V-1 INTRODUCTION
One of the important criteria for any specific application of a phosphor is its efficiency of energy conversion. Basically this efficiency may be defined as the ratio of energy converted into luminescence emissions by the phosphor to the energy incident on it for exciting luminescence. Alternately one may define quantum fluorescence efficiency as the ratio of the number of photons emitted to that absorbed by a phosphor, when the incident and emitted beams are electromagnetic radiation. However, when the incident beam consists of particles like electrons and α particles one may opt to determine the power conversion efficiency, which can be defined as the ratio of the powers emitted and incident radiations.

Measurement of these efficiencies involves complex experimental techniques and calculations are based on several assumptions and approximations. Errors in these estimates are reported to be of the order of 10 to 15% (113,114).

Two types of measurements are often used for efficiency determination (115-117). The first is the deduction of efficiency of an unknown phosphor in comparison with a phosphor of known efficiency. The second is the direct optical method without using any assumptions and consequently often described in the literature as tedious and time consuming. Here we measure quantum fluorescence efficiency of phosphors by direct optical method using experimental techniques and by using manufacturers data for the spectral response function of the detector, which is the modified form of the second method.
V-2 EXPERIMENTAL SETUP

The quantum fluorescence efficiency measurements of the phosphors were done at the rare earth division laboratory of Bhabha Atomic Research Centre, Mumbai. The apparatus used for the measurement of quantum fluorescence efficiency $Q$ is as shown in Fig.5.1. It consists of a stainless steel (SS) assembly of two chambers – (1) the upper and (2) the lower. The upper chamber consists of an SS tube of internal diameter 5 cm and length 25 cm. A high-pressure mercury vapour lamp (3) 125 W with out its outer shell is placed vertically in this chamber. This lamp provides UV radiation of frequency 254, 312 and 365 nm. The light beam from the lamp is collimated with two aluminium rings (4) of 2 cm internal diameter, fitted inside the SS tube. The thin metal plate (5) introduced through the side cutting on the tube act as the shutter.

The lower chamber, which is an SS tube of 10 cm diameter and 10 cm height, holds the interference filter (6) and quartz lens (7) on suitable supports. The aluminium sample holder (8) and silicon photo diode (SPD) (9). The base of the apparatus (10) is a graphite disc (2 cm thick and 10 cm diameter). A channel (11) is cut in this disc to slide the sample holder from the side inwards to the center. The sample holder is an aluminium plaque of internal diameter 2 cm and depth 3 mm. The plaque is loaded with a 3 mm phosphor layer of uniform thickness. The SPD mounted on a cylindrical bakelite frame (12) placed at the viewing port (13) will view the light coming out from the phosphor surface at an angle of 45°. The interference filter selects the 254 nm for UV excitation. The quartz lens (7) focuses the UV on to the phosphor surface. The light falling on the SPD surface (area 10x10 mm) produces a photocurrent, which is measured by an electrometer amplifier. A pyrex filter (14) introduced through the viewing port (13) cuts off UV when required. The beam of UV strikes the phosphor surface and the fluorescence emission falls on the SPD (Type no. S. 1337- 1010 BQ Hamamatsu make). The light collected by the SPD is proportional to the solid angle subtended by it on the phosphor surface.
Experimental setup used for quantum fluorescence efficiency studies.

(1) stainless steel (SS) upper chamber, (2) SS lower chamber, (3) mercury vapour lamp, (4) aluminium rings, (5) metallic shutter, (6) interference filter, (7) quartz lens, (8) aluminium sample holder, (9) silicon photo diode (SPD), (10) graphite base, (11) channel in the graphite base, (12) bakelite frame for mounting SPD, (13) viewing port and (14) pyrex filter.
V-3 THEORETICAL ASPECTS

