3.1A General

A luminescent material, when excited absorbs energy either through the host lattice or through the activator. The actual absorption spectrum of a crystal not only depends on the position of excited states but also on various transition probabilities. The absorption in pure ionic crystals may be of two types. One is connected with the charge transfer transitions between orbits of opposite ions and is known as fundamental lattice absorption. The other, called ionic or characteristic absorption is associated with an electronic transition between the two orbits of the same ion. (1) The characteristic absorption band of a simple ionic solid generally lies on the long wavelength side of the fundamental lattice absorption; the latter is very sensitive to changes in lattice dimensions. Pure lattice absorptions have been found in simple compounds such as NaCl, ZnS, ZnO etc. The characteristic absorptions of positive ions near the fundamental absorption are observed with the rare earth salts and transitional elements, whereas absorption due to complex negative ions occurs in nitrates, tungstates etc. (2,3)

3.2A Absorption in activated crystals

Generally the crystal lattice is not perfect due to the presence of defects or impurities. These imperfections perturb the periodicity of the crystal and produce localised energy levels. Thus every impurity or lattice defect will in
general give rise to new absorption bands which are usually observed on the long wavelength side of the fundamental absorption.\(^{(4,5)}\) A foreign ion (positive or negative) replacing the corresponding host ion, trapped electrons and holes and cracks in the surfaces of the crystal are a few of the various imperfections causing a long wavelength tail of the fundamental absorption. Faint absorptions connected with the localised levels of these imperfections are observed only when the energy of these transitions is smaller than that corresponding to the fundamental absorption of the host crystal.\(^{(6-9)}\)

Incorporation of a considerable amount of activator or formation of mixed crystals changes the lattice dimensions, thereby changing the relative positions of the energy levels. The characteristic absorptions are however very little affected by such changes. But the fundamental absorption due to transfer transitions from a negative to a positive ion shifts towards shorter wavelengths if the lattice expands and towards longer wavelength if the lattice contracts.\(^{(10,11)}\) There is no essential difference, in principle, between the characteristic absorption of a pure substance and that of an activated substance. In cases, where the matrix compound can form a series of mixed crystals with the activator compound, a continuous change from one to another type may occur. For example, the optical properties of Lanthanum fluoride activated with cerium fluoride change gradually into those of pure cerium fluoride as the concentration of the latter is increased.\(^{(12)}\) The same is true for
the fundamental absorption of pure crystals and the transfer absorptions possible in activated crystals. In such cases it is reasonable to talk in terms of the fundamental absorption of the activator compound.

From a theoretical point of view, fundamental absorption in pure non-metallic crystals should give rise to photoconductivity. In alkali halide crystals such absorption produces no photocurrent. It has been assumed that such absorption creates 'excitons' which move through crystal and have no net charge.

For substances like zinc sulphide and silver halides the correct interpretation of the $N$ absorption spectrum is still in doubt. It is also not certain whether the radiation which stimulates photoconductivity and fluorescence is absorbed by ions of the perfect lattice, or only by ions specially situated at the surfaces of cracks or by atoms in interstitial positions. There is no general agreement as to whether the absorption spectrum in this region depends upon the activating impurity.

However, in zinc sulphide type phosphors excited by ultraviolet light, it may well be said that the centres are responsible for the long wavelength tail of the absorption band.\(^{13}\)

Although present, the lines of the trivalent rare earth ions have not been recorded in absorption spectra of sulphide and oxide phosphors activated with Sm, Eu, Pr etc. but they were observed in Sm activated tungstates. Zeeman effect in emission and absorption spectra of $\text{CaF}_2 : \text{Eu}^{3+}$ crystals was investigated by
FIG. 3A.1—ENERGY BAND MODEL FOR ABSORPTION

L  — GROUND STATE
L₁  — UNOCCUPIED STATE
L₂  — EXCITED STATE
T  — TRAPPING STATE
Zakharchenya(14)

The absorption and luminescence spectra of rare earth ions in a compound are affected by the crystal field of the host lattice around the ion. The fine structure of the absorption and luminescence spectra of rare earth activated class II - VI compounds are affected by heat treatment of the sample. This has been observed by Ibuki et al.(15) in ZnS : Tm phosphor. The absence of Pr^{3+} absorption in non heat-treated crystals was also observed by them. Typical broad band absorption of divalent rare earth was used by Arkhangel'skaya et al.(16) to observe the activator valence state changes as a result of electron transfer between the defect centres.

