CHAPTER IV

EMISSION SPECTRA
4.1 Introduction

The emission spectrum of a phosphor provides the luminescence intensity distribution as a function of wavelength of emitted radiation. The study of spectral properties leads to an understanding of the mechanism of electronic transitions in luminescent solids. From a theoretical point of view it gives information about the levels of the luminescence centre and the mechanism of energy transfer from one centre to another, and from an experimental point of view it helps in the development of luminescent materials for specific applications.

The emission spectra of inorganic phosphors consists of one or more bands displaced towards the longer wavelength side of the absorption. The position of these emission bands is determined by impurity systems commonly termed as activators.

The broadening arises due to the following reasons:

(i) The statistical distribution of impurities and imperfections and their corresponding effects on the energy band of the host crystal, and

(ii) The perturbation caused by the thermal agitation and the atomic re-arrangements accompanying the absorption and emission during luminescence process.

The band spectra so observed are due to electronic transitions involving the outer most valence electrons.

In the case of rare-earth activated phosphors the emission
spectra consists of sharp lines due to their characteristic transitions within well shielded incomplete inner most shells.\textsuperscript{9-10} The spectral distribution of intensity generally has the shape of a Gaussian error curve.

Fluorescence and phosphorescence spectra are typical examples of emission spectra.\textsuperscript{11}

4.2 Parameters influencing the emission spectrum

The emission spectrum of a phosphor depends upon a number of parameters such as the nature and concentration of the activator, crystal structure, temperature, presence of other impurities, mode of excitation and method of preparation.

(a) Effect of activator - The common characteristics of a phosphor are always influenced by the presence of activator because of the interaction between the emission centre and the host crystal lattice.\textsuperscript{12} In some cases electronic states of the activator are perturbed by the crystal field while in others the activator modifies the energy states of the pure crystal. Different activators with the same host crystal give rise to bands or lines in different spectral regions. ZnS : Cu emits green luminescence while ZnS : Mn emits yellow.\textsuperscript{13} Lehmann has reported that the different activators in CaO and CaS phosphors emit in different spectral regions.\textsuperscript{14-15}

The activator ion also influences the electric field of the
surrounding ions of the host crystal, which perturbs the ground and excited states of the activator and brings them nearer, thus reducing the transition energy. Hence different host crystals with the same activator give rise to emission in different regions. One of the examples of this may be found in the work of Blasse and Bril 17,18 who have reported the emission of Ce $^{3+}$ and Eu $^{3+}$ in different host systems. Other examples can be seen from the work of P.M. Jaffe et al. 19 and Warmaker et al. 20

When the activator substitutes for a cation of the host crystal, the interaction field between ions depend on the lattice spacing of the host crystal. Consequently the spectral position of the emission bands shift to longer wavelengths when a smaller cation of the host is replaced by a large activator resulting in a decrease of lattice spacing and to shorter wavelengths when a large cation of a host is replaced by a smaller activator resulting in an increase of lattice spacing 19,21 hence a decrease of perturbation.

Investigations of Lehmann showed that with the addition MgO to ZnO crystals the emission band shifts to shorter wavelengths while the addition of CdO to ZnO shifts the emission band to longer wavelength side of the spectrum. 22 In some cases opposite effects have also been observed. 23 Such effects have been explained as due to increase polarizability with size of the
cation and hence a greater intermeshing of the electronic orbits of cation and anion. This reduces the lattice size and hence shift is to longer wavelengths. The investigations of Smith\(^{24}\) with Mn activated Zn - Cd phosphates showed that an increase of Cd content shifted the emission band to shorter wavelengths and then to longer wavelengths than shown for zinc or cadmium phosphate alone. Haphazard results have been explained as due to change of structure.\(^{21}\) Several phase changes were also noted within this range of composition.

It has been observed that the emission characteristics of phosphores change significantly with the variation of activator concentration\(^{5,25}\) which is attributed to the presence of particular energy sinks in the crystal lattice.\(^{25}\) The absorbed excitation energy is lost radiationlessly at these sinks during the migration through the lattice. If the possibility of this transfer is low, the energy cannot escape to a quenching centre and the quantum efficiency is high even at high concentrations. On the other hand if the probability of the transfer is high the excitation energy can be lost at an energy sink even for low concentrations. Some new emission bands may also be produced at high concentrations of activator due to the production of pairs or other molecular complexes as has been reported in the case of KCl : Tl.\(^{27}\)

In the case of phosphores exhibiting multiple band emission
the relative intensities of emission bands in different spectral regions often depend on the concentration of the activator. 29

(b) **Effect of crystal structure of the host and solid solution**

The crystal structure of the host can affect the intensity or emission characteristics of the phosphor; e.g., Cu in ZnS (wurtzite) emits a band with peak wavelength 3230 Å, while Cu in ZnS (blende) emits with peak at 5150 Å. 29

