SYNTHESIS AND PHYSICAL PROPERTIES OF SOME NEW PHOSPHORS

A Thesis
submitted to the

UNIVERSITY OF POONA

for the degree of

DOCTOR OF PHILOSOPHY

(IN CHEMISTRY)

By

P. G. POL,
M. Sc.

National Chemical Laboratory,
Poona 8.

April 1971

Addendum to the thesis entitled "Synthesis and Physical Properties of some new Phosphors" submitted by Shri P.G. Pol, for the Ph.D. degree of Poona University.

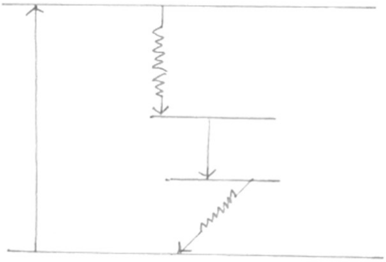
Page 9 - Line 4 - delete the words '21000 cm^{-1} above ground level'.

Line 5 - delete the words 'at 21000 cm^{-1}'.

Line 6 - change the words 'ground level' to 'an excited vibration level'.

Add line 7 - The antimony ion finally decays to the ground level by non-radiative transition.

Page 11 - The three level diagram should be changed to a four level diagram as follows:



Page 32 - Line 8 - change the words 'a new series of compounds' to 'a new series of solid solutions'.

Page 34 - Add the following sentence after the table:

The medium strong line with d = 2.68 may be attributed to an overlap of $20\bar{2}2$ (d = 2.73) and $30\bar{3}1$ (d = 2.61).

Page 51 - Delete the first two lines of paragraph two and the foot note i.e. 'It is clear that the energy levels of Th^{4+} and W^{6+} lie far above the region of excitation'.

'Although the exact energy levels are not known experimentally, an approximate idea can be got from the energy levels of isoelectronic Rn and Kr levels'.

Page 59 - Change the fourth line from below to read as:

"The effect of the concentration of copper and manganese activators on the luminescence of the mixed phosphor has also been studied".

Page 71 - Change the fifth line from below and the modified sentence should be:

"This showed that at least 20% (but not more than 30%) CdS remains dissolved in CaS having heated for two hours at 800°C and on cooling to room temperature (at 200°C/hr.) but that 10% CaS does not dissolve completely in CaS under similar conditions".

Page 72 The contents of table No.2.1 should be changed to:
X-ray diffraction data and 'd' values for $(Ca_{80\%} + Cd_{20\%})S$
a = 5.630.

Intensity	hkl	$d_{obs.}$	$d_{cal.}$
m	111	3.25	3.25
vs	200	2.81	2.82
s	220	1.99	1.99
w	311	1.70	1.70
m	222	1.63	1.63

Page 90 The table should be changed to following:

$1/\lambda$	$1/\lambda^2$
1.672×10^{-4}	139.8×10^{-8}
1.754×10^{-4}	104.6×10^{-8}
1.852×10^{-4}	61.76×10^{-8}

Page 116 Change the first sentence to "Calcium fluoride shows the well-known fluorite structure in which each calcium ion is surrounded by eight fluoride ions and there is cubic symmetry around Ca^{2+} ions.

Page 117 The contents of Table 3.1 should be changed to:
X-ray diffraction data and 'd' values for $NaYF_4$. a_o = 5.662.

Intensity	hkl	$d_{obs.}$	$d_{cal.}$
w	-	3.48	-
w	111	3.28	3.27
vs	200	2.83	2.83
s	220	2.00	2.00
m	222	1.63	1.63
m	400	1.41	1.42
m	-	1.41	-
ms	420	1.27	1.27

Page 118 Change the stntence beginning with 8th line as: "We have observed that the compound does not show appreciable fluorescence upto 6 per cent europium which may be attributed to weak absorption".

Page 124 Change the sentence beginning with the second line to: "The transitions thus induced by odd components of the crystalline field give forced electric-dipole transitions while the vibrations give vibronic transitions".

Page 132 Add after the last paragraph: "If there is no symmetry at all, then also the number of lines can be 1,3,5. The experimental data show more lines than the cited 3 and 5. Since Na and Y are disordered there may be several types of rare earth ions present in different crystal fields. Different fields mean different luminescent transitions".

---000---

PREFACE

In spite of the fact that the first synthetic phosphor was made two centuries back, the interest in this field is sustained even now. This arises from the tremendous technological importance of these materials which motivates continued effort towards progressive improvement in their properties.

Especially, during last few decades, semiconducting solids and junction concepts came of age, the laser was born and with that event, interest in the luminescence of rare earth ions increased dramatically. Electron spin resonance and the polarisation of luminescence were developed as important tools in luminescence research.

Today, as a result, we have a vast family of phosphors comprising of oxides, phosphates, sulphides, fluorides, silicates, etc. Each one is characterised by certain special properties which render them useful for certain specific applications. In the present work, we have studied compounds belonging to three different classes, namely halophosphates, sulphides and fluorides with a view to synthesise some new phosphors and study their structural and optical properties. These studies, we believe, have led to a better understanding of the role of substituents on the properties of the phosphors.

CONTENTS

---OOO---

ont scan

CHAPTER I : HALOPHOSPHATES

1.1 : GENERAL INTRODUCTION

The most widely used phosphor in fluorescent lamps is calcium halophosphate $Ca_{10}(PO_4)_6(F,Cl)_2$, activated by antimony and manganese. It was discovered in 1942 by McKeag and Ranby. A unique feature of this family of phosphors is that while some members emit highly coloured fluorescent light, the emission of others, is characterized by a broad spectral energy distribution, approaching white light suitable for general lighting purposes. The phosphors have the apatite structure.

A large amount of effort has been expended in preparing phosphors belonging to this family having different compositions with various activators and also measuring their luminescent efficiency, emission spectra, etc. with a view to find new and useful phosphors for fluorescent lamps. However, some amount of empericism still persists in this field because of the complex nature of the technically useful phosphors. A paper by Jenkins, McKeag and Ranby[1] provides a good sampling of the empericism of this work.

The apatite structure tolerates extensive substitution for calcium, phosphorus and halogens permitting the preparation of a considerable number of chemical combinations. The work done so far mainly describes the substitution for calcium by metals of the IInd group and for phosphorus by arsenic and antimony. However, the correlation between the substitution and properties of these phosphors does not seem to be well understood. In order to achieve more insight into the properties of substituted halophosphates the present investigation is carried out.

The host, calcium halophosphate, has been completely replaced by strontium fluorophosphate. Thorium and tungsten have been substituted for strontium and the effect of this substitution on the crystal structure and optical properties of the phosphors has been studied. Further, the effect of sensitizer and activator on the fluorescent properties of these phosphors has also been studied.

Structure and mechanism of halophosphate phosphor

Synthetically prepared calcium halophosphate $Ca_{10}(PO_4)_6(F,Cl)_2$ shows close resemblance in structure with mineral apatite. Synthetic calcium halophosphate was used first by McKeag and Ranby as the host for phosphor material. Attempts have since then been made to prepare different compounds having apatite structure.

The unit cell of halophosphate phosphor is found to be hexagonal and the space group[2] is $C_{6h}^{2}-C\,6_3/m$. The ions are located at:

4CaI in (f) : $\pm 1/3, 2/3, z$; $\pm 1/3, 2/3, 1/2-z$; $z_{Ca} = 0$.

6CaII in(h) : $\pm x, y, 1/4$; $\bar{y}, x-y, 1/4$; $y-x, \bar{x}, 1/4$;
$x_{Ca} = 1/4$, $y_{Ca} = 0$.

6P in (h) : $x_p = 5/12$; $y_p = 13/36$.

6 'O$_I$' in (h) : $x_1 = 1/3$; $y_1 = 1/2$.

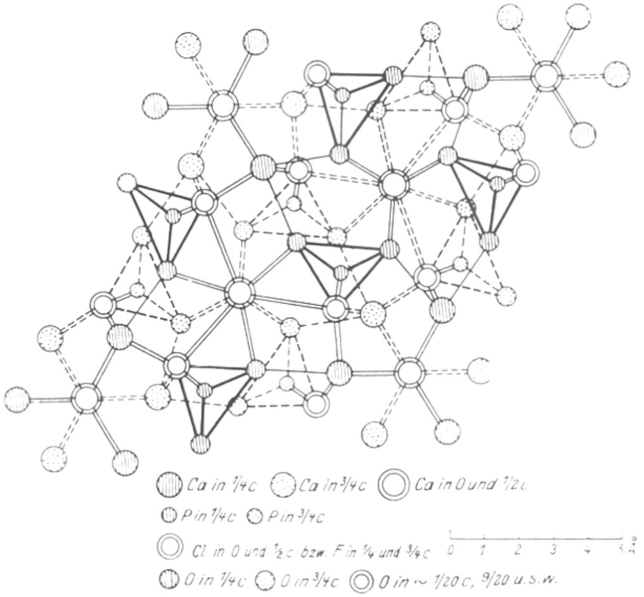
6 'O$_{II}$' in (h) : $x_{II} = 3/5$; $y_{II} = 7/15$.

12 'O' in (i) : $\pm(x,y,z;\ \bar{y},x-y,z;\ y-x,\bar{x};z;\ x,y,1/2-z;$
$\bar{y},x-y,1/2-z;\ y-x,\bar{x},1/2-z)$.

$x_{III} = 1/3$; $y_{III} = 1/4$; $z_{III} = 1/16$.

Figure 1.1 shows the apatite structure. The structural details are tabulated below:

Atom site	Symmetry			Distances
Ca I	C_3-3	9 'O'	3I,3II,3III.	2.32, 2.38, 2.85.
Ca II	C_s-m	1 F		2.34,
		bzw.2Cl		2.91, (2.93),
		6 'O'	2III, 2III, 1 II, 1 I.	2.29, 2.44, 2.67, 2.82.
P	C_s-m	4 'O'	1 II,2III, 1 I.	1.49, 1.60, 1.82.
F	C_{3h}-$\bar{6}$	3 Ca	II	2.34,
		6 'O'	III	3.10^{c},
		2 F		3.44.
Cl	C_{3i}-$\bar{3}$	6 Ca	II	2.91, (2.93),
		6 'O'	III	2.85^{c}, (2.89),
		2 Cl		3.44^{c}, (3.43).
O$_I$	C_s-m	11 'O'	1 II, 2III, 2I, 2III, 2II, 2III.	2.67^{a}, 2.67^{a}, 2.71^{bb}. 2.98^{b}, 3.48^{b}, 3.55^{b}.
O$_{II}$	C_s-m	11 'O'	2III, 1 I, 2II, 2III, 2III, 2I.	2.63^{ab}, 2.67^{a}, 2.86^{bb}, 3.10^{bc}, 3.21^{c}, 3.48^{b}.
O$_{III}$	C_1-1	1F		3.10,
		bzw.1 Cl		2.85, (2.89),
		8'O'	III, II, I, III, I, II, II, I.	2.58^{ac}, 2.63^{ab},2.67^{a},2.94^{c}, 2.98^{b},3.10^{bc},3.21^{c}, 3.55^{b}.



APATITE STRUCTURE

(Taken from Struktur Bericht, Vol.2,1928-1932, p. 100)

Fig. 1.1.

