Chapter 3

INFLUENCE OF (GROUP II B) CODOPANTS ON THE THERMOSTIMULATED LUMINESCENCE SENSITIVITY OF CaSO₄:Dy/Tm PHOSPHORS

3.1. Introduction

Among the different types of TLD materials, rare earth (RE) doped metal sulphates especially CaSO₄:Dy or CaSO₄:Tm phosphors developed by Yamashita et al. [Ya 71] is in use in many countries for radiation dosimetry purpose due to its high sensitivity, stability and low cost. The need for a more sensitive TLD phosphor in the field of personal dosimetry has arisen as a result of downward revision in the dose limitation by International Commission for Radiological Protection [ICRP 60]. Therefore further development of TLDs especially their sensitivity may become essential if TLDs are to remain in the race as the official radiation protection dosimeter.

Several attempts were made by different groups to improve the dosimetric properties of CaSO₄:Dy. Schmidt et al. [Se 74] have studied the effect of a number of codopants (23 studied but 14 reported) and came to the conclusion that none of these codopants improve the sensitivity of CaSO₄:Dy. Improvement in the photoluminescence (PL) and thermostimulated luminescence (TSL) efficiency of CaSO₄:Dy was tried in several ways. Monovalent impurities provide charge compensation and hence result in the increased incorporation of Dy³⁺ but addition of the monovalent impurities induces undesirable changes in the glow curves. Atone et al. [At 93] proposed an alternative charge compensator P⁵⁺ at sulphur (S⁶⁺) substitutional sites. With these codopants CaSO₄:Dy has shown a 40-100% increase in its TSL sensitivity. However, other independent studies showed that the TSL sensitivity of CaSO₄: Dy,P is reduced due to post-irradiation annealing at 400°C unlike CaSO₄:Dy [Sh 93]. The possibility that phosphorous is situated in interstitial positions rather than at sulphur sites cannot be ruled out since the ionic radius of P⁵⁺ (29 pm) is lower than that of S⁶⁺ (35 pm). In that case, the migration of phosphorous could take place easily at higher temperatures and this explains well the annealing temperature dependent behaviour of the TSL sensitivity of CaSO₄:Dy,P. However, even if phosphorous is situated in interstitial positions, the Ca⁺⁺ vacancies would be eliminated which should have shifted the TSL glow peak to 130°C.
Bhatt et al. [Bh 96] have independently confirmed that co-doping of phosphorous in CaSO$_4$:Dy/Tm increases its TSL sensitivity by 40%. Fluorescence intensity also increased with phosphorous co-doping. The ESR spectrum for CaSO$_4$:Dy and CaSO$_4$:Dy,P recorded at 300 K [At 95] after irradiation with $\gamma$-irradiation was found to be identical, implying that there is no increase in the production of radicals that act as trapped hole centres.

Another possible way of improving the TSL efficiency CaSO$_4$:Dy is by increasing the trap concentration through coactivators. Following the success of co-doping with phosphorous at substitutional sites Atone et al. [At 93] looked for other codopants that may replace the sulphate ion. Similar to the case with phosphorous, Mo or SO$_3$ codopants was found to increase the TSL sensitivity of CaSO$_4$:Dy by 40 to 100%. The SO$_3$ group can act as a reducing agent, and that may expected to increase the redox reactions that are responsible for the TSL processes in CaSO$_4$: RE phosphors [At 95]. Following SO$_3$ co-doping, TSL indeed show an increase by 80-100% in the CaSO$_4$:Dy/Tm phosphors. However, it was observed that the increase in the TSL sensitivity is ‘short lived’. When the phosphors were stored, the TSL sensitivities decreased.