Similarly, α and β forms of calcium orthophosphates when activated by Eu²⁺ emit bands with peaks at 4800 Å and 4190 Å respectively. 31 Van Itert and Soden 32,33 found that the increased interaction with the surroundings can either depress efficiency by coupling with the phonons or increase efficiency by facilitating energy transfer from host to activator. The emission properties of a phosphor can also change if the composition of the phosphor is altered by the formation of a solid solution with another compound with a consequent change in lattice spacing. 23,32

(c) **Effect of other impurities**

The presence of minute traces of cationic impurities considerably affect the luminescence properties of phosphors. 14,33-35 Addition of flux in phosphors gives a
marked change in its luminescence spectra. The fluorescence intensity has been found to be dependent upon the quantity of flux used. Incorporation of Na or Li in ZnS may give rise to fluorescence or quenching centres depending on whether chloride is present or not. The presence of other ions such as sulphates or oxide ions are observed to influence the luminescence characteristics of phosphors.

(d) **Effect of temperature** - There are two fundamental competing transition processes in phosphors: (i) radiative and (ii) non-radiative. The non-radiative processes are invariably temperature dependent while the radiative processes are not. Hence there is a critical temperature for some phosphors at which its efficiency is maximum. The change in temperature of a phosphor influences the intensity and sometimes the colour of luminescence. The following effects may be observed in spectral distribution with increase in temperature:

1. A broadening of emission band to both sides without change in peak position.
2. A broadening towards longer wavelength side.
3. A shift of the peak besides a broadening to both sides.
4. A change of relative intensity between two peaks besides broadening.

Glaeser and Bril have discussed in detail the
relation between absorption (or emission) and quenching temperature. Many substances which are not luminescent at room temperature show fluorescence at lower temperature. The lowering of temperature sometimes helps in resolving the broad bands into sub-bands and even into fine structure. Low temperature fluorescence gives information about the energy levels of interacting atoms or ions in the phosphor.

Rachkko et al. observed a continuous shift of narrow band (7.5 eV) of MgO to longer wavelength with rise of temperature while the broader (6.7 eV) remained constant. But the intensity of broader band increased while that of the narrow band decreased.

(e) Effect of excitation intensity - It is seen that at low excitation intensities the fluorescence is proportional to the square of exciting intensity while at higher intensities it changes to a linear variation. The shift in emission band of (Zn-Cd)S phosphors towards longer wavelength with an increase in excitation intensity has been reported by Sondek. A shift towards shorter wavelength has also been reported by Fehr and his coworkers in (Zn-Cd)S:Ag with increase of excitation intensity.

It is observed that in ZnS and some other phosphors the luminous efficiency for U.V. light excitation is dependent on the
wavelength and intensity of exciting radiation as well as on the temperature. 50

A non-linear variation of luminescence emission with excitation intensity was observed by Bisolf and Kröger 53 and was explained by Schön 54 and Klasens. 55 They assume that the non-radiative transfer of electrons between different centres is affected by the migration of positive holes in the phosphor crystal. At high temperature however, this non-linear effect has been found to decrease with wavelength of exciting radiation. 55

4.3 Methods for measuring emission spectra

There are two basic methods which are used for studying emission spectra i.e., (i) Photoelectric method, (ii) photographic method.

(i) Photoelectric method - In the photoelectric method some workers 57-60 have used a spectroradiometer coupled with a photomultiplier tube and recorder or galvanometer as detector while others have used thermopiles as detector. 51,52 A method based on a grating monochromator coupled with photomultiplier tube has been given by Ellis and Rossiter. 53 The emission spectra at room temperature and liquid nitrogen temperature were measured by Shionoya and Amano, 54 using a double monochromator and IP 32 photomultiplier tube connected to a recorder.
Hughes and Pells \(^{55}\) measured the emission spectra of a phosphor using Hilger monospekck 100 grating monochromator and EMI 4255 S photomultiplier.

(ii) **Photographic method** - It is an advantage that photographic method can reveal the structure of emission band which may not be possible with a photoelectric device, \(^{55}\) because of its high sensitivity and its feature of integrating the light which falls on emulsion over the entire period of an exposure. Plymale \(^{57}\) studied the emission spectrum using both photoelectric and photographic methods, and concluded that they have the same degree of accuracy.

An energy recording spectrometer has been described by Slavin et al., \(^{62}\) who recorded fluorescence spectra in terms of an absolute energy scale, independent of wavelength. Ofen \(^{59}\) has also designed a high pressure apparatus for studying the emission spectrum.

