CHAPTER 5

ABSORPTION, PHOTOLUMINESCENCE, X-RAY AND EMISSION SPECTRA

5.1  INTRODUCTION

A basic understanding of the thermoluminescence mechanism involves the identification of the trapping centers for the observed light emission. Normally, electrons and holes trapped at defects or impurities form color centers and introduce optical absorption bands into the transparent crystal. The defect energy levels lie in the forbidden gap of the insulating crystal. Therefore, occupation and detrapping of the charge carriers could be correlated with the changes in the optical absorption bands. A study of these changes coupled with photoluminescence spectra can give additional information about the thermoluminescence process.

5.2  ABSORPTION SPECTRA

Absorption spectra of TLD-100 powder, as determined by reflection method described in sec 2.2.4, is shown in Fig. 5.1. There is an absorption band around 450 nm ($M$ band). Smaller bands around 360 nm ($R$ band) and 550 nm ($N_2$ band) are also present. These results exactly reproduce the observations of Vaughan and Miller (1970) and Claffy et al (1971). In fact the absorption
FIG 5.1 OPTICAL ABSORPTION AND PHOTOLUMINESCENCE SPECTRA OF TLD-100
UNIRRADIATED   \gamma-IRRADIATED
B: EXCITATION SPECTRUM A: ABSORPTION SPECTRUM
C: EMISSION SPECTRUM D: EXCITATION SPECTRUM
E: EMISSION SPECTRUM
spectra of single crystals of LiF: Mg, LiF: Ti and TLD-100 have been extensively studied (Hakajima 1971 and Zimmermann et al 1967). The present set of observations, taken with powder sample, is shown here only to indicate the utility of the method adopted.

TLD-200 powder, a commercial quality of CaF$_2$:Dy, exhibits an absorption spectra on γ irradiation at RT, as shown in Fig. 5.2. Absorption bands are observed at 310, 360, 390, 410, 435, 470, 500 and 550 nm. Fong (1964) observed bands around 314, 421, 458, 488, 544, 577, 715 and 910 nm for CaF$_2$:Dy single crystals whereas Kiss (1965) reported bands at 303, 337, 383, 406, 446, 475, 531 and 566 nm for a similar material. These bands are characteristic of Dy$^{2+}$.

CaSO$_4$:Dy (0.05 mol%) exhibits gamma ray induced absorption bands as shown in Fig. 5.3a. Within experimental limits, the bands are characteristic of Dy$^{2+}$ ions. Undoped CaSO$_4$, for the same gamma irradiation level, shows almost a uniform coloration over the wavelength range 300 - 600 nm, and the apparent optical density is lower by a factor of three. Isothermal annealing studies at 120°, 150°, 250°, 300° and 400°C failed to establish the correspondence of any of the TL glow peaks observed around 85°, 120°, 220°, 275°, 375°, 500° and 570°C with any of the optical absorption bands observed in the irradiated phosphor.
2.5.2 Optical absorption and fluorescence spectra of TLD-200

A: Absorption, y-irradiated
B: Excitation
C: Emission
CaSO$_4$ :Tm (0.05 mol) powder, on gamma ray irradiation, exhibits absorption bands as shown in Fig. 5.4a. The bands are characteristic of Tm$^{2+}$, and are similar to those observed in the case of CaF$_2$:Tm on irradiation. Kiss (1962) reported bands around 208, 230, 310, 335, 410 and 450 nm with a small hump around 570 nm for CaF$_2$:Tm$^{2+}$ crystals.

On gamma irradiation of undoped MgF$_2$ phosphor, intense absorption bands around 260 nm and 360 nm with a minor hump at 400 nm have been observed (Fig. 5.5). Doped MgF$_2$ phosphors also show a similar absorption spectrum. The present studies failed to reveal any additional bands attributable to the impurity ions.

BaSO$_4$ phosphor, by its intrinsic nature, is difficult to color on gamma irradiation. A feeble absorption band around 350 nm is observed on intense gamma irradiation ($10^6 - 10^7$ R).

5.3 PHOTOLUMINESCENCE AND X-RAY EXCITED OPTICAL LUMINESCENCE (SEOL).

Photoluminescence spectra of unirradiated TLD-100 phosphor has an excitation peak at 220 nm with a broad emission around 420 nm (Fig. 5.1). The extended nature of the emission curve on higher wavelength side indicates that it is an envelop of various bands. On
FIG 5-4 ABSORPTION AND FLUORESCENCE SPECTRA OF Co-SC^Tr

A - ABSORPTION

B - EXCITATION

C - EMISSION

WAVELENGTH (nm)

RELATIVE FLUORESCENCE

APPEARANT OPTICAL DENSITY

A: ABSORPTION

B: EXCITATION

C: EMISSION
irradiation, the spectra undergo a drastic change with excitation maxima around 425 and 470 nm and emission peaking at 520 nm with humps around 550-570 nm and 635 nm. Emission bands of the photoluminescence spectrum of the irradiated phosphor coincide with TL emission bands at 300, 420, 520 and 650 nm (Jittenden et al 1974).

