Chapter 4

EFFECT OF DOPANT CONCENTRATION AND HEAT TREATMENT ON THE TL.

4.1 Effect of dopant concentration on the TL glow curve patterns

Dy and Tm have been found to be the most efficient activators in CaSO₄ (sec. 3.1) and these have been studied in detail for concentration effects. CaSO₄(Dy) samples with dopant concentrations of 0.018, 0.027, 0.036, 0.054, 0.072, 0.126, 0.18, 0.27, 0.36, 0.72 and 1.8 per cent by weight of Dy in CaSO₄ and CaSO₄(Tm) samples with dopant concentrations of 0.02, 0.033, 0.05, 0.067, 0.1, 0.2, 1.0 and 10 percent by weight of Tm in CaSO₄ were prepared as described in sec. 2.1.1. TL glow curves from each of the samples were taken after gamma irradiation to about 5 x 10⁴ R. The TL glow peak intensity patterns obtained for different concentrations were different, with Dy and Tm behaving in the same way in CaSO₄. The results obtained for the case of CaSO₄(Dy) are illustrated in figs. 15 and 16.

It is seen that all the prominent glow peaks excepting the peak occurring around 480°C, show a sharp increase during the initial additions of the dopant, reach a maximum for an optimum concentration of about 0.1% by weight and start declining for any further increase in the Dy concentration. However, the high temperature peak at 480°C seems to build up very slowly
FIG. 15. EFFECT OF ACTIVATOR CONCENTRATION ON THE TL GLOW CURVES
OF $\gamma$ IRRADIATED CaSO$_4$: Dy
[DOSE: $5 \times 10^4$ R]
FIG. 16. EFFECT OF DOPANT CONCENTRATION ON THE VARIOUS TL PEAKS OF GAMMA IRRADIATED 
CaSO$_4$ (Dy)
even for further increases beyond 0.1%. At the optimum concentration, the laboratory made CaSO₄(Dy) compares well with the TL sensitivities of the commercially available phosphores for dosimetry work (fig.17).

4.2 Concentration quenching:

The total TL intensity emitted for the same gamma irradiation from CaSO₄ doped with different concentrations of either Dy or Tm follows a specific pattern of a sharp increase in the TL output during the initial increase of dopant concentrations reaching a maximum at an optimum concentration level (about 0.1% by wt. of the dopant) after which the TL output gradually falls off for any further increase in the concentration of the dopant. Fig.18 represents the result obtained for CaSO₄(Tm).

The falling off in the TL output when the dopant is present in much larger concentrations, is thought in terms of a 'concentration quenching effect' which has been dealt in detail in sec. 1.3.2 a. The equations of Johnson & Williams (eqn.22) and Bowes & Lee (eqn.23) were tried using a computer code, arbitrarily assigning various ranges of values for the constants involved and looking for the best least square fit with the experimentally observed points. The modified equation of Bowes and Lee seemed to give somewhat the nearest fit although it was generally realised that both the very low and very high concentration points were found not accommodated in any of the
FIG. 17. COMPARISON OF TL SENSITIVITIES OF CaSO$_4$ : Dy PHOSPHORS PREPARED IN DIFFERENT LABORATORIES.

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H - HARSHAW CHEMICAL CO, U.S.A.
fits. The theoretical fit arrived at using eqn.23, along with the experimental points for Dy & Tm are shown in fig.19. It is worth noting here that the theoretical equations for concentration quenching do not take into account any spectral differences due to concentration variations. This aspect was not pursued in the present investigations either.

4.3 Effect of high temperature treatment:

4.3.1 Experimental:

Freshly evaporated samples of CaSO₄ with various dopants and without the dopant (sec.3.1.1) after cleaning and drying, were treated in separate batches at 400°C, 600°C and 800°C for two hours in this study. The heat 'treatments' were always done in two different ways for the same temperature: in one, called 'fast cooling' the samples were removed from the furnace quickly and allowed to attain RT under ambient conditions; and in another, called 'slow cooling', the samples were allowed to attain RT in the furnace itself after switching off the furnace. 5 mgms of samples after each such treatments were drawn and their TL glow curves recorded after a gamma exposure of 300 R using a linear temperature programmer described in sec. 2.2.1 b.

a) Effect of rate of cooling:

In general it was found that 'fast cooling' as compared to 'slow cooling' always suppressed to a good extent the TL emission
FIG. 19. THEORETICAL FIT FOR THE CONCENTRATION QUENCHING OBSERVED IN Dy- AND Tm-DOPED CaSO$_4$ PHOSPHORS.