The number of UV photons/s striking the phosphor surface for excitation is determined by measuring the number of reflected photons/s from a standard magnesium oxide (MgO) powder of known reflectivity $\rho (= 0.91)$ for UV radiation\textsuperscript{118}. In the above experimental setup aluminium plaque is loaded with magnesium oxide powder. The reflected UV photons/s (from the MgO) falling on the SPD generates a photocurrent proportional to the number of UV photon/s striking its surface. This current $C_1$ can be written as

$$C_1 = K\rho Y I_e \quad \text{(1)}$$

(where, $K$ is a constant representing the geometry of the apparatus, $Y$ is the number of UV photons/s striking the MgO surface and $I_e$ is the photo current (in amperes) produced in the SPD by a single UV photon striking its surface/s expressed in A/photon/s). If the plaque is replaced by one loaded with phosphor, the UV photons striking the phosphor gets partly absorbed and partly reflected. The net effect is the generation of a photocurrent $C_2$ in the SPD due to the combined effect of visible fluorescence emission (in number of photons/s) spread over a range of wavelengths and reflected UV (in number of photons/s).

Thus

$$C_2 = C_1 + C_4 \quad \text{(2)}$$

(where $C_2$ is the photo current due to fluorescence emission and $C_4$ due to the reflected UV). Due to the flatness of the quantum response of the SPD in the visible region of emission (Fig.5.2), $C_3$ can be written as

$$C_3 = KQ(l-\gamma)Y I_f \quad \text{(3)}$$

(where $Q$ is the quantum fluorescence efficiency, $\gamma$ the reflectivity of the phosphor for UV and $I_f$ the photo current in amperes generated in the SPD by a single fluorescence photon striking its surface/s expressed as A/photon/s) and

$$C_4 = K\gamma Y I_e \quad \text{(4)}$$

Substituting for $Y$ in terms of $C_1$ from equations (1) in (2) we get

$$C_2/C_1 = [(l-\gamma)Q I_f]/\rho I_e + \gamma/\rho \quad \text{--- (5)}$$

So

$$Q = [C_2/C_1 - \gamma/\rho] [\rho/(l-\gamma)] [I_e/I_f]$$

And from equations (1) and (4)

$$\gamma = \rho (C_4/C_1)$$

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Therefore

\[ Q = \left( \frac{C_2}{C_4} - \frac{C_4}{C_3} \right) \left[ \frac{I_e}{I_f} \right] \left[ \frac{\rho}{(1-\gamma^2)} \right] \]

Since

\[ C_2 - C_4 = C_3 \]

\[ Q = \left( \frac{C_3}{C_4} \right) \left[ \frac{I_e}{I_f} \right] \left[ \frac{\rho}{(1-\gamma^2)} \right] \]

The values of \( Q \) are determined by using equation (6) substituting all the known values in which \( C_2 \) and \( C_3 \) are actually measured and \( I_e \) and \( I_f \) can be deduced from the characteristic curve of the SPD given in Fig. 5.2.

**V-4 MEASUREMENTS**

The aluminium plaque is loaded with MgO and placed in the apparatus. The UV (254nm) light is focused on to a small area of the sample using the quartz lens. The reflected UV rays from MgO produces the photocurrent \( C_1 \) in the SPD, which is measured by the electrometer amplifier. The plaque is now emptied and filled with the phosphor and the photocurrent \( C_2 \) is measured. The pyrex glass filter is then placed in front of the SPD to cut off the reflected UV from the phosphor and the current due to the remaining fluorescence emission \( C_3 \) alone is also measured. From these we get \( C_4 \), which is equal to \( C_2 - C_3 \). But \( C_3 \) is not the exact current component in \( C_2 \) due to fluorescence alone. The measured current is \( C_3' \), which is an attenuated value of \( C_3 \) due to the transmission coefficient \( \tau_f \) of the Pyrex filter. The real \( C_3 = C_3' / \tau_f \). The transmission coefficient \( \tau_f \) of the filter measured using Shimadzu spectrophotometer is 0.92±1% for visible region of emission. Knowing all these values \( Q \) was calculated for different samples whose \( Q \) values are given in the Table 5.1.