3.3A Physical picture of the absorption process

Different types of absorption can be represented by the model shown in Fig. 3A.1. The various possible transitions leading to absorption are given below.

(i) Lattice absorption producing free electron and free hole.
(ii) Lattice absorption resulting in exciton formation.
(iii) Absorption in the centre producing an electron in the conduction band.
(iv) Absorption in the filled band raising an electron to unoccupied centre.
(v) Absorption in the filled band raising an electron into the trap.
(vi) Absorption within the centre giving an excited state of the centre.
3.4A Methods of studying absorption spectrum

The absorption spectrum of transparent crystals is studied by the measurement of transmitted light, whereas reflectance is usually taken as a measure of absorption in the case of crystalline opaque materials. It is common practice to compare the reflectance of powdered crystalline phosphors with that of a standard material such as MgO or MgCO₃, to determine the spectral regions of strong absorption. (17-19)

Johnson and Studer(20) have compared the transmission through a single transparent crystal with the reflectance from powders formed by pulverizing samples of the same material. They found that all the absorption bands observable in the transmission curve are found in the reflectance curve also, thus justifying the use of reflectance data in obtaining absorption characteristics. Dips in the reflectance curve correspond to absorption bands. In reflectance measurement, to minimise scattering losses the grain size of the specimen should be large compared to the wavelength of light used.

Different workers have measured diffuse reflectance by different methods. (21,22) Johnson(17) has also derived an equation relating the diffuse reflectance of crystalline powders to particle size and index of refraction, enabling one to calculate the absolute optical absorption coefficient. Absorption coefficients calculated by means of this equation are shown to be in satisfactory agreement with absolute absorption measurements on single crystal.
**FIG. 3A.2(a)** - ABSORPTION SPECTRUM OF CaS: Eu (0.05%).

**FIG. 3A.2(b)** - ABSORPTION SPECTRUM OF CaS: Tb (0.1%).
Recently Yamashita and co-workers\(^{23,24}\) have measured the reflection spectra of CaS phosphors, activated with Sb\(^{3+}\), Bi\(^{3+}\) and Sn\(^{2+}\). The intensity of light after being reflected by the sample was measured and compared with that obtained from non-luminescent powder of MgO. From these intensities reflectivity and hence absorption coefficient were calculated.

For measuring absorption regions of transparent substances, direct recording spectrophotometers of commercial type such as Beckman DU or Cary Model 14R are used these days. For the study of opaque powders, a reflectance unit is attached with these.

3.3A Present method

The absorption spectra of the samples were recorded by Unicam SP8000 UV recording spectrophotometer. This is a double beam recording instrument covering UV and visible regions of the electromagnetic spectrum. It is also provided with an integral chart recorder for plotting spectra of linear absorbance against linear wavelengths. The instrument is linear in absorbance and has two basic absorbance ranges viz. 0 – 1 A and 0 – 0.2 A. The photomultiplier tubes used in this instrument are EMI 964 QA and 9558 QA (red sensitive model). The base line of the instrument was set using MgO as the reference material.

3.6A Results

The absorption spectra of CaS : Eu and CaS : Tb phosphors are shown in Fig. 3A.2. The absorption spectrum of CaS : Eu
contains a broad band extending from yellow to violet apart from UV band (200 - 400 nm), so that the sample can be excited by optical as well as by UV irradiation (254 nm). The absorption spectrum of CaS : Tb shows a broad band extending from 200 to 350 nm. Lehmann has also studied the absorption bands for these phosphors and has reported similar results. (25, 26)
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CHAPTER III B

EMISSION SPECTRA
3.1B Introduction

The emission spectrum of a phosphor gives the luminescent intensity as a function of wavelength of the emitted radiation. From a theoretical standpoint it gives information about activator levels and the mechanism of energy transfer from one centre to another and from a practical point of view it helps in the development of luminescent materials for specific applications.\(^{(1,2)}\) The emission studies in conjunction with absorption and excitation studies help in the investigation of energy levels and their distribution in luminescent solids and thus constitute an important phase of phosphor research.

Due to interaction between the emission centre and crystal lattice, the emission spectra of inorganic phosphors consist of one or more bands displaced towards the longer wavelength side of the absorption spectra.\(^{(3)}\) These bands can peak anywhere between the ultraviolet and infrared regions, their positions being determined by activators.\(^{(4,5)}\) In exceptional cases of phosphors, activated by rare earths the emission may be in the form of line spectra, as these are due to transitions within well shielded electron shells.\(^{(6-8)}\)

The intensity distribution in the emission bands is generally symmetrical and has the shape of a Gauss error curve.