4.4 **Present method**

(A) **Experimental arrangement**

A photoelectric method has been employed to record the emission spectra of all prepared phosphors. The experimental arrangement consists of the following parts:

(i) **The excitation source** - White X-ray radiations (consisting of all possible wavelengths but
effectively (Kα line) were selected as the source of excitation for the present study. These X-rays were obtained from Philips X-ray machine (type PW 1010) with copper target, operated at 30kV and 10 mA. All the measurements were made under similar operating conditions.

(ii) The Phosphor holder assembly — Fig. 4.1 represents the schematic diagram of this assembly. It consists of a hollow brass cylinder (B) with its inner surface covered with lead sheet (L). O₁ and O₂ are the two circular openings perpendicular to each other and at the same height of the cylinder. A₁ and A₂ are brass tubes fitted into O₁ and O₂. The top of the cylinder consists of an aluminium disc (D). A rectangular brass plate (P) used as sample mounting plate is fixed vertically at the centre of the disc (D). Its height and inclination with respect to the X-ray beam can be adjusted with the help of knob (K). Its position is indicated by pointer (I). The plate (P) is provided with a circular hole in centre to fit a removable brass sample holder (C). This brass sample holder has a small cavity of one cm diameter and 2 mm depth. The phosphor can be pressed uniformly in the cavity. This cavity also has a fine hole to hold a tip of the thermocouple (T). A heating element (H) of Kanthal strip was attached behind the sample holder to maintain it at different temperatures so that the same set up can be used for studying thermoluminescence as well as
FIG. 4.1 - SAMPLE HOLDER ASSEMBLY.
temperature dependence of fluorescence. Two terminals $T_1$ and $T_2$ were provided on the disc (D) for making connections to the heating element. Two holes $O_3$ and $O_4$ with glass tubes were also provided on the disc (D) for thermocouple leads to go across. A collimated beam of X-rays is allowed to fall on the sample through the tube $A_1$ and the emitted luminescence radiations emerges through the tube $A_2$. An electronic shutter (S) with an operating switch is provided with the X-ray machine to cut off the X-ray beam at will.

(iii) Bellingham and Stanley Spectrometer - The Bellingham and Stanley direct wavelength reading spectrometer employs quartz, glass or rock salt prisms and three calibrated drums for three different regions viz., ultra-violet, visible and infra-red. Since the studies were carried out in the visible region, the glass prism and the corresponding drum were employed. This calibrated drum reads wavelength from 4000 Å to 8000 Å with an accuracy of 1 Å between 4000 to 5300 Å and 3 to 5 Å between 5300 to 8000 Å. The drum was again calibrated with a standard mercury vapour lamp before using the B.S. Spectrometer.

(iv) The Photomultiplier tube IP21 and Photonmeter - A IP21 photomultiplier tube was used in all the present measurements, Fig.(4.2A). It has a circular dynode arrangement with Sb-Cs cathode (type 931)
$R_1 = 150 \, k\Omega$, $R_2 = 100 \, k\Omega$, $R_4 = 100 \, k\Omega$ (POTENTIOMETER),
$R_5 = 1 \, M\Omega$, $A =$ ANODE, $C =$ PHOTOCATHODE, $M =$ 1 $M\Omega$ (METER).

FIG: 4.2A. PHOTOMULTIPLIER CIRCUIT.
having improved sensitivity and reduced dark current. Its current amplification factor is $2 \times 10^5$ and the current in the P.M. tube is proportional to intensity for currents up to 150 $\mu$A. The spectral response curve has a maximum at 4720 A (Fig. 4.23).

The photomultiplier tube was coupled with a photonmeter (Genco No. 95407) which has a built-in power supply for FP21 P.M. tube and a sensitive galvanometer. Some specifications of the photonmeter are given below:

Current sensitivity : 10 to 0.001 A
Luminous sensitivity : 1 Picolumen/scale division
Input impedance :
  Maximum sensitivity : 1000 Meg ohms
  Minimum sensitivity : 100 K ohms
Linearity : 0.5% at recorded output
Stability of amplifier : 0.1%
Output voltage : 95 volts
Input voltage : 103 to 105 volts at 50 c/s.

