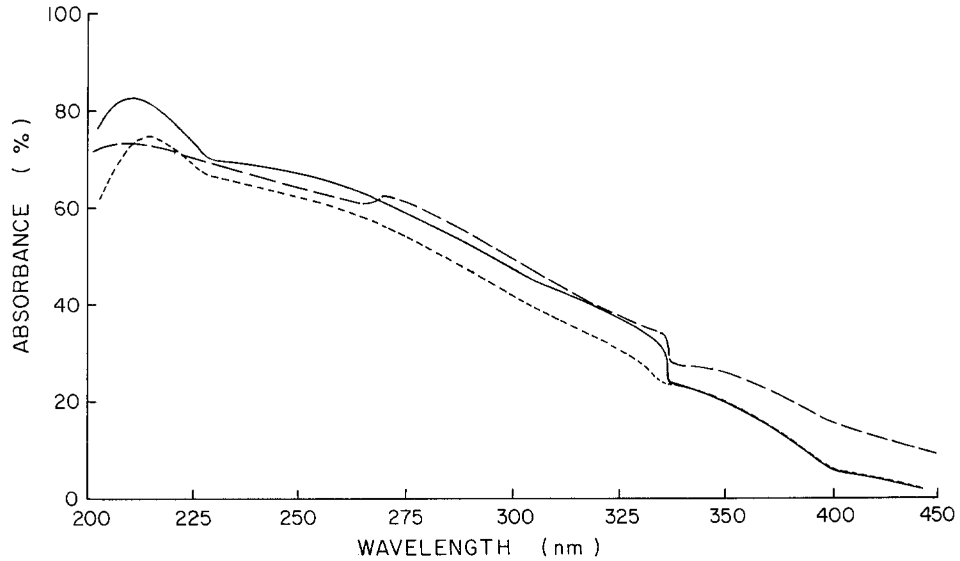

Figure 8 Diffused reflectance of Sr_2SiO_4 : Dy samples: dysprosium concentration (mol %) (—) 0.01, (——) 0.05, (---) 0.10.

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