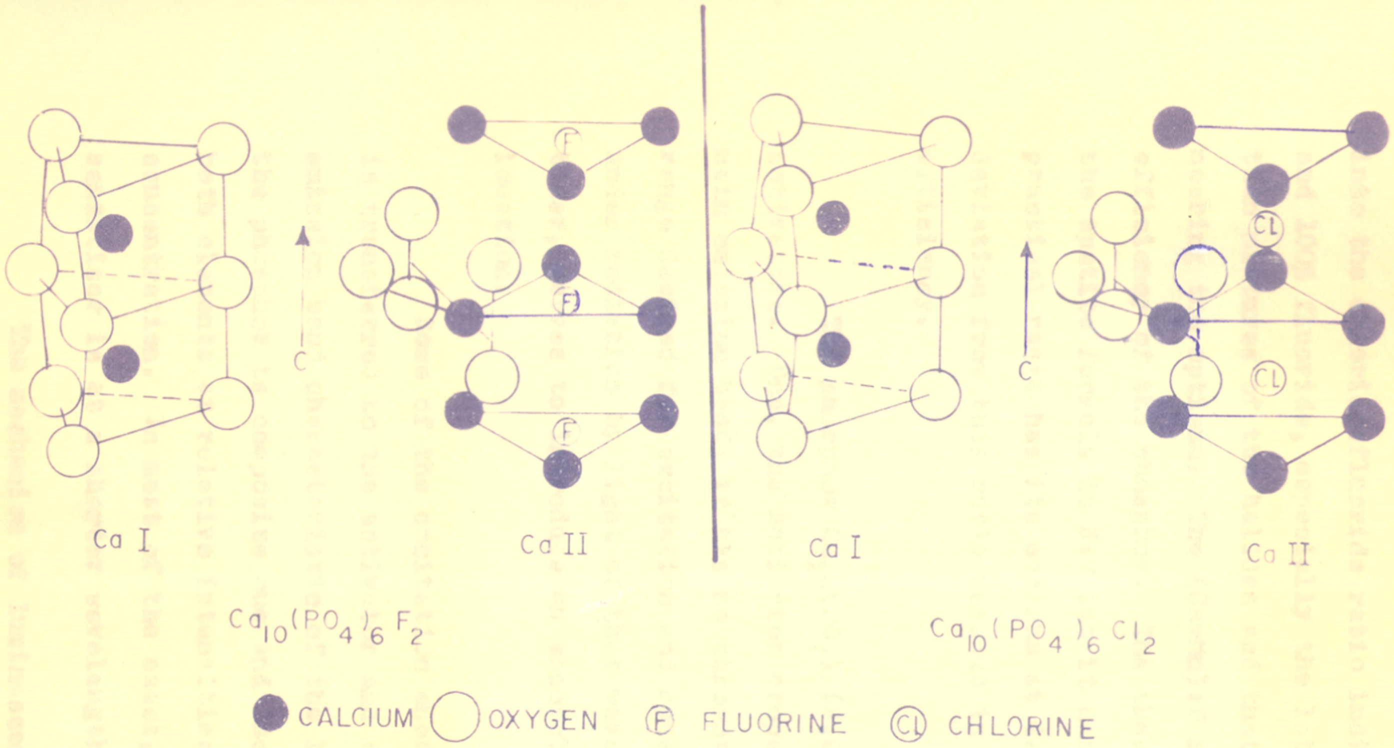
The lattice constants for some of the synthetic apatites are given below:

	Apatite	Lattice constants		
		a(Å)	c(Å)	c/a
1	$Ca_{10}(PO_4)_6F_2$	9.37	6.88	0.735
2	$Ca_{10}(PO_4)_6Cl_2$	9.52	6.85	0.719
3	$Ca_{10}(PO_4)_6Br_2$	9.71	6.76	0.696
4	$Sr_{10}(PO_4)_6F_2$	9.72	7.28	0.748
5	$Sr_{10}(PO_4)_6Cl_2$	9.87	7.18	0.727
6	$Sr_{10}(PO_4)_6Br_2$	9.96	7.18	0.720
7	$Ba_{10}(PO_4)_6F_2$	10.22	7.665	0.750
8	$Ba_{10}(PO_4)_6Cl_2$	10.28	7.647	0.744
9	$Ba_{10}(PO_4)_6Br_2$	10.34	7.648	0.737
10	$Pb_{10}(PO_4)_6F_2$	9.760	7.29	0.746
11	$Pb_{10}(PO_4)_6Cl_2$	9.97	7.32	0.734
12	$Pb_{10}(PO_4)_6Br_2$	10.07	7.37	0.732

In the calcium halophosphate structure there are two types of calcium ions present; one of which is indicated as Ca(I). This type of calcium ion is surrounded by six oxygen atoms and is several atomic diameters distant from the halide ion so that the strength of the calcium-oxygen bond would be very little affected by a substitution of chloride for fluoride. The second type of calcium ion present is indicated as Ca(II). These ions are directly bonded to the halide ions and their surroundings include both the halide and oxygen ions. Due to the different position of fluoride and chloride in the lattice the surroundings of these Ca(II) ions are considerably different in the two cases. The local symmetry around the two calcium sites in fluorapatite and chlorapatite is shown in Figure 1.2.

When calcium halophosphate is activated by antimony alone the emission has a principal band in the visible spectrum peaking at approximately 4800Å. The inclusion of manganese depresses the blue band and produces a second principal band with a peak at approximately 5850Å. The manganese content and to a lesser degree the fluoride:chloride ratio can be varied to produce a range of phosphors giving colours from light blue to orange as also near-white combinations. In terms of fluorescent lamp colours, light blue, colour matching white, daylight and warm white can be prepared with a single halophosphate in each case. Whilst this is an attractive feature of the halophosphate, it is probably less valuable than the two attributes of high efficiency and excellent maintenance characteristics which make the halophosphates the principal lamp phosphor today. The relative ease of preparation and the low cost of the halophosphates also make them attractive to the lamp makers.

The maintenance of the characteristics of this phosphor is mostly related to the concentration of the ions present in the



THE LOCAL SYMMETRY AROUND THE TWO CALCIUM SITES IN FLUORAPATITE AND CHLORAPATITE

[Taken from Phillips Research Reports Supplements, No.2. (1968) p. 5.]

Fig 1·2

host material. The investigations of Nagy, Wollentin and Lui[3] into the chloride:fluoride ratio indicate that both 100% chloride and 100% fluoride, especially the latter, give lower luminescence than mixtures of the halides and that the ratios 2:1 or 1:2 are nearing the optimum. The (Ca+Mn):P ratio also affects the efficiency of the phosphor. The theoretical ratio derived from the apatite formula is 5:3 but it has been found that the practical range has its optimum at 4.9:3 and that even slight deviation from this ratio results in an appreciable loss of efficiency.

The phosphor $Ca_{10}(PO_4)_6(F,Cl)_2$:Sb, Mn, contains two activators. One, the activator proper, is responsible for the main emission band; it has no absorption band in the spectral range desired for excitation and consequently shows no fluorescence under radiation by light of that wavelength. The other, the sensitiser, serves to introduce an absorption band at the desired location.

Some of the excitation energy absorbed by the sensitiser is transferred to the activator and reappears as light in an emission band characteristic of the latter. The fluorescence of the phosphor is composite one and includes the emission bands of both elements at relative intensities which depend upon their concentration. In most of the cases, the emission band of the sensitiser is at a shorter wavelength than that of the activator.

The mechanism of luminescence when Sb alone is present as activator can be described in three steps:

CHAPTER III : FLUORIDES

1) Absorption of a photon of 41000 cm^{-1} by the antimony center, exciting it to a higher energy level.

2) Decay of the excited antimony ion to a lower level (21000 cm^{-1} above ground level) by a non-radiative decay process.

3) Decay of excited antimony ion at 21000 cm^{-1} to the ground level by a radiative transition emitting the radiation in blue.

The third process is competed by a non-radiative process where the entire energy is lost through lattice vibrations and no photon emission takes place. The quantum yield or the luminous efficiency would, therefore, depend on the relative ratio of the radiative and non-radiative decay from the level at 21000 cm^{-1}. It is found that the probability of non-radiative transition increases as Sb^{3+} concentration is increased. Thus a phosphor containing about 1% Sb gives a lower intensity than that containing about 0.3%. On the other hand, it is clear that the initial absorption of energy would be proportional to the absorbing sites and hence to the concentration of antimony ion. Therefore, there is an optimum concentration at which the maximum efficiency is achieved. This appears to be around 0.3%.

When antimony and manganese both are present together, one of the Mn^{2+} levels has the energy close to the 21000 cm^{-1} level of antimony. The initial absorption of the photon is by the Sb^{3+} site, as in the above case. The excited Sb^{3+}, decays non-radiatively to the level at 21000 cm^{-1}. At this stage, there are three possibilities: (1) direct radiative transition to the ground state emitting a photon of 21000 cm^{-1} (blue Sb emission), (2) resonance transfer of excitation from Sb^{3+} to the adjoining Mn^{2+} level and (3) non-radiative decay of the excitation.

In the second case, when the excitation is transferred to the Mn^{2+} ion, the excited Mn^{2+} ion decays non-radiatively to a lower excited state at 17300 cm^{-1}. This excited centre has again two possibilities for decay: (i) radiative decay giving an emission of 17300 cm^{-1} (yellow), (ii) non-radiative decay.

Summing up, after an absorption of a photon, we have the possibilities of obtaining a photon of 21000 cm^{-1} or of 17300 cm^{-1} or of a non-radiative decay; from one of the two levels mentioned above. The relative proportion of these would be governed by the various transition probabilities. Experimentally, it is found that when Mn^{2+} is present then the probability of direct decay from 21000 cm^{-1} is considerably decreased and correspondingly the Mn^{2+} emission (17300 cm^{-1}) is increased. This would mean that the resonance transfer probability from antimony to manganese is greater than that of direct decay from antimony. The luminescence mechanism of Mn^{2+} in Ca fluorophosphate has been shown in Fig. 1.3.