3.2B Factors affecting emission spectra

The emission spectra are very sensitive to a number of parameters such as the nature and concentration of activator,
presence of other impurities, crystal structure, temperature, mode of excitation and even the method of preparation. These have been discussed below:

(a) Effect of activator — It is an established fact that activator is an essential part of the 'emission centre'. In some of the cases the electronic states of the activator are perturbed by the crystal field, while in others the activator perturbs the energy states of the pure crystal. Thus the emission characteristics of a phosphor are always influenced by the activator.

With the same host crystal, different activators give rise to luminescence bands in different spectral regions. ZnS : Cu emits green luminescence, while ZnS : Mn emits yellow. Recent examples of this may be found in the cathodoluminescence of differently activated CaO and CaS phosphors reported by Lehmann. Similarly the same activator in different host materials may give rise to different emissions e.g. emission spectra of chromium in alkaline earth sulphides and europium in alkaline earth sulphides and pyrophosphate phosphores. When the activator substitutes for a cation of the host crystal, the interacting field between ions depends on the lattice spacing of the host crystal. Consequently the spectral position of the emission band shifts to longer wavelengths when a smaller cation of the host is substituted by activator resulting in a decrease of lattice spacing and to shorter wavelengths when a
large cation of host is replaced by activator resulting in an increase of lattice spacing.\(^{(13,15)}\) In some cases the opposite effect occurs and this has been explained as due to increased polarizability with size of cation.

It has been observed that the variation of activator concentration produces significant changes in the emission spectrum of a phosphor. At higher concentration the additional activator atoms destroy the matrix and a quenching of emission results. In phosphors exhibiting multiple emission, an increase of activator concentration causes the long wavelength band to predominate while lowering of activator concentration intensifies the short wavelength band.\(^{(4,16)}\)

(b) Effect of crystal structure - A crystalline modification of the host can affect the intensity or emission characteristics. Activators like Cu, Ag and Au incorporated in two different structures of ZnS emit bands with different peak values e.g. Cu in ZnS Wurtzite (hexagonal) emits a band with the peak wavelength at 5230 Å while with ZnS Blende (cubical), the peak is at 5350 Å.\(^{(17)}\) The emission properties are altered when the composition of a phosphor is changed by the formation of a solid solution with another compound and with a consequent change in the lattice spacing.\(^{(18,19)}\)

(c) Effect of other impurities - Fluxes were previously regarded as helpful in promoting low temperature crystallization only. However, the presence of minute traces of cationic impurities and
some other components from the flux affect considerably the luminescent properties of phosphors. (20-22) Addition of alkali metal ions to sulphide phosphors containing rare earths, tends to decrease the band emission while intensifying the sharp line emission. (23,24)

(d) Effect of temperature — Temperature has a marked influence on the intensity and colour of the luminescence. (25) The intensity of luminescence during excitation first increases to a maximum and then decreases rapidly, with rise of temperature. The initial rise of fluorescence in most cases is due to an increase in absorption of the exciting radiation and in some cases it is owing to emptying of traps. The fall of intensity is due to a competition between radiative transitions sensibly independent of temperature and non radiative transitions which rise rapidly with temperature. Many workers (26-30) have discussed in detail, the relation between emission and the quenching temperature. Many substances which are not luminescent at room temperature show fluorescence at lower temperature. The lowering of temperature resolves the broad fluorescence bands into sub-bands and sometimes reveals even fine structure. (31,32)

(e) Effect of excitation intensity — It was found that in zinc sulphide and some other phosphors the luminous efficiency for ultraviolet light excitation is markedly dependent on the wavelength and intensity of exciting radiation as well as on the temperature. (33)
A non-linear variation of luminescence emission with excitation intensity was first observed by Gisolf and Kroger. The satisfactory explanation of this non-linear increase of fluorescence with excitation intensity was given by Schon and was later on elaborated by Klasens. They assume that the non-radiative transfer of electrons between different centres is effected by the migration of positive holes in the phosphor crystal. At high temperature however, this non-linear effect has been found to decrease with the wavelength of exciting radiation.