4.5 Method for recording the emission spectra :

The various components described above were arranged as shown in Fig. (4.3). The power switch of the photonmeter was switched on and the instrument was heated for 15 minutes before H.T. was applied to photomultiplier tube. The photonmeter unit
FIG: 4.2B. SPECTRAL RESPONSE CURVE OF IP 21 PHOTOMULTIPLIER TUBE.
FIG. 4.3 - BLOCK DIAGRAM OF EXPERIMENTAL ARRANGEMENT FOR EMISSION STUDY.
was adjusted for dark current balance and maximum sensitivity. The phosphor was pressed in the cavity of the sample holder (C) and mounted in the sample mounting plate (P) attached with knob (K). The mounting plate (P) was then adjusted in such a way that the phosphor surface was completely exposed to X-rays and the fluorescence light falls on the slit of the B.S. Spectrometer properly (Effect of reflected and scattered X-rays is minimised by a lead sheet placed in the cylinder). B.S. Spectrometer was aligned by optical methods. Its slit towards sample was kept at 30 and that towards P.M. tube was kept at 20 for better response. After opening the X-ray shutter the phosphor was excited and the emitted fluorescence light focussed on the slit of the B.S. Spectrometer with the help of a converging lens system. Readings of the photometer were noted corresponding to various wavelengths as recorded from the drum. Necessary corrections for the response of the photomultiplier were made and spectral intensity as a function of wavelength was plotted as shown in Figs. 4.4 to 4.7.

4.6 Results

The fluorescence emission spectrum of all prepared phosphors were recorded at room temperature with the set up described. The spectra of different series reveal the following features:

1. All phosphors with ZnO as major component, show a structureless wide band in the yellow green region. The intensity
FIG. 4.4 [A, B] - EMISSION SPECTRA OF ZnO : MgO : Eu SERIES UNDER X-RAY EXCITATION.
**Fig 4.4 (C,D) - Emission Spectra of ZnO:MgO:Eu Series Under (1-x) (x) X-Ray Excitation.**
FIG: 4.5 [A, B] - EMISSION SPECTRA OF ZnO : MgO : Sm UNDER X-RAY EXCITATION.

WAVELENGTH $\lambda$ (nm)

INTENSITY (ARB. UNITS)

FIG. 4.6 (A,B) - EMISSION SPECTRA OF \( \text{ZnO} : \text{MgO : [Sm 0.01\%, Eu 0.05 \%]} \) \(_{(1-x)(x)}^{(1-x)}\) SERIES UNDER X-RAY EXCITATION.
FIG. 4.7 [A, B, C] - EMISSION SPECTRA OF ZnO : MgO (7:3) [\text{Sm(x)}, \text{Eu 0.05\%}] SERIES UNDER X-RAY EXCITATION.
FIG. 4.7 [D,E,F] - EMISSION SPECTRUM OF ZnO : MgO : [Sm(x), Eu 0.05%]

UNDER X-RAY EXCITATION.
of this band increases from 10:0 to 8:2 ZnO : MgO ratio
and then decreases rapidly beyond 7:3 ZnO : MgO ratio.
This band appears to be the host emission band of ZnO : MgO
phosphors.

(2) E - Series : All ZnO : MgO : Eu (10⁻¹ mole %)
(1-x) (x)
phosphors show emission lines at about 593 nm and 511 nm. The
emission intensity of 593 nm line increases up to 7:3 ZnO:MgO
ratio and then decreases. The intensity ratio of 511 to 593 nm
lines is nearly 1:1 up to 9:1 ZnO : MgO ratio and beyond that
this intensity ratio decreases rapidly as is clear from the results
given in Figs. 4.4A to 4.4D.

(3) S - Series : Phosphors of ZnO(1-x) : MgO(x) : Sm (10⁻² mole %)
series show emission lines at about 575 nm and 512 nm and a band of
comparatively low intensity peaking at about 650 nm. The intensity
of all of these lines and band increases up to 9:1 ZnO:MgO ratio
and then decreases gradually beyond this ZnO : MgO ratio as shown
in Figs. 4.5A and B.

(4) eu - Series : ZnO(1-x) : MgO(x) : Eu (0.05 mole %, Sm
0.01 mole %) phosphors show emission lines at about 575, 593 and
511 nm and a band of low intensity at about 650 nm, as shown in
Figs. 4.6 (A) and (B). The intensity of 575 nm line is much less
in comparison to that observed in S- series ( Figs. 4.5 A & B ).
An increase in intensity of 593 nm Eu line is clearly observed in
all samples. Hence it seems that 593 nm Eu emission is sensitized by Sm. Emission line at about 611 nm is observed in Eu as well as Sm series. Hence it seems that in this series this 611 nm line emissions due to both (Sm and Eu) are superimposed over each other. The 660 nm band is less intense than that in Sm series showing a quenching effect.

(5) X - Series : The results of this series i.e., ZnO : MgO (7:3) : (Sm (x), Eu (0.05 mole %)) of phosphors are shown in Figs. 4.7(A) to (F). It has been observed that low concentration (up to $10^{-3}$ mole %) of Sm enhances the 593 nm Eu emission, but with further increase in Sm concentration does not increase the Eu emission beyond this level. The intensity of 611 nm and 650 nm lines go on increasing with increase of Sm concentration up to $10^{-1}$ mole %.

It is observed that 575 nm line appears as concentration of Sm reaches $10^{-2}$ mole %.

All these results will be discussed in the concluding chapter.
# REFERENCES

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