TL emission spectrum (sharp bands at 485 nm and 580 nm) coincides with the photoluminescence spectrum of the CaF₂:Dy phosphor (Fig. 5.2c). Excitation part of the photoluminescence spectra (Fig. 5.2b) has peaks coinciding with the absorption bands observed on γ irradiation. X-ray excited optical luminescence (XEOL) studies indicate that Dy ion is in the Dy³⁺ state in the unirradiated phosphor (Fig. 5.6).

Photoluminescence and XEOL spectra of unirradiated CaSO₄:Dy are characteristic of the Dy³⁺ ion. On γ irradiation, these intensities diminish. This can be assigned to conversion of Dy³⁺ ions to Dy²⁺ on γ irradiation.

The photoluminescence spectra of the unirradiated CaSO₄:Tm are typical of the Tm³⁺ ions (Fig. 5.4) and this intensity diminishes on γ irradiation, as some ions get converted to Tm²⁺. On heating the phosphor, the ions get converted back to Tm³⁺ and the intensity of the photoluminescence gets restored.
FIG 5-6 XEOL SPECTRUM OF UNIRRADIATED CaSO$_4$:D$_y$
FIG. 57 XEOL SPECTRUM OF UNIRRADIATED CaSO₄: Tb
The photoluminescence spectra of $\text{Mg}_2\text{SiO}_4:\text{Tb}$ (Fig. 5.8) is typical of $\text{Tb}^{3+}$ ion and on irradiation, the luminescence gets diminished. This makes us infer that the number of $\text{Tb}^{3+}$ ions is reduced on irradiation and the original concentration of $\text{Tb}^{3+}$ ions gets restored on heating the TL phosphor.

Photoluminescence spectra of the $\text{MgF}_2$ samples are quite revealing. The spectra of the $\text{MgF}_2$ samples before and after irradiation at RT ($28^\circ$ - $30^\circ$C) are given in Fig. 5.9. Unirradiated starting sample as well as Mn doped samples do not show any fluorescence under 260 nm excitation. It is already known that $\text{Mn}^{2+}$ does not fluoresce on its own (Medlin 1968) unless the phosphor has some other absorption bands through which it receives excitation via energy transfer. On irradiation, $\text{MgF}_2:\text{Mn}$ samples show two fluorescence emission bands one at 420 nm and the other at 575 nm. The latter one matches with the $\text{Mn}^{2+}$ emission as observed in TL emission of $\text{MgF}_2:\text{Mn}$ (Sec. 5.4). 420 nm fluorescence emission band is present in all the $\text{MgF}_2$ phosphors doped as well as undoped. This intense band, related to the irradiated host matrix having an excitation maximum at 260 nm, may be assigned as an optical center, produced on $\gamma$ irradiation. The excitation maximum for 420 nm being at 260 nm and 380 nm
PHOTOLUMINESCENCE SPECTRA OF Mg$_2$SiO$_4$:Tb
A: EXCITATION, B: EMISSION
while that for Mn$^{2+}$ emission, at 260 nm, 380 nm and 420 nm goes to suggest that the Mn$^{2+}$ fluorescence is due to excitation energy transfer from the center responsible for 420 nm fluorescence emission or in other words, from one having absorption bands at 260 nm and 380 nm.

$\text{MgF}_2:\text{Tb}$, shows fluorescence even in the unirradiated state (Fig.5.9), which is characteristic of Tb$^{3+}$ ionic state and compares well with the characteristic Tb$^{3+}$ TL emission of $\text{MgF}_2:\text{Tb}$ (Sec. 5.4). On intense $\gamma$ irradiation, the characteristic fluorescence of Tb$^{3+}$ vanishes and the fluorescence observed is similar to that of the undoped samples. The absence of the fluorescence, on $\gamma$ irradiation, means absence of trivalent ions. The trivalent ions are converted, most probably, to divalent on irradiation.

Unirradiated $\text{MgF}_2:\text{Tm}$ shows fluorescence emissions bands at 360 nm and 460 nm under 260 nm excitation (Fig.5.9). These match very well with TL emission bands of Tm$^{3+}$ ions (sec. 5.4). On irradiation these bands diminish and a strong fluorescence band at 420 nm, having excitation bands at 260 nm and 380 nm, is observed. The decrease of the fluorescence emission typical of Tm$^{3+}$ ions means that Tm$^{3+}$ ions get reduced on irradiation. On heating the sample, this fluorescence intensity gets restored to that of undoped sample.
Similarly in case of MgF₂: Dy, fluorescence emission of undoped samples at 460 and 570 nm under 360 nm excitation is associated with Dy³⁺ ions and on Γ irradiation, a strong emission at 420 nm is observed whereas 460 nm and 570 nm bands diminish (Fig. 5.9).

