III X-RAY EXCITED OPTICAL LUMINESCENCE STUDIES

III-1 INTRODUCTION
X-rays have been found to be very effective in exciting luminescence particularly from the much higher energy levels of rare earth ions in crystals. Luminescence from four of the five 5d levels ($\Gamma_7^{III}$, $\Gamma_7^{II}$, $\Gamma_7^I$, $\Gamma_6^{I-2} F_{7/2}$) of rare earth ion Ce$^{3+}$ in YPO$_4$ has been reported$^{(53)}$. X-ray excited fluorescence from CaS doped with rare earth ions Dy$^{3+}$, Tb$^{3+}$, Dy$^{3+}$Tb$^{3+}$, Eu$^{2+}$, Eu$^{2+}$Tb$^{3+}$ also have been studied in detail$^{(94-97)}$. X-Ray excited optical luminescence (XEOL) studies have been used for qualitative analysis of rare earth impurities in Uranium, which is necessary for its use as a reactor fuel$^{(98)}$.

Belsky et al. studied the luminescence spectra of CaS:Ce under excitation by radiations from X-ray tube and synchrotron$^{(99)}$. The comparison of these spectra with that of photoluminescence revealed two types of radiation induced Ce$^{3+}$ emission centres. One type is in which an activator ion is displaced from regular sites of symmetry as a result of coulomb interaction with charged defects created in its neighbourhood by the excitation in the fundamental absorption edge. The second type is due to the creation of sulphur vacancies in the first coordination shell of Ce$^{3+}$ by the exciting radiation.

Here, we have studied the effect of Ce$^{3+}$ on the fluorescence emission from CaS phosphor using X-ray excitation. The fluorescence emission occurs in the visible and UV region and the intensity and wavelength of the emission varies with the concentration of the dopant.
III–2 SAMPLE PREPARATION
Details of sample preparation at various dopant concentrations are given in section 3 in chapter II.

III–3 EXPERIMENTAL ASPECTS
The XEOL spectrum was recorded at the spectroscopy division laboratory at Bhabha Atomic Research Centre, Mumbai. The experimental arrangement employed for the XEOL studies is shown schematically in Fig.3.1.

Fig.3.1
Schematic diagram of experimental setup for
X-ray excited optical luminescence studies
The X-ray source used for irradiating the sample consists of a 1 kW power X-ray tube having tungsten target and the tube operates at 40 kV, 20 mA. An exploded view of the sample chamber is shown in Fig.3.2. This provides the complete safe exchange of samples even though the X-ray tube (a) continues in operation at full power. During excitation of the sample in this chamber, a small access door (b) is blocked in the closed position by a lever (c). To exchange samples the lever and the attached shutter (d) are rotated so that the X-ray beam is interrupted before the door can be raised. The sample is accurately and reproducibly positioned at an angle of 45° to the incident X-ray beam through the use of a vee way mounting block (e) and suitably fitting sample holder (f). The optical path is inclined at an angle of 45° to the sample surface and at 90° to the X-ray beam.

The optical luminescence produced by the sample is collected by the condensing and reflecting concave mirror, which renders the beam horizontal and subsequently focused on the entrance slit of a 25cm focal length grating monochromator of Jarrel Ash type, with the help of a quartz lens as shown in Fig.3.1. The plane reflection grating of the scanning monochromator shown in Fig.3.1 with 2360 grooves/mm and blazed at 600 nm serves as the dispersing element. The widths of the entrance and exit slits of the monochromator are set at 100 micrometre and the spectrum is scanned at the rate 20.825 nm/min using a motor. The fluorescence emission is detected using a photomultiplier tube EMI 9858 QB operating at 900 V. The photocurrent is amplified using the electrometer amplifier EA 810 A and recorded with a two pen strip chart recorder, one of the pens of which is one tenth as sensitive as the other which permits a greater range of spectral intensities to be recorded during a single scan of wave lengths.

A few milligram of the powdered sample is spread uniformly over approximately 1cm² area of a special planchet and glued to it and kept on the sample holder and the X-ray excited fluorescence spectra are recorded.
Fig. 3.2

Exploded view of sample chamber

(a) X-ray tube, (b) access door for inserting the sample holder, (c) lever,
(d) shutter, (e) vee way mounting block and (f) sample holder
RESULTS AND DISCUSSION

Fig.3.3 shows the fluorescence emission spectra at various dopant Ce$^{3+}$ concentrations in CaS phosphor. The undoped sample exhibits a single broad peak in the visible region of the spectrum at 485 nm (a) in Fig.3.3. There is no spectral emission in the UV region. The emission in the visible region is due to self-activation centres arising from lattice defects like vacancies.

On increasing the dopant concentration, the emission peak in the visible region shifts towards the longer wave length side and a well defined shoulder is developed on the longer wave length side of the main peak (b), (c), (d) & (e) in Fig.3.3. These results show that the presence of dopant modifies the distribution of self-activation centres in the host lattice.

Apart from the emission in the visible region, the spectrum of CaS:Ce phosphor shows broad twin peaks in the UV region at wave lengths 225nm and 278nm$^{(44)}$. The UV emission intensity is very small compared to that of the visible region. Results obtained from the present studies are summarized in Table 3.1.

Table 3.1

<table>
<thead>
<tr>
<th>Dopant Conc. (mole %)</th>
<th>Wave length of peaks (nm)</th>
<th>Intensity of peaks (Arb.units)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>0.0000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.0175</td>
<td>222</td>
<td>275</td>
</tr>
<tr>
<td>0.0350</td>
<td>224</td>
<td>277</td>
</tr>
<tr>
<td>0.1750</td>
<td>225</td>
<td>278</td>
</tr>
<tr>
<td>0.3500</td>
<td>228</td>
<td>282</td>
</tr>
</tbody>
</table>

Fig.3.4 shows the variation of the peak intensity of the fluorescence emission with dopant concentration indicating the usual concentration quenching for all
X-ray excited fluorescence emission spectra of CaS:Ce$^{3+}$ phosphor for various Ce concentrations (mol%) (A) undoped, (B) 0.0175, (C) 0.035, (D) 0.175 and (E) 0.35
Fig. 3.4

Variation of X-ray fluorescence emission intensity with dopant concentration in CaS:Ce for the three prominent peaks at (a) 225nm (b) 278nm and (c) 500nm in the emission spectrum.
the peaks. The relevant transitions in Ce$^{3+}$ ions corresponding to UV emission are given in Fig. 3.5.

\begin{center}
\begin{tikzpicture}
\node (5d) at (0,0) {$5d^1$};
\node (2E) at (1,1) {$2E$};
\node (2T) at (2,1) {$2T$};
\node (4f) at (0,-1) {$4f^1$};
\node (2F) at (2,-1) {$2F$};
\draw[->] (5d) -- (2E) node[midway,above] {225 nm};
\draw[->] (2E) -- (2F) node[midway,above] {278 nm};
\end{tikzpicture}
\end{center}

\textbf{Fig. 3.5}

Relevant transitions in Ce$^{3+}$ ions corresponding to UV emission.

III-5 CONCLUSION

From these observations it can be concluded that the free ion term 2D arising from 5d$^1$ configuration of Ce$^{3+}$ splits into $2E$ and $2T$ states in CaS lattice with doublet separation 8470 Cm$^{-1}$ giving rise to the doublet in the UV region of the X-ray excited fluorescence spectra of CaS:Ce.