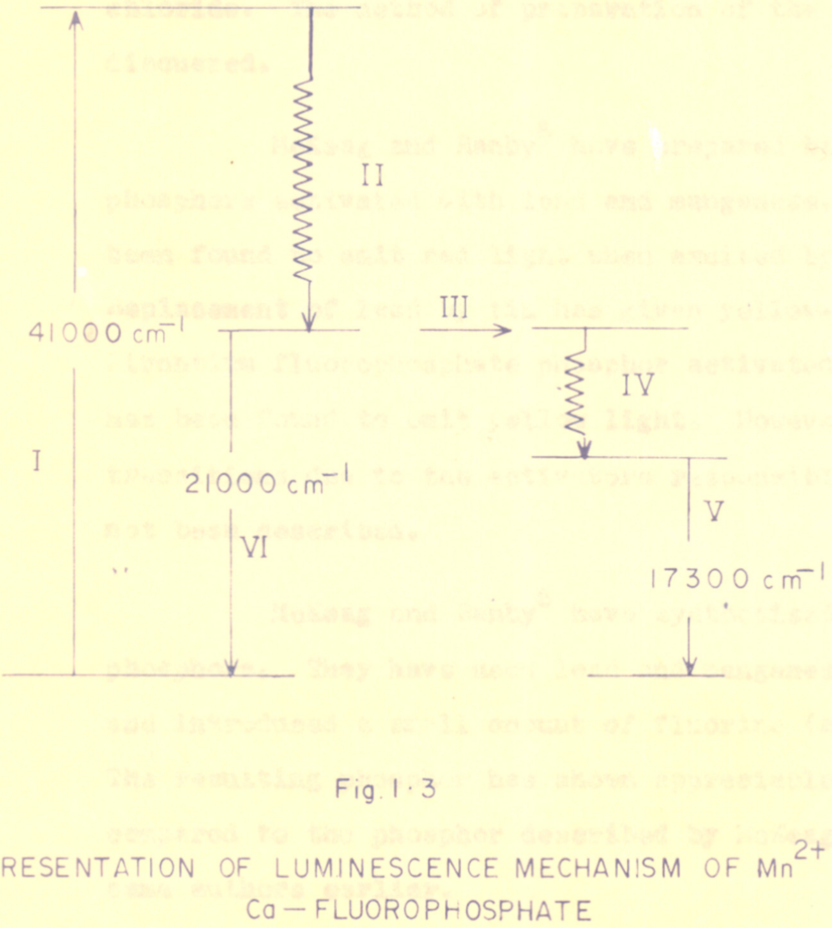


Fig. I·3

REPRESENTATION OF LUMINESCENCE MECHANISM OF Mn^{2+} IN Ca — FLUOROPHOSPHATE

I Excitation of Sb^{3+} ion by light (wave number 41000 Cm^{-1})

II Non-radiative transition

III Resonance transfer

IV Non—radiative transition

V Emission of Mn^{2+} ion with wavenumber 17300 Cm^{-1}

VI Emission of Sb^{3+} ion with wavenumber 21000 Cm^{-1}

1.2 : HISTORICAL INTRODUCTION

McKeag[4] has synthesised manganese activated luminescent cadmium chlorophosphate. He has replaced magnesium for cadmium by using magnesium chloride in place of cadmium chloride. The method of preparation of the phosphor has been discussed.

McKeag and Ranby[5] have prepared barium fluorophosphate phosphors activated with lead and manganese. The phosphors have been found to emit red light when excited by 2537Å radiation. Replacement of lead by tin has given yellow-green light. Strontium fluorophosphate phosphor activated with tin and lead has been found to emit yellow light. However, the energy transitions due to the activators responsible for emission have not been described.

McKeag and Ranby[6] have synthesised cadmium phosphate phosphors. They have used lead and manganese as activators and introduced a small amount of fluorine (about 2%) as CdF_2. The resulting phosphor has shown appreciable improvement as compared to the phosphor described by McKeag and Ranby, the same authors earlier.

McKeag, Jenkins and Ranby[1] have studied halophosphate phosphors replacing calcium partially or completely by strontium and barium. They have also used different activators such as Bi, Sn, Pb, As, in place of antimony. However, this work does not provide any information about the spectral energy distribution and the intensity of the substituted halophosphate phosphors.

Bundel and others[7] have studied Pb-Mn, Sb-Mn, Bi-Mn, activated calcium halophosphates. They have also seen the effect of partial substitution for Ca by other cations. In Sb-Mn activated calcium halophosphate the peak at 4800Å has been found to disappear as the manganese content is increased to 3%. When Ca is replaced by Sr, the Mn- and Sb- bands are found to be displaced in opposite directions. Fe, Cu, Cr and Pb have shown a quenching effect.

Anderson and Wells[8] have prepared barium and magnesium halophosphate using uranium, silver and thallium as activators. The phosphors have been excited by short and long wavelength mercury vapour. In both the phosphors uranium is found to show green luminescence and silver a poor bluish-violet luminescence. Thallium activated phosphor shows a poor luminescence in case of magnesium halophosphate whereas no luminescence has been observed in case of barium halophosphate. The spectral energy distribution has been given for phosphors activated with uranium. The paper does not describe the energy transitions responsible for emission and hence it does not throw any light on the role of the activator.

Fonda[9] has synthesised phosphors having the general formula $3Ca_3(PO_4)_2.vMX_2$ where v is more than 1, M = Mg, Sr, Cd or Zn and X = Cl or F. The phosphors have been activated with Sb and Mn. These phosphors show increased brightness with the wavelength peak shifted to deeper red as compared to $3Ca_3(PO_4)_2CaX_2$.

Wallaeys[10] has described the synthesis, structure and isomorphism of the apatites, in which chloride has been substituted by other ions such as bromide, hydroxyl, etc. on the basis of low-angle x-ray diffraction and thermogravimetric studies. He has prepared chloro-, bromo-, fluoro-, hydroxy-, calcium apatites. The unit cell parameters of all these apatites have been given.

Wollentine and others[11] have prepared manganese activated cadmium chlorophosphate phosphors. They have studied the effect of cation substitution on the properties of phosphors. Cadmium has been substituted by magnesium, barium, strontium and zinc in the form of chlorides. These cations have been introduced in the base material according to the formula $3Cd_3(PO_4)_2x(MCl_2):0.2$ Mn where M is any of the said four cations and X is varied from 0 to 5 moles. For zinc chloride the maximum brightness has been obtained with only one mole whereas for other chlorides more than one mole is required. The effect of simultaneous substitution of three cations has been studied in compounds with the formula $3Cd_3(PO_4)_2:2(Sr+Zn+Ba)Cl_2.0.2Mn$. The diagram showing the variation of relative brightness against the substituted cation concentration has been given. The optimum concentration of manganese and the emission peak is found to vary with the specific cation chosen to replace cadmium. The excitation spectra of the substituted halophosphate has also been studied.

In case of magnesium, zinc, strontium or barium substituted cadmium halophosphate, strontium has been found to produce the greatest expansion of the lattice spacings, while magnesium produces a moderate amount of contraction. Barium chloride gives only a slight expansion while zinc chloride does not show any change in lattice parameters.

Aoki and Hano[12] have prepared calcium-cadmium halophosphate phosphor having the base composition $Ca_3(PO_4)_2$67.7, $CdF_2$17.3, $Sb_2O_3$7, $MnNH_4PO_4$8 parts. The phosphors show orange fluorescence.

Prener[13] has synthesised a red light emitting manganese activated cadmium phosphate-zinc fluoride phosphor. The matrix has in its composition 5-20% ZnF_2 and 0.125-4% Mn activator. The effect of addition of zinc on the structure of the phosphor has not been discussed.

Hinonishi and Machida[14] have reported the properties of cadmium halophosphate phosphors. They have replaced cadmium partially by calcium, barium, magnesium and zinc and have simultaneously varied the chloride to fluoride ratio. All the phosphors show orange-red emission. The effect on the lattice parameters of the substitution of cations has not been given.

Wanmaker and Ouweltjes[15] have prepared calcium halophosphate phosphors. They have partly substituted Ca by Sr. Phosphors with (Ca+Sr+Mn) to phosphate ratios ranging from 1.33 to 1.75 have been prepared. All of them show apatite structure with no indication of foreign substances except the presence of calcium antimonate. According to them, for good efficiency the ratio of Me:P should not exceed in any case beyond 1.65. Doherty and Harrison[16] have claimed that the optimum efficiency of the commercial daylight and warm white halophosphate phosphors is obtained when the ratio of Me/P is exactly 4.9:3 and that of the halide is 2:1.

A phosphor containing $Cd_3(PO_4)_2$, $ZnCl_2$, $BaCl_2$, $SrCl_2$ and Mn has been reported by Wollentine and Nagy[17], where the total output in lumens/watt is about 40% more than the usual phosphor and stability is also improved. The peak of emission has been found to shift from about 5900Å to 5930-6080Å. Magnesium chloride can also be included. A triaxial diagram representing the lumen output of all possible combinations of Ba, Zn, Sr chlorides where the total amount present is 2 moles per 9 moles of Cd, has been given. The relation between the substituted cations and the improvement in stability and output has not been clearly explained.

Uhera[18] has reported mixed halophosphates having the base composition $(1-x)Sr_2P_2O_7$; $xBa_2P_2O_7(n-y)SrF_2.yBaF_2$ with $0 \leqslant x \leqslant 1$; $0 \leqslant y \leqslant n$ and $n = 0.01-0.1$. These phosphors emit whiter light than fluorescent Mg tungstate when stimulated with Hg 2537Å light.

Banno and others[19] have prepared the halophosphates having the general formula $3M_3(PO_{4-1n}nx_2)_2 \cdot M'X_2$, in which $1 \geqslant n \geqslant 0$ and M and M' are two alkaline earth metals, including Mg. They have used activators such as Mn, Sb, Sn and Pb. The above phosphor is reported to be isomorphous to apatite on the basis of x-ray diffraction studies.

Ranby and Henderson[20] have reported that the red emission from certain phosphors is intensified by the addition of Sm activator. They have incorporated Sm in a mixed calcium-strontium halophosphate matrix as well as the same matrix containing a little aluminium. The phosphors have been pre-activated by Sb and Mn. The emission spectra of the material with Sm have been found to be the same as without Sm but for the superposition of narrow bands or diffuse lines in the region 6600-6900Å. The role played by Sm in the electronic transitions as well as in increasing the intensity has not been explained.

Ouwletjes[21] has studied the calcium-strontium halophosphate phosphors activated with antimony and manganese. He has studied the killer effect of the impurity of iron. According to him, the greatest part of the killer effect of iron is a mere absorption of the emitted light.

Wanmaker and Verheyke[22] have done the thermogravimetric analysis of the mixed calcium-strontium halophosphates activated with antimony and manganese. They have found that the dissociation temperature of $CaCO_3$ is depressed by the presence of $CaHPO_4$ and $CaHPO_4 + SrCl_2$. The dissociation temperature of $CaCO_3$ is found to rise in mixtures producing fluorochloro-, chloro-, fluoro-, apatite in this order. The analysis of halophosphate firing mixtures has shown that the loss in Sb, Cl and F occurs only after complete dissociation of the $CaCO_3$. The loss of these elements is found to be high with a low $M/6PO_4$ ratio ($M = Ca+Sr+Mn$). The loss in chlorine may have occurred as a result of pyrohydrolysis of $SrCl_2$ or of the formation of $SbCl_3$.

Wollentine[23] has studied cadmium-fluorophosphate with lead and manganese activators. He has replaced cadmium fluoride by the fluorides of aluminium, calcium, strontium, barium, zinc, magnesium, potassium and sodium. The partial replacement of cadmium fluoride in the formulation $3Cd_3(PO_4)_{2.5}\cdot 2.5CdF_2$:0.70% Mn, 6.0% Pb, by the above mentioned fluorides results in decreased brightness, in all cases. In this respect, substitution of monovalent cations has been found to be most detrimental in the sense that small amounts cause a large loss in luminous efficiency and 2.5 moles results in a drop of 70%, while the same amounts of the divalent substituents have been found to decrease the efficiency by 45.0%. On the other hand, the same concentration of trivalent aluminium results in only 18% decrease in efficiency. Perhaps, the trend indicates that more the charge on the substituted cation less is the loss in efficiency.

The effect of these partial substitutions on the spectral emission of the phosphor is also studied. 1.2 moles of cadmium fluoride have been replaced by other fluorides. In the case of aluminium, strontium, barium and calcium, the emission spectrum remains unaltered with the peak wavelength at about 5900Å. Sodium, magnesium and zinc cause the peak to shift to about 5130Å. The excitation spectra for these mixed phosphors have been given as also their x-ray diffraction data.