The measured value of \( Q \) needs to be corrected for the reflectivity of the phosphor for its own emission. The true or intrinsic quantum efficiency \( Q_i \) is given by

\[ Q_i = \frac{2Q}{1 + R \alpha}. \]

Where, \( R \alpha \) is the reflection coefficient of an infinitely thick layer of phosphor for its own emission, which is close to unity. The thickness of the sample was taken as 3mm so that \( R \alpha = 1 \), so that \( Q = Q_i \).
Fig. 5.2

Spectral response characteristics of Photo diode type No. S 1337 – 1010 BQ

(Reproduced with courtesy, Hamamatsu Photonics, K. K. Solid State Division, Hamamatsu City, 435, Japan)
V-5 RESULTS AND DISCUSSION
Quantum fluorescence efficiency (Q) values given in Table 5.1 show that all the rare earth doped CaS samples show similar variation. i.e. as concentration of the dopant increases Q first increases and then decreases above an optimum concentration. This is due to the concentration quenching of luminescence emission as seen in the case of X ray fluorescence emission from CaS:Ce. Fig.5.3 shows concentration quenching effect of fluorescence emission from

### TABLE 5.1
Dopants and their concentrations, SPD currents and quantum fluorescence efficiencies of CaS:X phosphor samples

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Dopant concentration (wt.%)</th>
<th>SPD current (nA)</th>
<th>Quantum fluorescence efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₁</td>
<td>C₂</td>
</tr>
<tr>
<td>X = Ce</td>
<td>0.12</td>
<td>0.220</td>
<td>0.080</td>
</tr>
<tr>
<td></td>
<td>0.24</td>
<td>0.220</td>
<td>0.110</td>
</tr>
<tr>
<td></td>
<td>0.72</td>
<td>0.220</td>
<td>0.110</td>
</tr>
<tr>
<td></td>
<td>1.20</td>
<td>0.220</td>
<td>0.100</td>
</tr>
<tr>
<td>X = Sm</td>
<td>0.12</td>
<td>0.220</td>
<td>0.130</td>
</tr>
<tr>
<td></td>
<td>0.24</td>
<td>0.220</td>
<td>0.130</td>
</tr>
<tr>
<td></td>
<td>0.72</td>
<td>0.220</td>
<td>0.110</td>
</tr>
<tr>
<td></td>
<td>1.20</td>
<td>0.220</td>
<td>0.100</td>
</tr>
<tr>
<td>X = Nd</td>
<td>0.12</td>
<td>0.220</td>
<td>0.110</td>
</tr>
<tr>
<td></td>
<td>0.24</td>
<td>0.220</td>
<td>0.110</td>
</tr>
<tr>
<td></td>
<td>0.72</td>
<td>0.220</td>
<td>0.120</td>
</tr>
<tr>
<td></td>
<td>1.20</td>
<td>0.220</td>
<td>0.130</td>
</tr>
<tr>
<td>X = Pr</td>
<td>0.12</td>
<td>0.220</td>
<td>0.100</td>
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<td></td>
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<tr>
<td></td>
<td>1.20</td>
<td>0.220</td>
<td>0.100</td>
</tr>
</tbody>
</table>
Fig. 5.3

Variation of Quantum Fluorescence Efficiency of rare earth doped CaS with dopant concentration (wt.%)
these phosphors under UV illumination. Results show that Ce modifies quantum efficiency of CaS more than other dopants.

The low values of quantum fluorescence efficiency can be explained as due to higher efficiencies phosphorescence and thermoluminescence emission. Since thermoluminescence and phosphorescence efficiencies are higher, larger amounts of incident energy will be stored in these phosphors for these purposes. Another reason is the lower response of CaS to 254nm radiation as compared to 365nm radiation.

V- 6 CONCLUSION
Quantum fluorescence efficiency of rare earth doped CaS was measured using direct optical method. The method is suitable for the study of samples with low quantum fluorescence efficiency.