3.3B Methods of measuring emission spectra

There are two common ways of studying fluorescence spectra. One involves the use of energy detecting devices like photomultiplier tube and thermopile, while the other uses photographic plates. The convenience and sensitivity of the photoelectric method gives a marked advantage over the photographic method, which requires long exposures and consequent density evaluations.

The first automatic recording device consisting of a photomultiplier tube in conjunction with a spectrograph was designed by Zworykin and was further improved by Leverenz and Shrader. The use of double monochromator coupled with RCA - IP22 photomultiplier is recommended by Butler for more accurate measurements of emission spectra. An improvement in the sensitivity has been achieved by Zarowin. A method based on a grating
monochromator coupled with photomultiplier has been given by Ellis and Rossiter.\(^{(41)}\) The emission spectra at room and liquid nitrogen temperatures were measured by Shionoya and Amano\(^{(42)}\) using a double monochromator and IP22 photomultiplier connected to a d.c. amplifier and a millivolt recorder.

According to Byler\(^{(43)}\) photographic method can reveal the structure of an emission band which may not be possible with a photoelectric device. Fonda\(^{(44)}\) used a quartz spectrograph to record the emission spectra. Following Newton's method of crossed spectra, Germann and Woodruff\(^{(45)}\) have described an instructive method to study the luminescence spectra. 7. 3592

Plymale\(^{(46)}\) studied the spectral energy distribution curve using both photoelectric and photographic methods. He pointed out that these two methods gave results of the same degree of accuracy.

Patten and Williams\(^{(47)}\) studied the emission spectra at different temperatures. The phosphor was kept in a circular recess cut in a metallic disc which could be maintained at different temperatures. The emission spectra were recorded by a Littrow type spectrograph containing calibrated photographic plates.

Slavin et al.\(^{(48)}\) have described recently an energy recording spectrofluorometer. They have recorded fluorescence spectra in terms of an absolute energy scale, independent of wavelength. A high pressure apparatus, for studying the luminescence of solids, has also been designed by Offen.\(^{(49)}\)
FIG. 38.1 - SAMPLE HOLDER.
3.48 Present method

(a) Experimental arrangement — The emission spectrum were recorded using a photoelectric method. A Bellingham and Stanley direct reading spectrometer coupled with IP21 photomultiplier tube and a photometer were used in the present study. The experimental arrangement consists mainly of five parts.

1. The source of excitation
2. The sample holder
3. The Bellingham and Stanley spectrometer
4. The photomultiplier tube, IP21
5. The photometer.

The excitation was done by X-rays which were obtained from Philips X-ray machine (type 11704) operated at 35 kV and 12 mA. A copper target was employed in the X-ray tube and the 'white radiation' (consisting of all possible wavelengths but effectively Kα line) of X-rays was used for exciting the phosphors. Similar operating conditions were maintained during the entire study.

A schematic diagram of the sample holder is given in Fig. 3B.1. It consists of a hollow brass cylinder (B) with its inner surface covered with lead sheet (L). Two metal tubes A₁ and A₂ are fitted into the openings O₁ and O₂ of the cylinder, at right angles to each other. The top of the cylinder consists of an aluminium disc (D), at the centre of which a sample mounting plate (P)
is fixed. The plate (P) essentially a rectangular brass sheet can be raised or lowered and can also be rotated by means of a knob (K) and its position is indicated by a pointer (I). The plate is provided with a circular cavity in the centre to fit a removable brass sample holder (C) with a fine hole to hold a thermocouple (T). A heating element (H) of Kanthal strip was attached behind the sample holder to maintain it at different temperatures. Four terminals were provided on the disc (D), two for making connections to heating element (T₁, T₂) and two for thermocouple (T₃, T₄).

A collimated beam of X-rays is allowed to fall on the sample through the tube A₁ and the emitted luminescence radiation emerges through the tube A₂. A mechanical shutter (S) is also arranged at the end of tube A₁ to cut off the X-ray beam at will.

The Bellingham and Stanley spectrometer employs a glass, quartz or rock salt prism according to the regions to be investigated. It has three calibrated drums for three different regions viz. UV, visible and infrared. In the present work, since the studies were carried out in the visible region, the glass prism and the corresponding drum were used. The calibrated drum reads wavelengths right from 4000 to 8000 Å; with an accuracy of 1 Å between 4000 to 5300 Å and 3 - 6 Å between 5300 to 8000 Å. The calibration of the drum was checked with a standard mercury vapour lamp, before using the B.S. spectrometer.