Henderson and Ranby[24] have synthesised calcium-strontium halophosphate phosphors and in contrast to earlier work they obtained the optimum proportion of calcium to strontium as 4:1. The optimum concentration of the cerium and manganese activators has been found to be 6.0×10^{-2} and 0.039 gms. per atom of phosphor. Cerium emits at 3400Å while the mixture of cerium and manganese shifts the peak of emission to visible region. Replacement of Ca by Sr has been found to shift the Mn emission to a longer wavelength. X-ray diffraction studies have confirmed the formation of the apatite structure.

McKeag and Hunt[25] have, for the first time, prepared barium fluorophosphate phosphors activated with monovalent copper and copper and tin. The phosphor mixtures have been heated in a slightly reducing atmosphere, such as the gaseous mixture of nitrogen and hydrogen. The concentrations of copper and tin activators have been kept at 0.1-2% by weight of matrix. The phosphors containing only copper have shown strong red luminescence, whereas phosphors containing copper and tin together have shown strong orange-red emission when excited by 3650Å. However, the structural properties of these phosphors have not been discussed anywhere.

Wollentine[26] has synthesised lead and manganese activated cadmium-sodium fluorophosphate phosphors. They have the general formula $3Cd_3(PO_4)_2 \cdot xNaF:yMn:zPb:(g\ P_2O_5)$ where $2.5 < x < 5.5$; $0.029 < y < 0.29$; $0.038 < z < 0.54$; $0.03 < g < 1.5$. These phosphors show red fluorescence when excited by 2537Å radiation. The data do not provide any information about the effect of monovalent cation substitution for Cd, e.g. the creation of vacant sites due to the introduction of the monovalent sodium ion in the lattice.

Kamiya and Mizuno[27] have been the first to study the effect of anion substitution on calcium halophosphate phosphor, using lead, antimony, manganese as activators. They have replaced the phosphate by borate and silicate ions. The substitution of borate for phosphate decreases the intensity of the phosphor whereas the substitution of silicate does not show any appreciable effect on the intensity of the phosphor.

Wallaeys and others[28] have studied the x-ray diffraction of a series of solid solutions of alkaline earth halophosphates.

All these compounds have shown the apatite structure. The practically linear variation of the parameters as a function of composition has indicated that Vegard's Law is applicable to this type of substitution in apatite structure.

McKeag and Hunt[29] have prepared copper, tin and manganese activated halophosphates of the alkaline earth metals with varying fluorine and chlorine ratios. Strontium fluorophosphate activated with tin and manganese has been found to produce a strong yellow-green emission which changes to orange-yellow fluorescence as the manganese content is increased. Replacement of fluorine by chlorine has been found to diminish the brightness of these phosphors. The spectral energy distribution of the strontium fluorophosphate phosphor activated with tin and manganese has been given. Using Sn in place of Sb seems to shift the emission to smaller frequency. This is interesting in view of the fact that the final emitting centre is manganese in both the cases.

Butler[30] has prepared mixed calcium-strontium fluorophosphate phosphor activated with indium. 0.04 gm. mole In_2O_3 has been added per gram mole of the matrix which gives yellow emission when excited by 2.54 mu radiation.

Rimbach[31] has synthesised magnesium-calcium fluorophosphate phosphors. He has used cerium as a sensitizer and manganese as an activator. The phosphor has an optimum formula

$9MgO.3CaO.4P_2O_5.11.6\ CaF_2:0.80Mn:0.16Ce$. It produces yellow fluorescence with a peak around 5800Å. Substitution by SrF_2 for CaF_2 has been tried which shifts the emission towards the green. Other activators such as Pb, Sn, Bi, have been substituted for Ce. However, the effect of substitution on the structure is no where discussed.

Aia and Poss[32] have reported that the efficiency of calcium halophosphate phosphors increases by the addition of 0.02-0.5/3.0 gram atom of cadmium per gram mole of phosphate. The concentration of cadmium has been found to be critical. However, the data describe only the method of preparation of the phosphor and does not explain the role of cadmium in increasing the efficiency of the phosphor.

Rimbach[33] has synthesised a number of green-emitting, antimony and manganese activated strontium halophosphate phosphors. The phosphors have been heated to 1260°C and have the base composition $9SrO\ 3.1\text{-}3.35P_2O_5$, 1-1.5 Sr halide. The activator percentage has been kept 0.5-2.8% Mn and 0.5-6% Sb.

Suchow[34] has studied the effect of shortwave ultraviolet radiation on non-luminescent alkaline earth halophosphate base materials. This radiation has been found to produce colour centres in a typical commercial halophosphate base material, which has a formula $Ca_{4.87}Sr_{0.13}(PO_4)_{2.25}(P_2O_7)_{0.53}F_{0.87}Cl_{0.26}$. All the colours can be thermally bleached and some of them can also be bleached optically by exposure to 3650Å radiation. In all these preparations only strontium halophosphate has shown thermal bleaching accompanied by luminescence. In other cases only the optical bleaching is found to be accompanied by luminescence. The reflectance spectra and glow curves of all these phosphors have been given. The mixed phosphors have been found to show solid state miscibility with a continuous range and the Vegard's Law is followed.

Repsher[35] has prepared mixed calcium-strontium halophosphate phosphor activated with antimony and manganese. He has observed that the phosphor becomes more efficient when subjected to the following wash treatments. The phosphor is washed first with 0.01-0.3N HNO_3 and then with water to remove the residual acid. The powder phosphor is then washed once again with a suitable alcohol. It is dried and employed for coating in a fluorescent tube. Such a phosphor has been found to show higher efficiency.

Apple[36] has studied the effect of thermal treatment on the colour centers of calcium-cadmium halophosphates, unactivated as well as activated with antimony and manganese. The discharge from the tesla coil has been found to induce three colour centers in the 2500-7000Å region. The spectral distribution of these centers has been found to be dependent upon the Cl/F ratio. Incorporation of Sb and Cd and/or rapid quenching of the samples from elevated temperatures has lead to a decrease in induced colour center formation. Diffuse reflectance spectra of all these phosphors have been given.

Ouweltjes[37] has reported strontium halophosphate phosphor activated with antimony and manganese. Compared with the calcium halophosphate, the antimony emission band has been found to shift towards longer wavelength and the emission peak is found at 5000Å, the manganese emission band has been found to shift towards shorter wavelength giving a peak at 5600Å. The shifts of emission peaks of Sb and Mn have not been accounted for, when calcium is replaced by strontium.

Hoekestra[38] has listed the unit cell parameters of more than hundred different synthetic apatites. He has given the unit cell parameters of cation - as well as anion-substituted synthetic apatites which has made it possible to compare the parameters and hence to correlate some of the properties of substituted apatites.

Neurgaonkar and Sinha[39] have prepared lead and manganese activated calcium-cadmium halophosphate phosphors. In the spectral energy distribution, they have observed a double band emission peaking at 4500Å and 5800Å. The luminous output and spectral emission have been found to be effected by the activator concentration and the extent of cadmium substitution. The substitution of cadmium for calcium is found to shift the emission towards longer wavelength. X-ray intensity data have been given.

Neurgaonkar[40] has studied the effect of partial substitution of Mg and Be in calcium halophosphate on the optical and structural properties of the phosphor. In case of Ca-Be halophosphate, he has observed emission peaks at 4500Å and 5630Å, whereas in Ca-Mg halophosphate the emissions have been observed at 4500Å and 5670Å. The luminous output is found to be maximum at Mn = 0.5% and Pb = 5% in the first case and at Mn = 2%, Pb = 7% in the second case. Partial substitution of Mg and Be for Ca has been found to shift the emission peak towards higher wavelength. He has given the x-ray diffraction data of the substituted phosphors. With the help of intensity analysis the distribution of cations over the Ca(I) and Ca(II) sites has been determined. The data have indicated that the substituted ions having small radii prefer Ca(I) site and with large radius prefer Ca(II) site.

1.3 : EXPERIMENTAL TECHNIQUE

Synthesis.

Strontium carbonate, thorium dioxide, tungstic oxide, diammonium hydrogen phosphate, strontium fluoride, were taken as the starting materials of chemical purity. The synthesis of mixed halophosphate phosphors was carried out in two stages. In the first stage, only the basic halophosphate matrix was prepared according to the following formula:

$$9(Sr,M)CO_3 + 6(NH_4)_2HPO_4 + SrF_2 \rightarrow 3(Sr,M)_3(PO_4)_2.SrF_2 + 12NH_3 + 9CO_2 + 9H_2O$$

Appropriate amounts of the above materials were intimately mixed by grinding them in alcohol, in an agate pestle and mortar. The mixtures were ground for about 2-3 hours. They were then subjected to air-drying. These mixtures were transferred to crucibles, made of refractory material such as alumina. The crucibles were heated in air at about 1100°C for one hour in a specially prepared furnace. The mixtures were then cooled to room temperature. Heating and cooling were done at the rate of 200°C per hour. The halophosphates prepared in this way, without any activators, did not show any phosphorescence when excited by 2537Å radiation.

In the second stage, antimony and manganese were introduced in the basic matrix, as sensitizer and activator respectively. The concentration of antimony was kept constant at 3 per cent whereas the concentration of manganese was varied from 0.5 to 4 per cent by weight of matrix. As the amounts of the sensitizer and activator were very small, their compounds of chemical purity could be used. We used antimony trioxide and manganese carbonate of c.p. grade as the source of these activators. Appropriate amount of the basic material and activators (usually 2-3 gm. lot) were mixed thoroughly by grinding them in alcohol, in an agate mortar & [redacted] pestle, for about 2 hours. They were subjected to air-drying. Mixtures prepared in this way were found to be homogeneous and of suitable purity and desired particle size. These dried mixtures were then transferred to the crucibles made of refractory material. The crucibles were heated to about 1100°C for about 1 hour in nitrogen gas atmosphere in a specially prepared furnace. As manganese shows a tendency to get oxidized to higher valency state in air, at higher temperatures, the phosphor mixtures were heated in nitrogen. The nitrogen gas was purified by passing it through several traps such as concentrated sulphuric acid, potassium hydroxide, phosphorus pentoxide, etc. so that the impurities such as traces of water, oxygen, etc. could be removed. The furnace prepared for the heating purposes was fabricated as follows: A transluscent silica tube, about 1 meter in length and 2" internal diameter was taken. At both the ends B-65 self-male joints were prepared. This tube was inserted in a hollow crusilite silicon carbide element which was used as a heating source. Purified nitrogen gas was passed through one end whereas the other end was used as the outlet. For this purpose, two B-65 pyrex female joints, having an inlet, were fixed to the self joints of the silica tube. The silica tube was placed in the heating element in such a way that about 6"-7" portion from each side remained outside the heating element and both the ends of the silica tube could be kept sufficiently cold. In this fabrication, the heat losses were minimized by using lagging materials like fire-bricks, asbestos-cement sheets, asbestos rope, etc. A calibrated chromel-alumel thermocouple was introduced in the furnace and the zone of maximum heat was determined. The crucibles of alumina material, containing the phosphor mixtures, were kept in this zone of maximum heat and heated to about 1100°C.