\[ \text{CALCULATED } \eta = \frac{K}{1 + \frac{\alpha C}{\text{nc}}} \]

\( K = 100 \), \( \alpha = 0.037 \), \( n = 1000 \)
in the range RT to about 150°C while the emission beyond was increased slightly which was notably visible for the most sensitive TL peak IX used in dosimetry. This observation was confirmed for all the samples at all temperatures of treatment mentioned above. Fig. 20 presents the results obtained for the cases of Dy- and Tm-doped and the undoped CaSO₄ samples, for slow and fast cooling after treatment at 600°C for 2 hours.

b) Effect of temperature of treatment:

A slow cooled sample showed better consistency and reproducibility than a fast cooled sample and hence only the slow cooling results are considered. Likewise, samples annealed at 400°C were also found prone to TL glow curve inconsistencies possibly because of traces of sulphuric acid still present in the sample as was evident from the dirty coloration still persisting in the samples. All samples became perfectly white and showed TL stability after they were treated at other high temperatures of 600°C and 800°C. Nevertheless, the 400°C annealed samples as a rule, gave slightly higher TL outputs especially corresponding to the dosimetric peak IX compared to samples annealed at higher temperatures.

Comparison between 500°C and 800°C annealed samples, showed in general a marked suppression of the most sensitive dosimetry peak IX for higher temperature treatment and a slight increase in all other peaks (Fig. 21).
FIG. 20. SLOW (A) AND FAST (Q) COOLING EFFECTS ON THE TL GLOW CURVES OF CaSO₄ PHOSPHORS AFTER 600°C TREATMENT FOR TWO HOURS.

CaSO₄ (Dy) 
DOSE: 300 R

CaSO₄ (Tm) 
DOSE: 300 R

CaSO₄ (UNDOPED) 
DOSE: 300 R
4.3.2 Discussions

It has been mentioned earlier (sec.1.3.2b) that the lattice defects especially those related to ionic vacancies, increase with the temperature of the lattice and hence by rapid quenching of the sample, one can expect to 'freeze-in' larger number of these defects. If these host defects are the actual trapping sites which are thermally deactivated during the 'glow curve run', then it is only expected that some increase corresponding to these glow peaks should be observed in quenched samples. The observation here that all the peaks above about 150°C (i.e. peak VIII onwards which forms a major fraction of the total TL) show an increase after quenching, confirms that these should be due to host lattice defects (sec.3.1); the peaks V and VI, which show remarkable decrease after quenching may not be purely due to host lattice defects and might be also related to the impurities added. The impurities in fact have been found to influence the decay characteristics of these peaks (sec.5.5).

It is reasonable to expect that at higher temperatures, the dopant ions were likely to get dispersed which might otherwise be present in the form of agglomerates. Hence the results shown in fig.21 could be interpreted to hint that the emission under the highest TL peak IX is associated with the
dopant ions present in agglomerates in the crystal lattice. However, concentration quenching studies have indicated an optimum ratio of 1:1000 between activator and host lattice centres. The results could also be interpreted in another way in analogy to whatever has been proposed by Merz and Pershan (37) in CaF₂ phosphors. The RE emission corresponding to peak IX could be associated with RE³⁺ ions with non-locally compensated SO₄²⁻ ions. At higher temperature treatments (as well as at large dopant concentration), the probability of finding such RE sites with distant compensators is decreased (i.e. change in site symmetry) and accordingly the output is seen diminished.

4.4 Conclusions:

From the near-success achieved in fitting the experimentally obtained results of the present work with the theoretical equations of the Ewles and Lee for concentration quenching, it can be inferred that the rare earth elements act as activators in CaSO₄ phosphors and each activator centre is associated with a definite minimum number of lattice ions (∼ 1000 in the case of Dy and Tm in CaSO₄) and if the dopant ions are present more in number as to offset this minimum required ratio, quenching of the luminescence sets in.

Heat treatment studies have shown that the traps which are thermally deactivated are associated with
host lattice defects as evidenced by an increase in their number after fast cooling.

The TL emission corresponding to peak IX at about 200°C seems to be due to $\text{Er}^{3+}$ ions associated with distant charge comparators. For high concentrations of the dopant as well as for high temperature treatment of the optimally doped, there is considerable quenching of this emission since the number of such $\text{Er}^{3+}$ sites with distant charge compensators is reduced.