The photomultiplier tube used was IP21 which was a circular dynode arrangement with Sb-Cs cathode (type 931A) having improved sensitivity and reduced dark current. The current
FIG. 3B.2 - BLOCK DIAGRAM OF EXPERIMENTAL ARRANGEMENT FOR EMISSION STUDY.
amplification is $2 \times 10^6$ and the current in the photomultiplier tube is proportional to intensity for currents up to 150 $\mu$A. The spectral response curve has a maximum at 4720 Å.

The photomultiplier tube was coupled with a photonmeter (Cenco no. 86407), which had a built-in power supply and a sensitive galvanometer. Some specifications of photonmeter are given below:

- **Current sensitivity**: 10 to 0.001 A
- **Luminous sensitivity**: 1 Picolumen/scale div.
- **Input impedance**: Maximum Sy: 1000 Megohms, Minimum Sy: 100 K ohms
- **Linearity**: 0.5% at recorded output
- **Stability of Amplifier**: 0.1 %
- **Output Voltage**: 55 Volts
- **Input voltage**: 103 to 105 volts at 50 C/s

(b) Experimental procedure — The various components described above were arranged as shown in Fig. 38.2. The power switch of photonmeter was put on and the instrument was heated for 15 minutes, before H.T. was applied. The phosphor was pressed in the cavity of sample holder (C) and its plane was adjusted at an angle of 45° to the incident X-ray beam. After opening the shutter (S), the phosphor was excited and the emerging fluorescence light was focussed on the slit of the B.S. spectrometer with the help of a converging lens system. The readings of photonmeter, were
FIG. 3B 3(a) - EMISSION SPECTRA OF CoS: Eu SERIES.
FIG. 3B. 3 (b) - EMISSION SPECTRA OF CaS: T series.
noted corresponding to various wavelengths read on the
drum. After doing necessary correction for the response of
photomultiplier, the resulting spectra are shown in
Figs. 3B.3 (a - d ).

3.58 Results

Fluorescence spectra of four series of samples were
recorded at room temperature with the present arrangement. The
spectra of different series reveal the following features.

(i) E - Series : Calcium sulphide phosphor activated with
europium only, shows a broad band emission with peak at about
640 nm. As the concentration of europium is varied, the
intensity first increases, reaches a maximum corresponding
to a sample containing 0.05 mole % Eu, thereafter starts
decreasing. This concentration quenching will be discussed
in the last chapter. However, the peak wavelength remains
constant with the change in activator concentration Fig.3B.3(a).

(ii) T - Series : Calcium sulphide phosphors activated with
terbium only show line emission, with seven distinct peaks at
420, 437, 460, 487, 550, 585 and 620 nm. The peak intensities
of these lines also show a variation similar to that found in
E - Series. However, the optimum concentration of terbium
is found to be 0.1 mole %. Fine structures of these lines
are difficult to be observed without high resolution
Fig. 3B.3 (b).
Fig. 3b.3(c) - Emission spectra of CaS: (Eu, Tb) series
R₅ - (Eu 0.1%, Tb 0.1%)
R₆ - (Eu 0.1%, Tb 0.2%)
FIG. 3B.3(d) - EMISSION SPECTRA OF CaS: (Tb, Eu) SERIES.

N3 - (Tb 0.1%, Eu 0.001%)
N4 - (Tb 0.1%, Eu 0.01%)
(iii) R-Series — The variation in the luminescence intensity of CaS : ( Tb x, Eu 0.1 ) phosphors is shown in Fig. 3B.3c. It has been observed that only red emission of europium predominates in almost all the samples of the series. Moreover the intensity of Eu emission increases with the increase of Tb concentration, reaches a maximum value for the sample CaS ( Tb 0.1, Eu 0.1 ) and thereafter the Eu emission gets quenched progressively. At this concentration of Eu ( 0.1 mole %), terbium emission does not appear except at very high concentration of Tb ( 0.9 mole %).

(iv) N-Series — The results of this series CaS : ( Tb 0.1, Eu x ) are shown in Fig. 3B.3(d). Samples containing less than $10^{-3}$ mole % of Eu, show the Tb lines only, Eu emission being scarcely observable; those containing $10^{-3}$ to $10^{-2}$ mole % of Eu, show distinctly both Tb and Eu emissions. Whereas samples containing more than $10^{-2}$ mole % of Eu show only Eu emission, while Tb emission almost disappears. Hence it is evident that energy is transferred from Tb$^{3+}$ to Eu$^{2+}$ and consequently Eu emission is enhanced. This feature will be discussed in the last chapter. The peak wavelengths and corresponding intensities are given in Table 3B.1 (a) – (d).