X-ray diffraction studies

The x-ray powder diffraction technique was employed to see the completion of the reaction and to determine the extent of substitution in the mixed halophosphate matrix. The samples were filled in glass capillaries and Debye-Scherrer patterns were taken on a Radon X-ray diffraction machine using type A-2 diffraction tube with a copper target and a 9 cm. camera. The d values were obtained from the powder diffraction data. The diffraction lines were indexed with the help of a standard c/a vs.

log d chart for the hexagonal system and lattice parameters were determined by successive refinements. The visually estimated intensities of different diffraction lines were compared with the calculated intensities for different planes. With the help of this comparison the distribution of the substituted cations on the two sites in the apatite structure was determined.

Measurement of spectral energy distribution and intensity of emission under 2537Å excitation

The instrument used for measurement of spectral energy distribution and intensity of emission consisted of the following equipments: (1) the ultraviolet lamp used as the source of irradiation of the sample, (2) sample holder and beam chopping arrangement,(3) constant deviation spectrometer as the dispersion unit, (4) photomultiplier tube as the detector, (5) power supply unit, (6) spot galvanometer as the recorder.

For the irradiation purpose, a low pressure mercury vapour discharge lamp providing 2537Å wavelength was used (minevalight C 50-60 cyc., Model R51, Ultraviolet Produ. Inc., South Pasadona, Calif., 220V). The lamp was covered with a black paper with a hole at the centre. The spectrometer slit, the sample and the beam aperture were adjusted to be in a straight line. The sample holder was placed in such a way that the phosphor layer could face the UV radiation. The sample was prepared by applying a thin layer of the phosphor material, on a microscope slide with the help of an adhesive material. The layer thickness of all the samples was approximately the same. In order to stop the visible component of the UV radiation from entering the spectrometer, a beam chopping arrangement was introduced. The chopper consisted of two co-axial metallic discs having alternate holes in the same axis. The arrangement of alternate holes made it possible to pass only the emitted visible radiation through the spectrometer which was due to the phosphorescence of the halophosphate phosphor. The chopper was attached to a high speed motor, the speed of which was kept at 1500 r.p.m. The two discs of the chopper were blackened by a black paint. With the help of the beam chopping arrangement only the radiation due to the after-glow of the phosphor could be passed through the spectrometer. The micro-slide containing the sample was mounted in between the two discs of the chopper with the help of a wooden stand. The chopper was placed between the spectrometer and the source of irradiation. A photomultiplier tube (make - EMIE photomultiplier tube 6097B) was attached to the telescope of the spectrometer. The intensity of the emitted radiation due to the phosphorescence of the sample was measured by photomultiplier tube. The photomultiplier output was fed to the spot galvanometer and the intensity was measured in terms of galvanometer deflection.

Before starting the actual measurements the proper setting and alignment of the instrument was done. It included the adjustment of the position and distance of the UV lamp from the spectrometer, the position of the sample holder and beam chopping arrangement, the height of the micro-slide, the slit width of the monochromator as well as the telescope. The deflection on the spot galvanometer was adjusted to zero for the dark current. The spectrometer was set at various wavelengths, with a regular interval and the corresponding readings were recorded on the spot galvanometer. The readings were recorded for the wavelength region 4500 to 6500Å. These readings were corrected for the spectral response of the photomultiplier tube and the non-linearity of the wavelength scale. The graphs were plotted for relative intensity as a function of wavelength.

1.4 : RESULTS AND DISCUSSION

X-ray diffraction studies

Strontium in strontium fluorophosphate was partly replaced by thorium and tungsten. Attempts were made to prepare compounds having the general formula $(Sr_{1-x}M_x)_{10}(PO_4)_6F_2$ where M = Th or W. In these compounds some ThO_2 or WO_3 always remained unreacted which could be seen by x-ray diffraction patterns. This was attributed to the fact that thorium and tungsten could not be incorporated in the divalent state. A new series of compounds where Sr^{2+} was replaced by Th^{4+} and W^{6+} and the charge compensation was taken care of by keeping requisite metal deficiency was therefore attempted. These could be represented by a general formula $(Sr^{2+}_{1-x}Th^{4+}_{x/2}\square_{x/2})_{10}(PO_4)_6F_2$ and $(Sr^{2+}_{1-x}W^{6+}_{x/3}\square_{2x/3})_{10}(PO_4)_6F_2$ respectively. Following compounds of different compositions were prepared for the two systems:

	Sr-Th fluoro phosphate	Sr-W fluorophosphate
1:	$(Sr_{9.82}Th_{0.09}\square_{0.09})(PO_4)_6F_2$	$(Sr_{9.82}W_{0.06}\square_{0.12})(PO_4)_6F_2$
2:	$(Sr_{9.64}Th_{0.18}\square_{0.18})(PO_4)_6F_2$	$(Sr_{9.64}W_{0.12}\square_{0.24})(PO_4)_6F_2$
3:	$(Sr_{9.46}Th_{0.27}\square_{0.27})(PO_4)_6F_2$	$(Sr_{9.46}W_{0.18}\square_{0.36})(PO_4)_6F_2$
4:	$(Sr_{9.28}Th_{0.36}\square_{0.36})(PO_4)_6F_2$	$(Sr_{9.28}W_{0.24}\square_{0.48})(PO_4)_6F_2$
5:	$(Sr_{9.10}Th_{0.45}\square_{0.45})(PO_4)_6F_2$	$(Sr_{9.10}W_{0.30}\square_{0.60})(PO_4)_6F_2$
6:	$(Sr_{8.92}Th_{0.54}\square_{0.54})(PO_4)_6F_2$	$(Sr_{8.92}W_{0.36}\square_{0.72})(PO_4)_6F_2$
7:	$(Sr_{8.65}Th_{0.675}\square_{0.675})(PO_4)_6F_2$	
8:	$(Sr_{8.20}Th_{0.9}\square_{0.9})(PO_4)_6F_2$	

X-ray diffraction patterns were taken for all these compounds with the help of Cu-kα radiation on a Debye-Scherrer camera. In strontium-thorium system x in the general formula was varied from 0.018 to 0.18, whereas in the strontium-tungsten system x was varied from 0.018 to 0.108. Compounds with $x > 0.108$ in the first system showed the presence of unreacted ThO_2 whereas compounds with $x > 0.09$ in the second system showed the presence of unreacted WO_3.

The x-ray patterns were indexed with the help of a standard log d chart for hexagonal system. Using the d values for hko type reflections, preliminary value of 'a' parameter was determined from the relationship $a = [4/3(h^2 + hk + k^2)]^{1/2}d$. Similarly, c was determined from $d_{00\ell}$ using the relationship $c = d_{00\ell} \times \ell$. The method of successive refinements was then employed to get constant values of a and c. These constant values were then used to calculate the d values for all the observed reflections. The observed and calculated d values together with intensities of observed reflections and calculated a and c values for two representative compositions are recorded in Table Nos. 1.2 and 1.3. The observed values for our unactivated strontium fluorophosphate are also given in Table No. 1.1. The calculated values of a and c in case of unactivated strontium fluorophosphate match fairly well with the standard ones.

Table No. 1.1

X-ray diffraction data and d values for $Sr_{10}(PO_4)_6F_2$

a = 9.671, c = 7.226, c/a = 0.742.

Intensity	hkil	$d_{obs.}$	$d_{cal.}$
ms	0002	3.61	3.61
ms	$10\bar{1}2$	3.32	3.32
ms	$12\bar{3}0$	3.14	3.16
ms	$11\bar{2}2$	2.89	2.89
vs	$30\bar{3}0$	2.78	2.79
ms		2.68	
m	$22\bar{4}1$	2.30	2.30
m	$11\bar{2}3$	2.17	2.16
w	$20\bar{2}3$	2.09	2.09
w	$22\bar{4}2$	2.01	2.01
s	$13\bar{4}2$	1.96	1.95
s	$12\bar{3}3$	1.91	1.91
s	$32\bar{5}1$	1.87	1.86
ms	0004	1.81	1.81

Table No. 1.2

X-ray diffraction data and d values for $(Sr_{8.92}Th_{0.54}\ \square_{0.54})(PO_4)_6F$
a = 9.868, c = 6.654, c/a = 0.6742

Intensity	hkil	$d_{obs.}$	$d_{cal.}$
ms	0002	3.32	3.33
ms	$12\bar{3}0$	3.25	3.23
ms	$10\bar{1}2$	3.11	3.10
s	$12\bar{3}1$	2.92	2.90
vs	$30\bar{3}0$	2.84	2.85
s	$11\bar{2}2$	2.75	2.76
ms	$20\bar{2}2$	2.64	2.63
	$30\bar{3}1$	Not observed	2.62
vw	$22\bar{4}0$	2.49	2.47
w	$13\bar{4}0$	2.36	2.37
vw	$12\bar{3}2$	2.30	2.32
	$22\bar{4}1$		2.31
vw	$13\bar{4}1$	2.20	2.23
w	$30\bar{3}2$	2.15	2.17
	$10\bar{1}3$		2.15
ms	$40\bar{4}1$	2.02	2.03
	$11\bar{2}3$		2.02
ms	$22\bar{4}2$	1.99	1.98
	$20\bar{2}3$		
vw	$32\bar{5}0$	1.96	1.96
s	$31\bar{4}2$	1.93	1.90
	$32\bar{5}1$		1.88
s	$14\bar{5}0$	1.89	1.86
s	$21\bar{3}3$	1.84	1.83
s	$40\bar{4}2$	1.80	1.80
	$41\bar{5}1$		1.79
ms	$32\bar{5}2$	1.67	1.70
	0004		1.67

Table No. 1.3

X-ray diffraction data and d values for $(Sr_{9.46}W_{0.18}\square_{0.36})(PO_4)_6F_2$

$a = 9.637$, $c = 6.74$, $c/a = 0.6996$

Intensity	hkil	$d_{obs.}$	$d_{cal.}$
w	0002	3.35	3.37
ms	$12\bar{3}0$	3.15	3.15
	$10\bar{1}2$		3.08
s	$12\bar{3}1$	2.87	2.86
vs	$30\bar{3}0$	2.78	2.77
s	$11\bar{2}2$	2.70	2.76
w	$20\bar{2}2$		2.62
	$30\bar{3}1$		2.57
	$22\bar{4}0$	2.44	2.41
m	$31\bar{4}0$	2.31	2.31
	$21\bar{3}2$	Not observed	2.30
	$22\bar{4}1$	Not observed	2.27
w	$13\bar{4}1$	2.17	2.19
	$10\bar{1}3$	Not observed	2.17
	$30\bar{3}2$	Not observed	2.15
ms	$40\bar{4}0$		2.08
	$11\bar{2}3$	2.01	2.036
	$40\bar{4}1$		2.00
ms	$20\bar{2}3$		1.98
	$22\bar{4}2$	1.96	1.96
ms	$32\bar{5}0$	1.91	1.91
	$31\bar{4}2$		1.91
ms	$32\bar{5}1$	1.86	1.84
	$21\bar{3}3$		1.83
ms	$41\bar{5}0$	1.80	1.82
w	$40\bar{4}2$	1.77	1.77
	$41\bar{5}1$	Not observed	1.76
	$30\bar{3}0$	Not observed	1.75
w	0004	1.70	1.70

Discussion

The unit cell of the new substituted fluorophosphates has been found to be hexagonal. The unit cell dimensions of these compounds are determined by x-ray powder diffraction data. An examination of the x-ray lines and their intensities suggest that the compound is, no doubt, isomorphous with the well-known apatite structure.