It has been reported [Mo 89] that, when sulphate materials are doped with Mo or Cr, irradiation by $\gamma$-rays produces more hole–trapping radicals. Since Cr, Mo and W all exhibit +6 oxidation states, similar to S, all these elements can replace S substitutionally in CaSO$_4$ crystal lattice. During irradiation, the energy required to remove the electron from the radicals (SO$_4^{2-}$, CrO$_4^{2-}$, MoO$_4^{2-}$ and WO$_4^{2-}$) decreases with the increase in atomic number. In other words, the hole trapping probability should increase with Z in the order of S, Cr, Mo and W. As these radicals are supposed to play the role of hole traps in TSL of CaSO$_4$:RE, it was thought that co-doping with Mo would increase the number of populated hole traps, and in turn, the TSL sensitivities. As expected, the TSL sensitivity in CaSO$_4$:Dy found to increase by 60% when Mo was used as codopant. The PL and TSL emission spectra of the Mo co-doped phosphors remained unchanged. ESR signals correspond to SO$_3^-$ is stronger in co-doped CaSO$_4$:Dy samples. This shows that Mo co-doping results in the formation of SO$_3^-$ radicals in higher concentration. The increase in TSL is thus due to the higher concentration of populated traps. However, the exact mechanism, which links the enhancement in SO$_3^-$ population with Mo incorporation, is yet to be understood. Atone et al. [At 95] expected to obtain a
higher sensitive phosphor by combining the effects of Mo and P in CaSO$_4$:Dy,Mo,P phosphor but it showed only 30% increase in sensitivity.

Earlier all attempts on the enhancement TSL sensitivity of CaSO$_4$:Dy were based on improving the incorporation of more amount dopants (Dy or Tm) by charge compensation mechanism (co-doping of Na and P) or by increasing the number of populated hole traps through the Mo co-doping. Here we have made an attempt to increase the number of electron traps in CaSO$_4$:Dy/Tm by co-doping divalent ions having higher second ionisation potential (SIP) (group II B metals) than Ca$^{2+}$. Morgan and Stoebbe [Mo 89] came up with a model for the TSL emission process in CaSO$_4$:RE$^{3+}$ phosphors based on an energy transfer occurring between an unidentified recombination centre and the RE$^{3+}$ ions as mainly responsible for the TSL emission in CaSO$_4$:Dy. But this model is somewhat incomplete in certain aspects, i.e. only the trapping sites (hole traps) have been identified but the recombination centres (electron traps), have not been identified. Since the recombination centres appears to be common for different TSL peaks and different activators (RE$^{3+}$ as well as Mn$^{2+}$), Lakshmanan [La 99] has speculated that on irradiation, Ca$^{2+}$ ions spatially situated near the activator ions themselves perhaps act as electron traps. An independent way of testing this hypothesis is to replace Ca$^{2+}$ ions with other divalent ions having higher SIP and verify if there is an enhancement in the TSL sensitivity since the electron trapping probability of these ions are higher than that of Ca$^{2+}$.

This chapter describes the effect of codoping of Zn, Cd and Hg (IIB group elements in the periodic table having a higher SIP compared to that of Ca$^{2+}$- see Table 3.1 [Li 93]) on the TSL sensitivity and glow curve shape of CaSO$_4$:Dy/Tm phosphors. The optimum concentration of the dopants to get maximum sensitivity with favourable glow curve shape was found out. The TSL and PL in CaSO$_4$:Zn,Dy and CaSO$_4$:Dy were studied with the aim of comparing their sensitivities, dose response and the luminescence characteristics.

3.2. Experimental Details

CaSO$_4$ .2H$_2$O along with the dopants Zn (0.2 mol%) and Dy (0.2 mol%) were dissolved in concentrated sulphuric acid and recrystallised following the method of Rao et al. [Ra 80]. CaSO$_4$:Zn,Dy and CaSO$_4$:Cd,Tm phosphors were prepared with different Zn/Cd concentrations to obtain the optimal sensitivity following a similar recipe.
CaSO₄:Hg,Tm phosphor was prepared with both Hg and Tm at 0.2 mol% following a similar recipe. The residual samples were washed with triply distilled water and dried again in an oven at 100°C, followed by annealing in air in a furnace maintained at 700°C for 1 h. These samples were sieved to separate out the crystals of size 74 to 250 μm for TSL measurements. The γ-ray irradiations were carried out at RT using a 60 Co γ-cell with dose rate of 0.864 x 10³ Gy/h and a ¹³⁷Cs source with dose rate of 4.7 mGy/h at 1 m distance. The CaSO₄:Dy phosphor powder prepared by us has the same sensitivity as that of the commercial CaSO₄:Dy product made by Harshaw which is nearly 40 times more sensitive than that of LiF:Mg,Ti (Harshaw). The γ-ray induced TSL glow curves of the phosphor in powder form (74-250 μm size) were recorded using a computerised reader (PMT EMI 9924B) made by Nucleonix India Ltd., India. Heating rate used was 2 K s⁻¹ and 10 K s⁻¹. Heating was carried out in air. At the dose levels used in this work were ≥1 mGy, the contribution of non-radiation induced spurious TL was negligible and hence no nitrogen was flushed during read out. The PL measurements were carried out using a Fluorolog 3-11 version (Jobin Yvon-Spex) fluorimeter in air at room temperature. Its spectral resolution is 0.2 nm. Spectral corrections were not made for the instrumental response.