3.6B (a) The chromaticity diagram : If we assume three primary colours red (A), green (B) and blue (C) then any colour may be defined by three quantities $X$, $Y$ and $Z$ which
FIG. 3B 4 - CHROMATICITY DIAGRAM SHOWING SPECTRAL COLOURS AND "ILLUMINANT C", POINT O REPRESENTS ZnS:Cu AS GIVEN BY CURIE (1921).
are known as tristimulus values and represent the respective amounts of A, B and C which must be mixed to obtain a match to that colour. The quantities

\[
x = \frac{X}{X+Y+Z}; \quad y = \frac{Y}{X+Y+Z}; \quad z = \frac{Z}{X+Y+Z}
\] (3.1)

are the trichromatic or chromaticity co-ordinates for the particular colour. They are governed by the identity

\[x + y + z = 1\] (3.2)

and so specification of two of them (x and y) will define the colour. A graph obtained by plotting known co-ordinates of various spectral colours, is known as chromaticity diagram Fig. 3B.4. White light, known as illuminant C, has the co-ordinates

\[x = 0.31, \quad y = 0.316\]

(b) Dominant wavelength and purity: A zinc sulphide phosphor (wurtzite) with a green emission band, having its co-ordinates \(x = 0.19\) and \(y = 0.625\) can be represented on the chromaticity diagram by the point \(O\). The straight line \(CO\) cuts the position of the spectral colour at a point \(P\) which determines the dominant wavelength.

The colour \(O\) can be obtained by adding to the spectral colour \(P\) a certain amount of white \(C\). The purity is defined as \(CO/CP\). The dominant wavelength of
ZnS : Cu phosphor is thus found to be 524 nm and its purity is about 60%. (50)

(c) Application of Chromaticity diagram: Leverenz (51) has given the colour diagram locations of ZnS – CdS phosphor with copper and silver activators. A remarkable application of such a diagram is to be found in the work of Kroger et al. (52) who show that white colour can not be obtained with a mixed ZnS – CdS : Cu, Ag phosphor. Moreover, a change in colour in passing from wurtzite to blende form of ZnS can be obtained by reducing the energy gap for wurtzite.

From efficiency and economic points of view the most useful material for electroluminescence devices would be the one capable of emitting white light. The most encouraging results have been obtained with ZnS$_{1-x}$S$_x$ and with GaN. The latter has produced not only nearly saturated colours shown along the periphery of chromaticity diagram but also white light. (53) Loebner (54) has speculated on the possibility of using the direct gap alloy In$_{1-x}$Ga$_x$N to make electroluminescence devices capable of emitting at virtually any co-ordinate inside the chromaticity diagram.

The chromaticity diagram is thus helpful in choosing appropriate phosphors for monochrome and colour television.
(d) Measurement of chromaticity co-ordinates of the phosphors:

A Spectra Brightness Spot Meter (Model UB 1/0) was used in the present study. The source of excitation and the sample holder were the same as described in Section 3.4B.

(i) Description of the instrument - Spectra Brightness Spot Meter is a direct reading instrument. When an object is viewed through the telescopic sight, light is picked up by the high speed fL - 9 objective lens and imaged on the reticule of the eyepiece. A partial reflecting mirror just ahead of the reticule reflects a portion of the light downward to the photomultiplier tube. An aperture plate is located at the focus of this light beam directly above the photomultiplier tube, the output from which is fed to the input grid resistor circuit and the range selector switch. The voltage produced across this resistor is duplicated and the current amplified as much as one million times by a special three stage d.c. amplifier. This output current is indicated by the microammeter which is calibrated in foot lamberts (fL). Range multipliers of 0.01/0.1/1/10/100 are available on the range switch enabling the instrument to measure brightness from 0.003 fL to 10,000 fL, to an accuracy of ±1% of full scale deflection.

Three complete and separate power supplies are provided with the instrument to supply necessary voltages
FIG. 3B.5(a) - CHROMATICITY DIAGRAM SHOWING THE POSITIONS OF E SERIES AND T SERIES OF SAMPLES.
FIG. 383 (b) - CHROMATICITY DIAGRAM SHOWING THE POSITIONS OF R SERIES AND N SERIES OF SAMPLES
to d c amplifier, filament and photomultiplier tube.