It is known that in apatite structure the metal ions occupy two types of sites which we might designate as (I) and (II) sites. These two metal ions along with their surrounding oxygens are shown in Fig. 1.2. Sr(I) site is surrounded by six nearly equidistant oxygen ions and three others at a slightly longer distance. Sr(II) ion is surrounded by six oxygen ions, the closest three are nearly equidistant, followed by two at a slightly larger distance and one more still farther away. The metal oxygen distances in terms of c and a are given below:

Sr(I) is surrounded by:

3 oxygen at $(a^2/36 + c^2/16)^{1/2}$
3 oxygen at $(7a^2/225 + c^2/16)^{1/2}$
and 3 oxygen at $(13a^2/144 + c^2/16)^{1/2}$.

Sr(II) is surrounded by:

2 oxygen at $(a^2/144 + 25c^2/256)^{1/2}$
1 oxygen at $\sqrt{217}\ a/60$
2 oxygen at $(7a^2/144 + 9c^2/256)^{1/2}$
1 oxygen at $(13a^2/144)^{1/2}$.

Table No. 1.4 shows the calculated values of the metal-oxygen distances in the two compounds.

Table No. 1.4

Metal-Oxygen distances in

$(Sr_{8.92}Th_{0.54}\Box_{0.54})(PO_4)_6F_2$

and

$(Sr_{9.46}W_{0.18}\Box_{0.36})(PO_4)_6F_2$

Position of Sr(I) site	Sr-Th system (in Å)	Sr-W system (in Å)
3 oxygen at	2.34	2.33
3 oxygen at	2.41	2.39
and 3 oxygen at	3.40	3.35
Position of Sr(II) site		
2 oxygen at	2.24	2.30
2 oxygen at	2.51	2.47
1 oxygen at	2.42	2.11
1 oxygen at	2.97	2.90

The distribution of the substituted cation on the Sr(I) and Sr(II) sites has been studied with the help of x-ray intensity analysis. As an approximation, it has been assumed that the substitution does not affect the values of the various site parameters and the same values as those known for strontium halophosphate have been taken. Thus, it has been assumed that the substituted metal ion has distributed itself over the two available strontium sites without disturbing the position of these or the other sites. In view of the qualitative interest of the result such an approximation is expected to serve the purpose.

The observed intensities have been estimated visually. The intensities have been calculated using the formula

$$I \propto |F| \cdot p \cdot \frac{1 + \cos^2 2\theta}{\cos\theta \sin 2\theta}$$

where F is the structure factor, p is the multiplicity and $(1 + \cos^2 2\theta / \cos\theta \sin 2\theta)$ is Lorentz and polarization factor. No corrections for the absorption and temperature effects have been applied as the errors introduced are in opposite directions and hence they nearly cancel each other. The structure factor values have been calculated from the equation:

$$|F_{hkl}|^2 = A_{hkl}^2 + B_{hkl}^2$$

$$A_{hkl} = \sum_i f_i \cos 2\pi(hx_i + ky_i + lz_i)$$

$$B_{hkl} = \sum_i f_i \sin 2\pi(hx_i + ky_i + lz_i).$$

The simplified form of this equation has been given in the International Table[41] for this space group, which has been used in actual calculations. Appropriate equations for different reflections have been obtained by substituting the values of hkl and atomic coordinates xyz for the various ions of the apatite structure.

The values of the scattering power f have been taken from International Table[42] for x-ray crystallography. The multiplicity factors have been obtained from International Table for that space group. The calculated intensities have been normalised so that $x\sum I_{obs.} = \sum I_{cal.}$ The models A-D chosen for the calculations have been given in Table No.1.5.

Table No.1.5

Different models of structure

$(Sr_{8.92}Th_{0.54}\square_{0.54})(PO_4)_6F_2$

Model	Sr(I)	Sr(II)
A	4Sr	4.92Sr + 0.54Th + 0.54 □
B	2.92Sr + 0.54Th + 0.54 □	6Sr
C	3.46Sr + 0.54Th	5.46Sr + 0.54 □
D	3.46Sr + 0.54 □	5.46Sr + 0.54Th

$(Sr_{9.46}W_{0.18}\square_{0.36})(PO_4)_6F_2$

Model	Sr(I)	Sr(II)
A	4Sr	5.1Sr + 0.3W + 0.6 □
B	3.1Sr + 0.3W + 0.6 □	6Sr
C	3.7Sr + 0.3W	5.4Sr + 0.6 □
D	3.4Sr + 0.6 □	5.7Sr + 0.3W

The intensities calculated using these models have been presented along with the observed intensities of the reflections in Table Nos. 1.6 and 1.7.

For strontium-thorium fluorophosphate, it can be seen that $30\bar{3}0$ is the strongest observed reflection. As compared to that observed $12\bar{3}1$ reflection is weak. However, calculated reflection $12\bar{3}1$, in model A is strong, in model B slightly less

Table No.1.6

Comparison of the observed intensities with those calculated using different models of structure $(Sr_{8.92}Th_{0.54}\square_{0.54})(PO_4)_6F_2$

S.No.	hkil	I_{cal}				I_{obs}
		A	B	C	D	
1	0002	20	16	10	28	30
2	$12\bar{3}0$	10	11	14	8	30
3	$10\bar{1}2$	32	33	35	30	40
4	$12\bar{3}1$	99	90.5	76	116	60
5	$30\bar{3}0$	95	99.7	108	87.5	100
6	$11\bar{2}2$	75	80	91	66	80
7	$20\bar{2}2$	16	19	25	11	50
8	$30\bar{3}1$	0.25	0.25	0.25	0.25	
9	$22\bar{4}0$	3	4	7	1	10
10	$13\bar{4}0$	19	16	12	24	20
11	$12\bar{3}2$	2	0.8	0.02	4	
12	$22\bar{4}1$	0.2	0.2	0.2	0.2	5
13	$13\bar{4}1$	1	1	1	1	5
14	$30\bar{3}2$	3	5	9	1	
15	$10\bar{1}3$	1	1	1.4	1.4	15
16	$40\bar{4}1$	2	2	2	2	
17	$11\bar{2}3$	13	12	10	16	30
18	$22\bar{4}2$	44	47	54	40	
19	$20\bar{2}3$	1.5	1.5	1.5	1.5	40
20	$32\bar{5}0$	7	7	7.5	2	5
21	$31\bar{4}2$	20	22	24	20	
22	$32\bar{5}1$	28	24	20	32	50
23	$14\bar{5}0$	39	41	45	35	50
24	$21\bar{3}3$	51	55	47	70.5	50
25	$40\bar{4}2$	39	37	34.5	42	
26	$41\bar{5}1$	3.4	3.4	3.4	3.5	50
27	$32\bar{5}2$	13	15	18	10	
28	0004	19	19	19	19	30

Table No.1.7

Comparison of observed intensities with those calculated using different models of structure: $(Sr_{9.46}W_{0.18}\square_{0.36})(PO_4)_6F_2$

Sr. No.	hkil	I cal. A	I cal. B	I cal. C	I cal. D	I obs.
1	0002	14	20	12.5	25	15
2	$12\bar{3}0$	32	31	32	29	55
3	$10\bar{1}2$	24	25	26	24	
4	$12\bar{3}1$	79	88	71	96	75
5	$30\bar{3}0$	84	81	90	77.34	100
6	$11\bar{2}2$	70	65	75	60	75
7	$20\bar{2}2$	18	15	21	13	20
8	$30\bar{3}1$	0.2	0.2	0.2	0.2	
9	$22\bar{4}0$	3	2	4	1	
10	$31\bar{4}0$	27	28	27	28	30
11	$21\bar{3}2$	1	2	0.2	4	Not observed.
12	$22\bar{4}1$	0.2	0.2	0.2	0.2	Not observed.
13	$13\bar{4}1$	6.5	6.4	6.4	6.5	10
14	$10\bar{1}3$	1	1	1	1	Not observed.
15	$30\bar{3}2$	3	2	6	1	Not observed.
16	$40\bar{4}0$	7	9	5	11	40
17	$11\bar{2}3$	11	12	10	14	
18	$40\bar{4}1$	2	2	2	2	
19	$20\bar{2}3$	2	2	2	2	40
20	$22\bar{4}2$	40	38	43	36	
21	$32\bar{5}0$	1	6	6	6	40
22	$31\bar{4}2$	10	10	10	8	
23	$32\bar{5}1$	22	24	20	27	40
24	$21\bar{3}3$	26	28	23	30	
25	$41\bar{5}0$	43	42	45	40	40
26	$40\bar{4}2$	31	33	30	34	20
27	$41\bar{5}1$	3.4	3.4	3.4	3.4	Not observed.
28	$30\bar{3}3$	0.2	0.2	0.2	0.2	Not observed.
29	0004	19	19	19	19	20

strong and in model D strongest, as compared to calculated reflection $30\bar{3}0$. Only model C shows appreciable difference in two calculated reflections. Observed reflection $14\bar{5}0$ is medium strong. Model A, B and D all give relatively lower intensities of this reflection, whereas model C gives nearly equal intensity. In case of reflection $21\bar{3}3$ model A, B and D all give more or less stronger reflection than the observed one. Only model C matches close to the observed reflection. It is also observed that, in general, observed intensities match fairly well with the calculated intensities of model C.

For strontium-tungsten fluorophosphate, reflection $12\bar{3}0$ is equally strong for all models. Observed reflection $12\bar{3}1$ is strong. Models A and C show this reflection nearly equally strong, whereas models B and D show it to be stronger as compared to the observed one. $30\bar{3}0$ is the strongest observed reflection. As compared to this observed reflection $12\bar{3}1$is much less strong. There is appreciable difference in intensities of these two reflections. Calculated values, in model A, of intensities of $12\bar{3}1$ and $30\bar{3}0$ are nearly same. Models B and D show higher intensity of $12\bar{3}1$ than that of $30\bar{3}0$. However, model C shows, as expected, a lower value of $12\bar{3}1$ as compared to that of $30\bar{3}0$. Observed reflection $11\bar{2}2$ is strong. Models A and C show it to be strong. But models B and D give lower intensities than the observed one. Observed reflection ($20\bar{2}3$ + $22\bar{4}2$) is medium strong. All models show more or less same intensities as the observed one. For reflection ($32\bar{5}1$ + $21\bar{3}3$) the observed and calculated intensities of model C match to a good extent, whereas all other models show higher intensities of this reflection. In general, model C shows good agreement with the observed intensities of the different reflections.

It is clear from Table Nos. 1.6 and 1.7 that calculated intensities of model C in both the systems match fairly well with the observed intensities of the x-ray diffraction patterns. It can be concluded that thorium and tungsten ions are substituted for strontium at Sr(I) site, leaving a metal vacancy at Sr(II) site.

Emission spectrum studies

Strontium halophosphate phosphor activated with antimony and manganese as activators, has already been studied[37]. In the present work, strontium has been partially replaced by thorium and tungsten in the fluorophosphate matrix. An attempt has been made to study the effect of this substitution on the optical properties of the mixed phosphors. Pure strontium halophosphate phosphor activated with antimony and manganese is known to show a double band emission at about 4750Å and 5450Å. These emission peaks have been attributed to emission of antimony and manganese respectively.