3.3. Results and Discussion

3.3.1. Comparison of TSL glow curves

Figure 3.1 compares the glow curves of CaSO₄:Dy, CaSO₄:Zn,Dy, CaSO₄:Cd,Tm, CaSO₄:Hg,Tm and CaSO₄:Mo,Zn,Dy at the γ-dose level of 2.4 Gy. All the dopants were at the concentration level of 0.2 mol%. The codopants Zn and Cd increase the TSL intensity of the dosimetric peak of CaSO₄:Dy but the high temperature peak near 300 °C has decreased slightly. About 45% increase in the TSL efficiency is seen in Zn and Cd (each 0.2 mol%) codoped samples but the presence of Hg codopant reduces the TSL sensitivity of CaSO₄:Tm. No appreciable change is seen with Mo as codopant in CaSO₄:Zn,Dy.

Since among the divalent ions, IIB group elements Zn²⁺, Cd²⁺ and Hg²⁺ have higher SIP than Ca²⁺ ion, each of these elements was codoped with Dy/Tm in CaSO₄. Results showed improvement in the TSL sensitivities for CaSO₄:Dy/Tm phosphors codoped with Zn and Cd in agreement with the above prediction. But Hg codoping showed a reduction in TSL sensitivity. This may be because Hg can exist in monovalent
as well as divalent valence states. Further more, the ionic radii of Hg$^{1+}$ and Hg$^{2+}$ are slightly higher than that of Ca$^{2+}$ (table 3.1). However the ionic radii of Zn$^{2+}$ and Cd$^{2+}$ are lower than that of Ca$^{2+}$. Hence, Zn$^{2+}$ and Cd$^{2+}$ can replace Ca$^{2+}$ much more easily in the CaSO$_4$ lattice than Hg.

3.3.2. Optimum concentration of dopants

Figures 3.2a and 3.2b compare the TSL glow curves of CaSO$_4$:Zn,Dy (for different concentrations of Zn and Dy) with that of CaSO$_4$:Dy (0.2 mol%). In figure 3.2a concentration of Dy was kept at 0.2 mol% and the Zn concentration was changed from 0.05 to 0.4-mol%. TSL glow curves of the $\gamma$ -irradiated sample shows gradual increase of high temperature peak with increase of Zn concentration and small change in dosimetric peak temperature. The maximum TSL intensity and peak temperature was observed for both Dy and Zn at 0.2-mol% concentration. Figure 3.2b shows the TSL glow curves at different concentrations of Dy and Zn. The optimum concentration of both the dopants were found to be at 0.2 mol% for the maximum TSL sensitivity.

Table 3.2 compares the TSL intensities - both peak area (161-310 °C) as well as peak heights - of the dosimetric peak of standard CaSO$_4$:Dy with codoped CaSO$_4$ phosphors at different concentrations of the codopants (Zn, Cd and Hg). The concentration referred to the amount of dopants that are dissolved. The actual amount of activator / co-activator actually got into the CaSO$_4$ crystal is unknown. A concentration of 0.2 mol% for both Dy/Tm and the codopant shows the maximum TSL sensitivity. At concentrations higher than 0.2 mol%, the TSL intensities were reduced due to concentration quenching [Ay 74, Na 74].

Figure 3.3 compares the TSL glow curves of CaSO$_4$:Cd,Tm (for different Cd concentrations from 0.2 to 5 mol% with Tm at 0.2 mol%) with that of CaSO$_4$:Tm (0.2 mol%). For low Cd concentrations, the TSL sensitivity increases but at higher Cd concentrations, the TSL sensitivity decreases when compared to that of CaSO$_4$:Dy. Further, the dosimetric peak shifts gradually to low temperature with increasing Cd concentration accompanied by an increase in the low temperature peak near 100 °C.