(ii) Spectral response characteristics : The spectra spot meter employs a six position knob labelled FL, ZERO, RED, BLUE, OPEN and X-100. When the knob is in the RED, FL or BLUE positions, the spectral sensitivities of the instrument are approximations of the CIE X, Y and Z tristimulus values. This allows the instrument to be used directly for the determination of chromaticity coordinates (x, y and z) of a luminous source.

(iii) Experimental procedure : The power switch of the Spot meter was put on and the instrument was allowed to be heated for 15 minutes before H.T. was applied. The phosphor was excited by X-rays and the emerging fluorescence radiation was focussed on the reticule of the Spectra Brightness Spot meter. The tristimulus values (X, Y and Z) of all the phosphors were thus measured by positioning the knob at RED, FL and BLUE respectively. The chromaticity coordinates for the colours emitted by each phosphor were then calculated by applying relation (3.1).

(iv) Results : The American Standard chromaticity diagram was used for showing the relation between the chromaticity of the sample and that of the spectral colours Fig. 38.5(a) and 38.5(b). The dominant wavelengths and purity of all the samples were thus calculated. The results are given in Table 38.2 (a) - (d).
It is evident by seeing the data of the Table 3B.2 that the dominant wavelengths of CaS : Tb and CaS : Eu phosphors are 503 and 584 nm respectively, but for the mixed series CaS : (Tb 0.1, Eu x) the dominant colour shifts from 506 to 586 nm as the concentration of europium is increased. At a concentration of 0.1 mole % of Eu, the emission of terbium completely disappears and only the emission of europium persists. This once again confirms the transfer of energy from terbium to europium.
Fluorescence Spectra

Table 3B.1

(a) CaS : Eu phosphors

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Conc. of Eu mole %</th>
<th>Peak wavelength nm</th>
<th>Peak Intensity Arb. Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₁</td>
<td>0.001</td>
<td>640</td>
<td>13.5</td>
</tr>
<tr>
<td>E₂</td>
<td>0.01</td>
<td>640</td>
<td>26.0</td>
</tr>
<tr>
<td>E₃</td>
<td>0.05</td>
<td>640</td>
<td>34.0</td>
</tr>
<tr>
<td>E₄</td>
<td>0.1</td>
<td>640</td>
<td>25.0</td>
</tr>
<tr>
<td>E₅</td>
<td>0.3</td>
<td>640</td>
<td>13.0</td>
</tr>
</tbody>
</table>

(b) CaS : Tb phosphors

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Conc. of Tb mole %</th>
<th>Tb $^5D_3$ manifold</th>
<th>Tb $^5D_4$ manifold</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Peak wavelength nm</td>
<td>Peak Int. Arb. Units</td>
</tr>
<tr>
<td>T₂</td>
<td>0.01</td>
<td>437</td>
<td>2</td>
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<td>0.05</td>
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<td>8</td>
</tr>
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<td>T₄</td>
<td>0.1</td>
<td>437</td>
<td>17</td>
</tr>
<tr>
<td>T₅</td>
<td>0.3</td>
<td>437</td>
<td>4</td>
</tr>
</tbody>
</table>

Continued ........
(c) CaS: (Eu 0.1%, Tb x%) phosphors

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Conc. of Tb mole %</th>
<th>Peak wavelength nm</th>
<th>Peak Intensity Arb. Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁</td>
<td>0.00001</td>
<td>645</td>
<td>21</td>
</tr>
<tr>
<td>R₂</td>
<td>0.0001</td>
<td>645</td>
<td>23</td>
</tr>
<tr>
<td>R₃</td>
<td>0.001</td>
<td>645</td>
<td>28</td>
</tr>
<tr>
<td>R₄</td>
<td>0.01</td>
<td>645</td>
<td>30</td>
</tr>
<tr>
<td>R₅</td>
<td>0.1</td>
<td>640</td>
<td>46</td>
</tr>
<tr>
<td>R₆</td>
<td>0.2</td>
<td>645</td>
<td>34</td>
</tr>
</tbody>
</table>