In strontium-thorium fluorophosphate system $(Sr_{1-x}Th_{x/2}\square_{x/2})_{10}(PO_4)_6F_2$ nine compositions in the range

$0 < x < 0.18$, and in strontium-tungsten fluorophosphate system $(Sr_{1-x}W_{x/3}\square_{2x/3})_{10}(PO_4)_6F_2$, seven compositions in the range $0 < x < 0.11$, have been studied. Each composition has further been studied for spectral emission of the activators. The concentration of antimony was kept constant at 3% as even small amount of it is sufficient to work as a sensitizer. The concentration of manganese activator has been varied from 0 to 4%. A mercury vapour lamp providing 2537Å radiation has been used as the source of excitation. It is known that the excitation radiation is first absorbed by Sb^{3+} ions. A part of it is lost by non-radiative transfer to lower excited levels of Sb^{3+} ion. Then from lower excited level of Sb^{3+} ion, another part of the energy is transferred to Mn^{2+} ion which emits in the visible region. Figures 1.4 and 1.5 show the variation of intensity as a function of wavelength of emission, for various concentrations of Mn activator for the typical compositions of the two systems.

In all the figures, a small and broad peak is present at about 4800Å which has been attributed to emission from the antimony activator. The emission peak of antimony is suppressed by Mn^{2+} activator. The peak of Mn^{2+} emission appears at about 5450Å. The evidences as regards the effect of manganese concentration on the position of emission peak seem to be conflicting. Neurgaonkar and Sinha[39] have observed that higher concentration of Mn^{2+} leads to a shift towards longer wavelength in substituted halophosphates. Ostaszewis[43] has also reported that the position

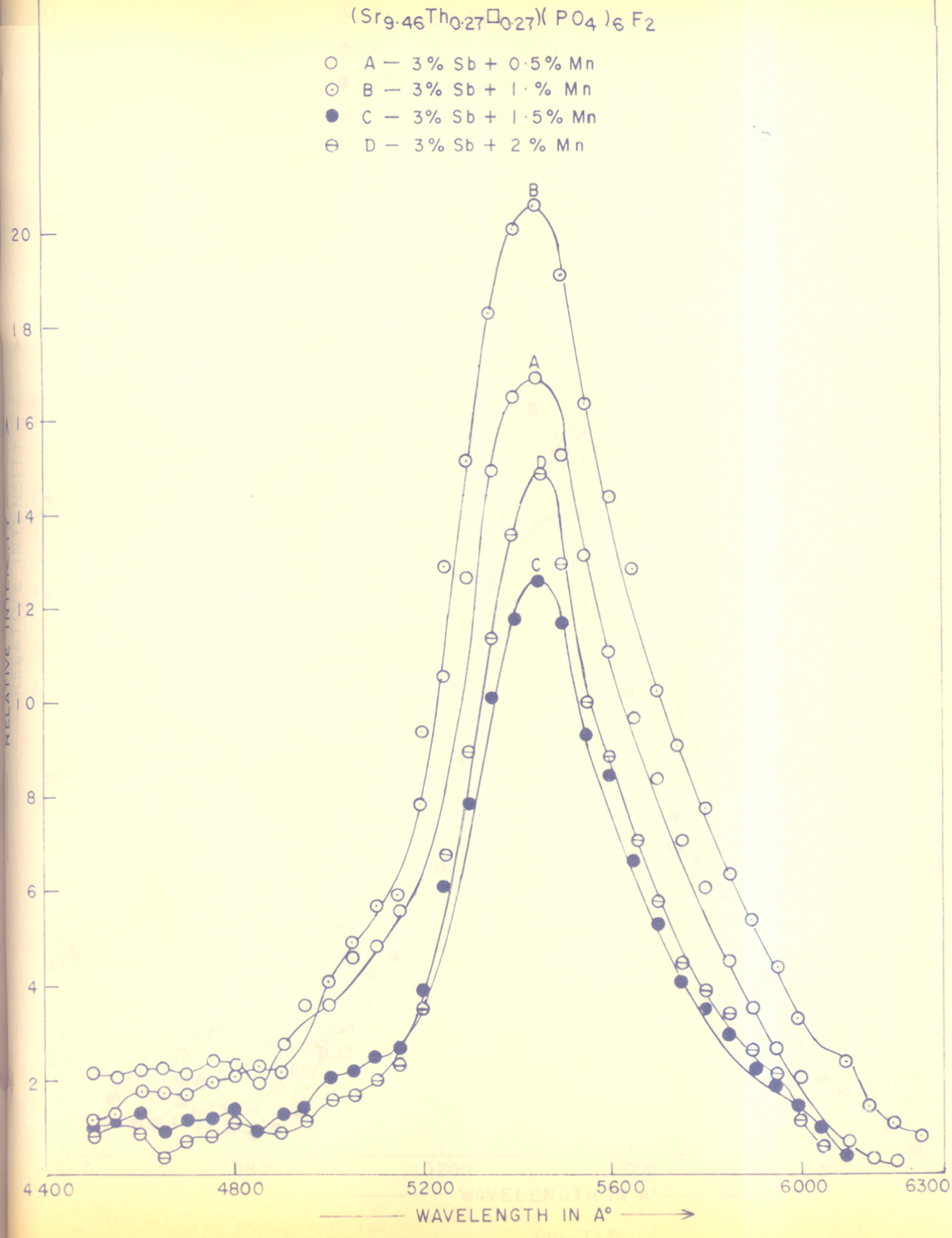

$(Sr_{9.46}Th_{0.27}\square_{0.27})(PO_4)_6F_2$
○ A — 3% Sb + 0·5% Mn
⊙ B — 3% Sb + 1·% Mn
● C — 3% Sb + 1·5% Mn
⊖ D — 3% Sb + 2 % Mn
B
A
D
C
20
18
16
14
12
10
8
6
4
2
RELATIVE INTENSITY
4400
4800
5200
5600
6000
6300
WAVELENGTH IN A°

FIG 1·4

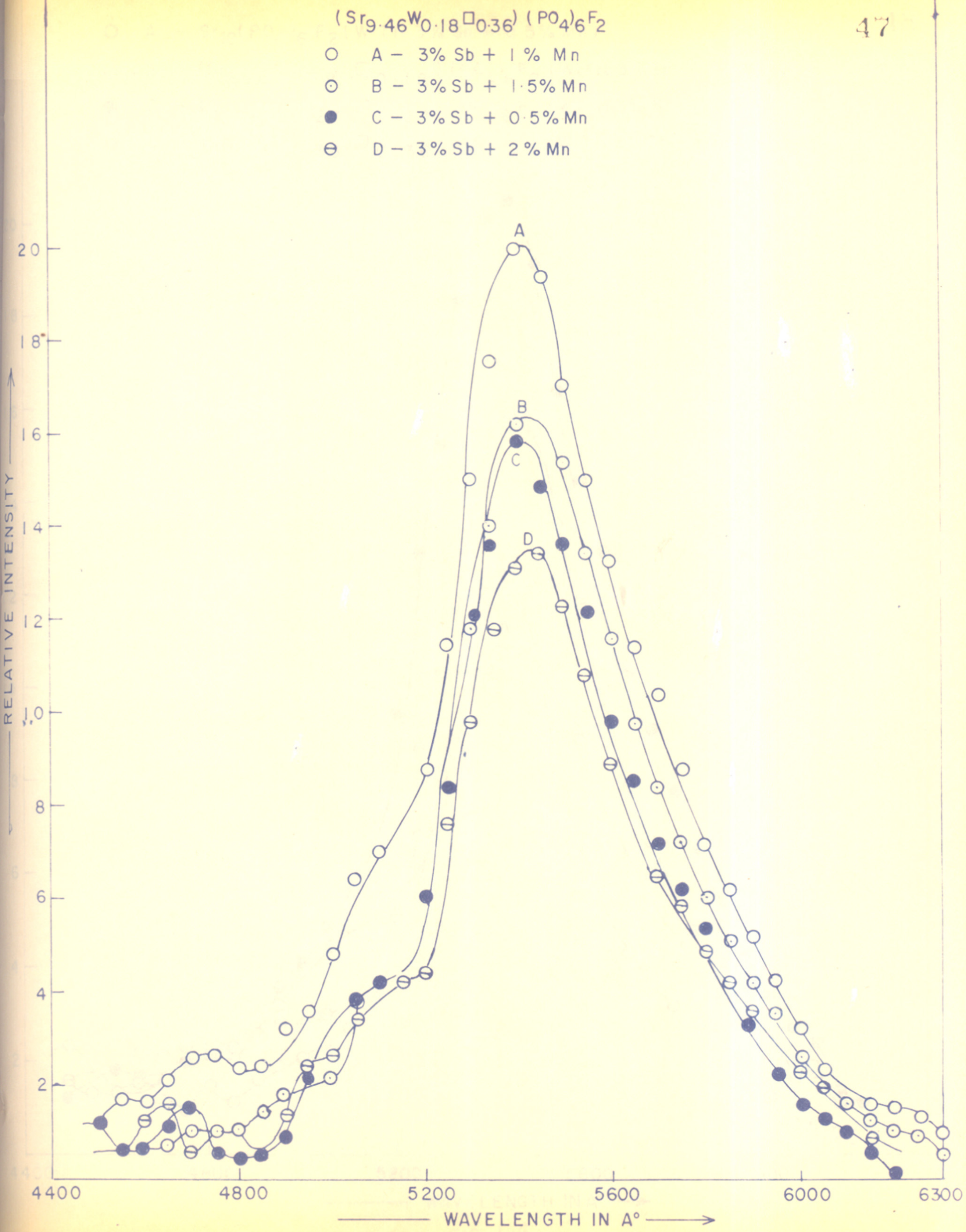

$(Sr_{9.46}W_{0.18}\square_{0.36})(PO_4)_6F_2$
○ A – 3% Sb + 1 % Mn
⊙ B – 3% Sb + 1·5% Mn
● C – 3% Sb + 0·5% Mn
⊖ D – 3% Sb + 2% Mn
A
B
C
D
20
18
16
14
12
10
8
6
4
2
RELATIVE INTENSITY
4400
4800
5200
5600
6000
6300
WAVELENGTH IN A°