3.3.3. Glow curve shape vs dose

Figures 3.4 and 3.5 compare the TSL glow curves of CaSO$_4$:Dy (0.2 mol%) and CaSO$_4$:Zn,Dy (0.2 mol% each) at different gamma doses ranging from 107 mGy to 5.97
kGy. The rising portion of the glow curve at low dose level above 350-400°C (curve-a in figs 3.4 and 3.5) is due to the infrared (IR) contribution from the heater strip. At higher dose levels the TSL contribution is much more than the IR signals. The high (~300°C) and low (~100°C) temperature glow peaks of Zn codoped material were comparatively smaller than that of CaSO₄: Dy. For CaSO₄:Dy the dosimetric peak shifts from 220 to 260°C with the increase of γ-dose up to ~50 Gy and further increase in the dose shifts the peak back to 220°C. But in CaSO₄: Zn,Dy, the glow peak shift is relatively minor, from 230 to 254°C and back to 230°C at the above mentioned γ-dose levels.

The reduced glow curve shift with increase in γ-dose in CaSO₄:Dy,Zn relative to that in CaSO₄:Dy, indicates a reduced contribution of the high temperature peak. The codopants in CaSO₄:Dy are known to influence its glow curve shape and dose response characteristics. For example in CaSO₄:Dy,Cu the high temperature peaks near 300°C is quenched much more than that of the dosimetric peak at 200°C and its non-linearity is also reduced [Sr 92]. Similar but less pronounced effects are noticed in the case of CaSO₄:Dy,Zn.

3.3.4. Dose vs TSL response

Figure 3.6 compares the γ-dose versus TSL response (integrated area) of CaSO₄:Zn,Dy and CaSO₄:Dy is more or less, linear up to ~50 Gy beyond which it started showing a supra linear response upto ~5 kGy and then the saturation in agreement with earlier results in CaSO₄:Dy by Oliveri et al. [Ol 78]. The dosimetric properties such as glow curve shape, peak temperatures and dose response characteristics of CaSO₄:Dy and CaSO₄:Dy,Zn are very similar. This shows that the codoping did not change drastically its dosimetric properties but only enhanced its electron trapping ability.

3.3.5. Photoluminescence spectra

Figures 3.7a and 3.7b compare the PL excitation and emission spectra of CaSO₄:Zn,Dy and CaSO₄:Dy before and after ~43 mGy of ⁶⁰Co γ-ray irradiation. PL emission spectra of CaSO₄:Zn,Dy shows the characteristic Dy³⁺ emission peaks at 482 and 573 nm. Co-doping of 0.2 mol% Zn in CaSO₄:Dy results in a slight reduction of its PL emission intensity (~13% at 482 nm and ~17% at 573 nm) as well as a change in the relative intensities of the spectral lines in the excitation spectra. In CaSO₄:Dy, the Dy³⁺ PL excitation peaks at 348 and 363 nm are equally intense. But in CaSO₄:Zn,Dy the PL emission intensity of 348 nm peak is higher than that of the 363 nm peak by ~10%.
This shows that the surroundings of Dy$^{3+}$ in the crystal lattice of the two phosphors are different. A spatial association of Zn and Dy ions in the CaSO$_4$ lattice is one such possibility. Similar results were observed in CaSO$_4$:Eu on P and Na codoping [Va 90]. After γ - irradiation both the phosphors showed a reduction in the Dy$^{3+}$ PL emission intensities but the reduction in CaSO$_4$:Zn,Dy (~9% at 482 nm and ~6.5% at 573 nm) is relatively smaller compare to that in CaSO$_4$:Dy (~21% at 482 nm and ~18% at 573 nm). Hence both the irradiated samples showed almost equal Dy$^{3+}$ PL emission.

In contrast to the enhancement in TSL sensitivity, CaSO$_4$:Dy and CaSO$_4$:Dy,Zn samples showed a reduction in the Dy$^{3+}$ PL intensities with Zn codoping. Hence the observed increase in TSL sensitivity is not due to increased luminescence efficiency of Dy$^{3+}$ but is related to the increase in the number of electron traps created from the presence of Zn$^{2+}$ ions. But our other on going studies have shown that in post-irradiation annealing at 700°C, the PL intensities of Dy$^{3+}$ in CaSO$_4$:Dy are not restored fully unlike the case with the TSL intensities. This shows that the redox process (RE$^{3+}$ ⇌ RE$^{2+}$) proposed earlier [Na 74] perhaps has little relevance with the TSL process. The energy transfer model of Stoebbe [Mo 89] is more in tune with present result.

About 8% thermal fading (145-330°C area) was observed for γ-irradiated CaSO$_4$:Dy,Zn phosphor stored at room temperature (~25-30°C) for 1 month storage period. Codoping of Zn/Cd had no effect on the ultra violet (UV) induced TSL glow curve and UV sensitivity of CaSO$_4$:Dy/Tm phosphors.