(d) CaS: (Tb 0.1%, Eu x%) phosphors

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Conc. of Eu mole %</th>
<th>Peak wavelength nm</th>
<th>Peak Int. Arb. Units</th>
<th>Peak wavelength nm</th>
<th>Peak Int. Arb. Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₁</td>
<td>0.00001</td>
<td>550</td>
<td>21</td>
<td>640</td>
<td>3</td>
</tr>
<tr>
<td>N₂</td>
<td>0.0001</td>
<td>550</td>
<td>23</td>
<td>640</td>
<td>4</td>
</tr>
<tr>
<td>N₃</td>
<td>0.001</td>
<td>550</td>
<td>25</td>
<td>640</td>
<td>20</td>
</tr>
<tr>
<td>N₄</td>
<td>0.01</td>
<td>550</td>
<td>7</td>
<td>640</td>
<td>34</td>
</tr>
<tr>
<td>N₅</td>
<td>0.2</td>
<td>550</td>
<td>0</td>
<td>640</td>
<td>20</td>
</tr>
</tbody>
</table>
Table 3B.2 

(a) CaS : Eu phosphors

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Tristimulus values X</th>
<th>Y</th>
<th>Z</th>
<th>Chromaticity co-ordinates x</th>
<th>y</th>
<th>z</th>
<th>Dominant wavelength in nm</th>
<th>Purity per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_2</td>
<td>0.08</td>
<td>0.07</td>
<td>0</td>
<td>0.533</td>
<td>0.466</td>
<td>0</td>
<td>584</td>
<td>100</td>
</tr>
<tr>
<td>E_3</td>
<td>0.096</td>
<td>0.084</td>
<td>0</td>
<td>0.533</td>
<td>0.466</td>
<td>0</td>
<td>584</td>
<td>100</td>
</tr>
<tr>
<td>E_4</td>
<td>0.06</td>
<td>0.054</td>
<td>0</td>
<td>0.526</td>
<td>0.473</td>
<td>0</td>
<td>583</td>
<td>100</td>
</tr>
</tbody>
</table>

(b) CaS : Tb phosphors

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Tristimulus values X</th>
<th>Y</th>
<th>Z</th>
<th>Chromaticity co-ordinates x</th>
<th>y</th>
<th>z</th>
<th>Dominant wavelength in nm</th>
<th>Purity per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_3</td>
<td>0.05</td>
<td>0.23</td>
<td>0.017</td>
<td>0.111</td>
<td>0.511</td>
<td>0.377</td>
<td>504</td>
<td>60.7</td>
</tr>
<tr>
<td>T_4</td>
<td>0.09</td>
<td>0.039</td>
<td>0.03</td>
<td>0.115</td>
<td>0.5</td>
<td>0.384</td>
<td>503</td>
<td>61.1</td>
</tr>
<tr>
<td>T_5</td>
<td>0.08</td>
<td>0.034</td>
<td>0.013</td>
<td>0.145</td>
<td>0.618</td>
<td>0.236</td>
<td>515</td>
<td>60.0</td>
</tr>
</tbody>
</table>

Continued ...............
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Tristimulus values</th>
<th>Chromaticity co-ordinates</th>
<th>Dominant wavelength in nm</th>
<th>Purity per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁</td>
<td>0.046 0.04 0</td>
<td>0.534 0.465 0</td>
<td>583</td>
<td>100</td>
</tr>
<tr>
<td>R₂</td>
<td>0.065 0.057 0</td>
<td>0.532 0.467 0</td>
<td>583</td>
<td>100</td>
</tr>
<tr>
<td>R₃</td>
<td>0.06 0.05 0</td>
<td>0.528 0.471 0</td>
<td>582</td>
<td>100</td>
</tr>
<tr>
<td>R₄</td>
<td>0.06 0.052 0</td>
<td>0.535 0.464 0</td>
<td>583</td>
<td>100</td>
</tr>
<tr>
<td>R₅</td>
<td>0.056 0.05 0</td>
<td>0.528 0.471 0</td>
<td>582</td>
<td>100</td>
</tr>
<tr>
<td>R₆</td>
<td>0.07 0.062 0</td>
<td>0.530 0.469 0</td>
<td>583</td>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(d) CaS : ( Tb 0.1%, Eu x% ) phosphors</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₁</td>
</tr>
<tr>
<td>N₂</td>
</tr>
<tr>
<td>N₃</td>
</tr>
<tr>
<td>N₄</td>
</tr>
<tr>
<td>N₅</td>
</tr>
<tr>
<td>N₆</td>
</tr>
</tbody>
</table>
REFERENCES


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