In case of BaSO₄: Tb and BaSO₄: Dy, the photoluminescence spectra of the unirradiated samples are characteristic of Tb³⁺ and Dy³⁺, respectively. (Fig. 5.10). Eu exists in Eu²⁺ as well as Eu³⁺ ionic form in unirradiated BaSO₄: Eu phosphor (Fig. 5.11). Fluorescence emission at 375 nm is attributed to Eu²⁺ ions whereas lines at 597, 625 and 700 nm are due to Eu³⁺ (Nambi et al. 1974). According to Bapat (1977), Eu³⁺ gets reduced to Eu²⁺ on Γ irradiation of CaSO₄ and reoxidizes back to Eu³⁺ on heating. As the figure shows, the same process holds good in BaSO₄: Eu. Eu²⁺ fluorescence increases on irradiating the sample while the fluorescence corresponding to Eu³⁺ decreases. The fluorescence of Eu²⁺ and Eu³⁺ gets restored to their original levels, on heating the phosphor for TL.

5.4 TL EMISSION SPECTRA

(a) Experimental details

High dose (10⁵ - 10⁶ R) samples were used for determining the emission spectra, so as to get sufficient
Fig 5.10 Photoluminescence spectra of BaSO$_4$:Tb and BaSO$_4$:Dy

1. BaSO$_4$:Tb  a: Excitation
2. BaSO$_4$:Dy  b: Emission
FIG. 5.11 PHOTOLUMINESCENCE SPECTRA OF BaSO₄:Eu

- Excitation Spectrum, Unirradiated
- Emission, Irradiated
- Emission, Unirradiated
emissions through monochromator for detection. The fast heating assembly was used for heating the phosphor (~10 mg). After attaining the appropriate temperature, it was held constant. The emission spectrum was recorded by automatic scanning using the motor drive of the grating (100 nm/min). A 600 nm biased grating was employed for the entire range 300-700 nm. Temperatures were so chosen that the sample is maintained around 20°C below the temperature of the glow peak whose emission is to be recorded. These spectra were taken mainly to detect various lines of emission from the samples and thus to arrive at the nature of the recombination centres.

(b) Results and Discussion

Even though the nature of the TL glow curves for various doped samples for a given matrix (CaSO₄, BaSO₄, or MgF₂) was the same, the emission spectra differ from one sample to another. The emission lines are characteristic of the dopant added (Figs. 5.12, 5.13 and 5.14). In case of Rare-earth dopants, the spectra are typically characteristic of RE³⁺ ion and are similar to fluorescence spectra of RE doped CaF₂ phosphors (Nerz and Pershan 1967). The only exceptions are those of Eu and Mn which exist in divalent state in CaSO₄, MgF₂ as well as BaSO₄.

In MgF₂ phosphors, the emission of Mn, Tb, Dy, or Tm occurs in the TL emission of respective doped samples.
FIG 5.12 TL EMISSION SPECTRA OF CaSO₄ PHOSPHORS
FIG 5.13 TL EMISSION SPECTRA OF BaSO₄ PHOSPHORS
A: UNDOPED, B: BaSO₄: Eu, C: Tb doped
D: Dy doped, E: Sm doped
FIG 5.14 TL EMISSION SPECTRA OF MgF$_2$ PHOSPHORS
but the 420 nm emission, even though predominantly observed in fluorescence, is completely absent in the TL emission. This is because in TL emission process, the recombination energy excites the host centers in higher excited states wherefrom transfer of excitation to the impurity ions is much more efficient than relaxation to a lower state of host center which could result to 420 nm emission. It may also be noted that a feeble emission around 575 nm is observed for all the MgF₂ samples. It is due to the unavoidable trace quantity of Eu present in the starting material itself.

5.5 CONCLUSIONS

Study of the absorption, photoluminescence, X-ray and emission spectra leads us to the following conclusions:

(i) With the exception of Mn²⁺ and Eu²⁺, all the activators incorporated in CaSO₄, BaSO₄ and MgF₂ matrices exist in triply ionized state, when the phosphors are unirradiated.

(ii) In general, on Y irradiation

\[ \text{RE}^3+ \rightarrow \text{RE}^2+ \], and on heating

\[ \text{RE}^2+ \rightarrow \text{RE}^3+ \]
(iii) With the exception of In and Eu, the emission centers in all the three phosphors are the trivalent rare-earth ions. In case of In and Eu, these are In$^{2+}$ and Eu$^{2+}$, respectively.