3.4. Conclusions

The TSL phosphors CaSO$_4$:Dy,Zn and CaSO$_4$:Tm,Cd were found to be ~50% more sensitive than CaSO$_4$:Dy. Optimum concentration was seen as 0.2 mol% for both Zn and Dy. Relatively reduced glow curve shape changes with γ-dose, less pronounced peak at low temperature (100°C) as well as at high temperature (300°C) are some of the salient features of CaSO$_4$:Dy,Zn phosphor. The enhancement in TSL sensitivity is achieved by codoping II(B) group elements Zn$^{2+}$ and Cd$^{2+}$, which have higher SIP than Ca$^{2+}$. This result is in agreement with earlier predication that on irradiation of CaSO$_4$:Dy, Ca$^{2+}$ ions spatially situated near the activator ions themselves perhaps act as electron traps. These phosphors can substitute CaSO$_4$:Dy/Tm for low exposure measurements in environmental and personnel monitoring.
3.5. References


Atone M S, Moharil S V and Gundurao T K  

Ayyangar K, Chandra B and Lakshmanan A R  

Bhatt B C, Shinde S S, Srivastava J K and Gundurao T K  

Lakshmanan A R  
*Prog. Mater. Sci.* 44 (1999) 1

Lide D R (ed)  

Morgan M D and Stoebe T G  

Nambi K S V, Bapat V N and Ganguly A K  
*J Phys C: Solid St Phys* 7 (1974) 4403

Oliveri E, Fiorella O and Mangia M  
*Nucl Instrum Meth* 154 (1978) 203


Schmidt K, Linemann H and Giessing R  
*Proc. 4th Int. Conf. On Luminescence Dosimetry (Krakow, Poland)* vol 1 (1974) ed T Niewiadomski

Shinde S S, Bhatt B C, Srivastava J K, Sanaye S S and Iyer P S  
*Bull Radiat Prot* 16 (1993) 95

Srivastava J K, Bhatt B C and Supe S J  

Van Der Voot D and Blasse G  
*J Solid St Chemistry* 87 (1990) 350

Yamashita T, Nada N, Onishi H and Kitamura S  
*Health Phys.* 21(1971) 295
### Table 3.1. Second ionisation potential of the elements [Li 93]

<table>
<thead>
<tr>
<th>Element</th>
<th>Second ionisation potential (eV)</th>
<th>Ion charge</th>
<th>Ionic radii for coordination no. 6 (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>15.04</td>
<td>+2</td>
<td>72</td>
</tr>
<tr>
<td>Ca</td>
<td>11.87</td>
<td>+2</td>
<td>100</td>
</tr>
<tr>
<td>Sr</td>
<td>11.03</td>
<td>+2</td>
<td>118</td>
</tr>
<tr>
<td>Ba</td>
<td>10.00</td>
<td>+2</td>
<td>136</td>
</tr>
<tr>
<td>Mn</td>
<td>15.64</td>
<td>+2</td>
<td>67</td>
</tr>
<tr>
<td>Zn</td>
<td>17.96</td>
<td>+2</td>
<td>74</td>
</tr>
<tr>
<td>Cd</td>
<td>16.91</td>
<td>+2</td>
<td>95</td>
</tr>
<tr>
<td>Hg</td>
<td>18.76</td>
<td>+1, +2</td>
<td>119, 102</td>
</tr>
<tr>
<td>Pb</td>
<td>15.03</td>
<td>+2</td>
<td>119</td>
</tr>
</tbody>
</table>

### Table 3.2. The TSL intensities, both peak area (161-310°C) as well as peak heights of the dosimetric peak of CaSO₄:Dy/Tm with different concentrations of codopants (Zn and Cd). $^{60}$Co γ- dose ~2.4 Gy.

<table>
<thead>
<tr>
<th>Dopant concentration in CaSO₄ (mol %)</th>
<th>TSL (arb. units)</th>
<th>Dosimetric Peak Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak area</td>
<td>Peak height</td>
</tr>
<tr>
<td>Dy=0.2</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Dy=0.2, Zn=0.05</td>
<td>1.17</td>
<td>1.24</td>
</tr>
<tr>
<td>Dy=0.2, Zn=0.1</td>
<td>1.28</td>
<td>1.32</td>
</tr>
<tr>
<td>Dy=0.2, Zn=0.2</td>
<td>1.42</td>
<td>1.47</td>
</tr>
<tr>
<td>Dy=0.2, Zn=0.3</td>
<td>1.31</td>
<td>1.38</td>
</tr>
<tr>
<td>Dy=0.2, Zn=0.4</td>
<td>1.32</td>
<td>1.39</td>
</tr>
<tr>
<td>Dy=0.1, Zn=0.3</td>
<td>1.35</td>
<td>1.33</td>
</tr>
<tr>
<td>Dy=0.4, Zn=0.4</td>
<td>1.33</td>
<td>1.36</td>
</tr>
<tr>
<td>Dy=0.2, Zn=0.2, Mo=0.2</td>
<td>1.47</td>
<td>1.53</td>
</tr>
<tr>
<td>Tm=0.2, Cd=0.2</td>
<td>1.43</td>
<td>1.35</td>
</tr>
<tr>
<td>Tm=0.2, Cd=0.6</td>
<td>1.02</td>
<td>0.98</td>
</tr>
<tr>
<td>Tm=0.2, Cd=1</td>
<td>0.89</td>
<td>0.88</td>
</tr>
</tbody>
</table>
Figure 3.1. The TSL glow curves of CaSO$_4$:Dy (a), CaSO$_4$:Zn,Dy (b), CaSO$_4$:Cd,Tm (c), CaSO$_4$:Mo$_2$Zn,Dy (d) and CaSO$_4$:Hg,Tm (e) at the $\gamma$-dose of $\sim$2.4 Gy. All the dopants are at the concentration level of 0.2 mol%. The intensities of various glow curves are not exactly normalised to the same weight of the TSL phosphor.
Figure 3.2a. The TSL glow curves of CaSO$_4$:Zn$_2$Dy with constant Dy (0.2 mol\%) and different concentrations of Zn in mole \%: 0.0 (a), 0.05 (b), 0.1 (c), 0.2 (d) and 0.4 (e). $^{60}$Co $\gamma$- dose $\sim 2.4$ Gy.

Figure 3.2b. The TSL glow curves CaSO$_4$:Zn$_2$Dy for different concentrations of Zn and Dy in mol\%, CaSO$_4$:Dy (0.2) (a) and CaSO$_4$:Zn$_2$Dy (0.2,0.2) (b), (0.3,0.1) (c) and (0.4, 0.4) (d). $^{60}$Co $\gamma$- dose $\sim 2.4$ Gy.
Figure 3.3. The TSL glow curves of CaSO$_4$:Cd,Tm with constant Tm (0.2 mol%) and different concentrations of Cd in mol %: 0.0 (a), 0.2 (b), 0.6 (c), 1(d), 2 (e) and 5 (f). $^{60}$Co γ-dose ~2.4 Gy.

Figure 3.4. The TSL glow curves of CaSO$_4$:Dy at varies $^{60}$Co γ-doses: 107 mGy (a), 1.2 Gy (b), 7.34 Gy (c), 42.6 Gy (d), 142 Gy (e), 852 Gy (f) and 5.97 kGy (g). The intensities of different glow curves have not been normalised and hence are not to be inter compared.
Figure 3.5. The TSL glow curves of CaSO₄:Zn,Dy at various γ-doses: 107 mGy (a), 7.34 Gy (b), 42.6 Gy (c), 142 Gy (d), 852 Gy (e) and 5.97 kGy (f). The intensities of different glow curves have not been normalised and hence are not to be inter compared.

Figure 3.6. The γ-dose versus TSL response (integrated area) of CaSO₄:Zn,Dy and CaSO₄:Dy is more or less, linear upto ~50 Gy beyond which it started showing a supra linear response upto ~5 kGy and then the saturation
Figure 3.7a. The PL spectra of CaSO₄:Dy (0.2 mol%). Emission spectra for λₑₓ = 363 nm: unirradiated (a) and irradiated (b) and Excitation spectra for λₑₘ = 482 nm: unirradiated (c) and irradiated (d). ⁶⁰Co γ-dose ~43 mGy.

Figure 3.7b. The PL spectra of CaSO₄:Zn,Dy (0.2 mol% each). Emission spectra for λₑₓ = 348 nm: unirradiated (a) and irradiated (b) and Excitation spectra for λₑₘ = 482 nm: unirradiated (c) and irradiated (d). ⁶⁰Co γ-dose ~43 mGy.