FIG. 1·5

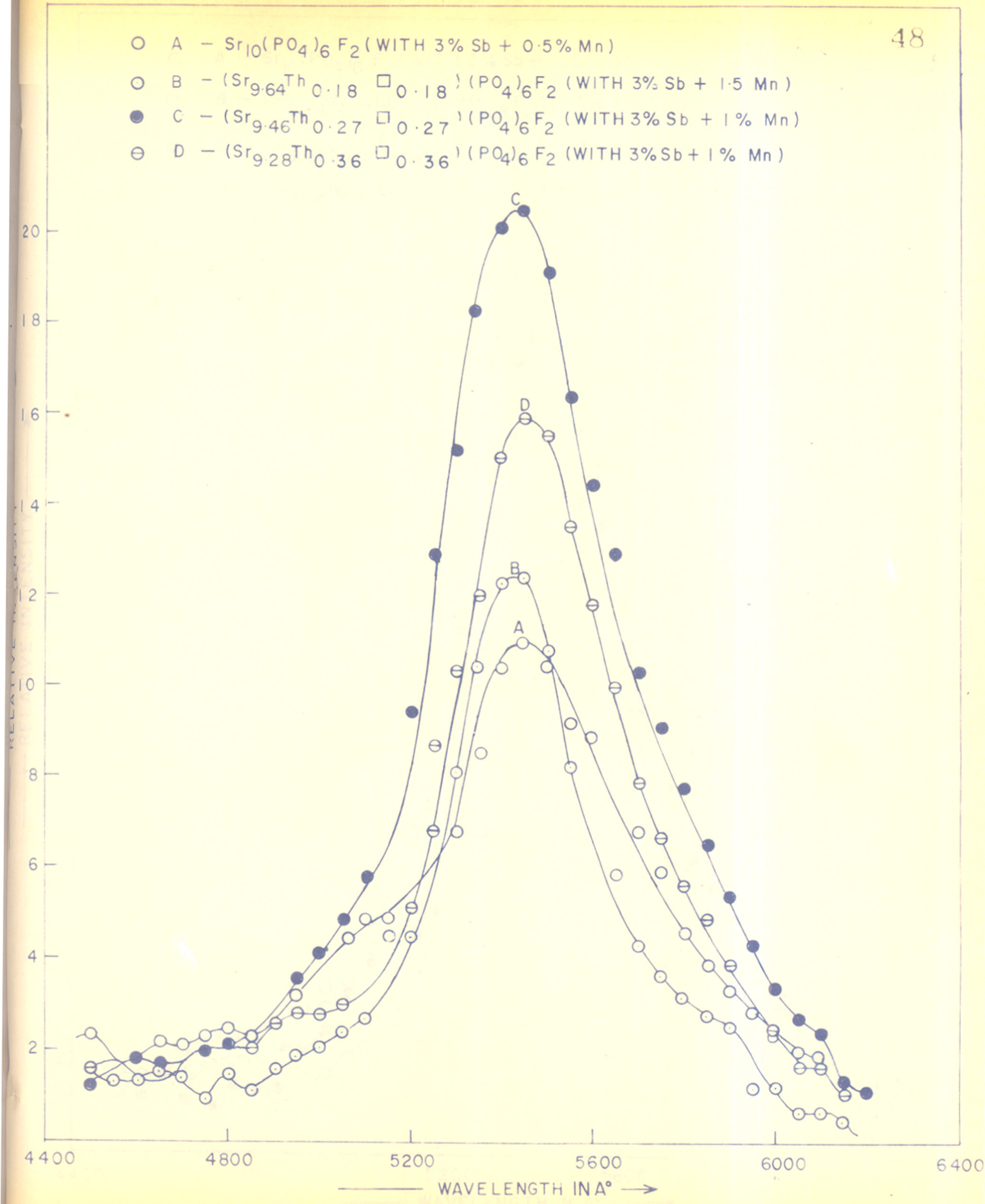

○ A – $Sr_{10}(PO_4)_6F_2$ (WITH 3% Sb + 0·5% Mn)
○ B – $(Sr_{9·64}Th_{0·18}\square_{0·18})(PO_4)_6F_2$ (WITH 3% Sb + 1·5 Mn)
● C – $(Sr_{9·46}Th_{0·27}\square_{0·27})(PO_4)_6F_2$ (WITH 3% Sb + 1% Mn)
⊖ D – $(Sr_{9·28}Th_{0·36}\square_{0·36})(PO_4)_6F_2$ (WITH 3% Sb + 1% Mn)
C
D
B
A
RELATIVE INTENSITY
20
18
16
14
12
10
8
6
4
2
4400
4800
5200
5600
6000
6400
WAVELENGTH IN A° →

FIG. 1·6

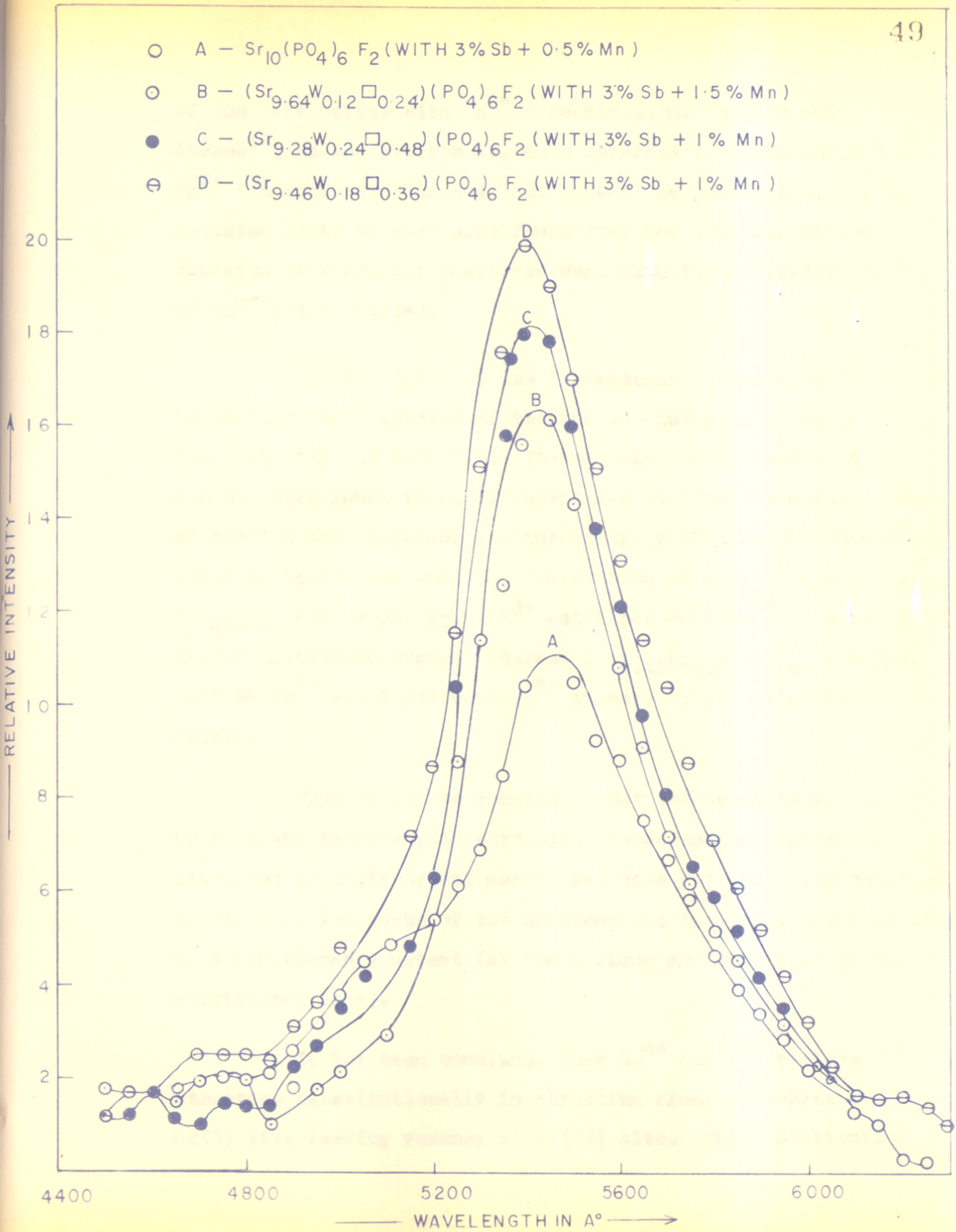

○ A — $Sr_{10}(PO_4)_6F_2$ (WITH 3% Sb + 0·5% Mn)
⊙ B — $(Sr_{9.64}W_{0.12}\square_{0.24})(PO_4)_6F_2$ (WITH 3% Sb + 1·5% Mn)
● C — $(Sr_{9.28}W_{0.24}\square_{0.48})(PO_4)_6F_2$ (WITH 3% Sb + 1% Mn)
⊖ D — $(Sr_{9.46}W_{0.18}\square_{0.36})(PO_4)_6F_2$ (WITH 3% Sb + 1% Mn)
D
C
B
A
RELATIVE INTENSITY
20
18
16
14
12
10
8
6
4
2
4400
4800
5200
5600
6000
WAVELENGTH IN A°

FIG. 1·7

of the peak varies with Mn^{2+} concentration. Butler and Jerome[44], on the other hand, have observed that change in Mn^{2+} ion concentration does not affect the position of the emission peak. We have also found that the position of the emission peak remains unaltered even when the concentration of Mn^{2+} ion is varied.

The intensity of the fluorescence changes with increasing concentration of thorium and tungsten which is shown in Figs. 1.6 and 1.7. The optimum concentration of Mn^{2+} ion has been found to be different for different concentrations of thorium and tungsten. The intensity of the phosphor has been found to be maximum when the composition is $(Sr_{9.46}Th_{0.27}\square_{0.27})(PO_4)_6F_2$ with 3 per cent Sb^{3+} and 1 per cent Mn^{2+} in case of strontium-thorium system, whereas $(Sr_{9.46}W_{0.18}\square_{0.36})(PO_4)_6F_2$ with 3% Sb^{3+} and 1 per cent Mn^{2+} in case of strontium-tungsten system.

Thus it can be concluded that the substitution of thorium and tungsten, in strontium fluorophosphate phosphor activated by antimony and manganese, does not shift the position of the emission peaks of the phosphor but increases the intensity to a considerable extent (at the optimum concentration of the substituted ions).

It has been concluded that Th^{4+} and W^{6+} replace strontium substitutionally in strontium fluorophosphate at Sr(I) site leaving vacancy at Sr(II) site. This substitution increases the intensity of the phosphor without shifting the peak of emission.

It is clear that the energy levels of Th^{4+} and W^{6+} lie far above the region of excitation (see footnote*). Hence it appears less likely that the substituted cations will take part in energy transfer process electronically. It, therefore, appears that the effect of these ions is only indirect, e.g. (i) affecting the energy levels of Sb^{3+} or Mn^{2+} ions by changes in the crystal field, perturbations or (ii) by affecting some of the transition probabilities.

Fonda[45] has speculated that the main cause of variation of the position of spectral emission would be the variation of the crystal field strength due to the change in lattice constants. Narita[46] has theoretically calculated the energy levels of the activating Mn^{2+} ion in calcium fluorophosphate and compared with the available experimental results. He has tried to correlate the shifts of the energy levels with change in lattice constants. The change in lattice constants due to replacement of ions may be isotropic or anisotropic. Assuming the isotropic change, when calcium is replaced by cadmium in calcium fluorophosphate, he has found that decrease by 2% in the lattice constant causes a shift of approximately 300 cm^{-1} to the lower energy side. The magnitude of the shifts corresponds to about 13% of the energy depression

---

*Although the exact energy levels are not known experimentally, an approximate idea can be got from the energy levels of isoelectronic Rn and Er levels.

due to the perturbation of the crystalline field of the original lattice constant. It is known from spectroscopic data that free Mn^{2+} ion does not have a level below 26800 cm^{-1} in its absorption spectrum. However, the emission spectrum has a peak near 17300 cm^{-1}. He has assumed that the Mn^{2+} ion is embedded in the crystalline field created by the surrounding ions and has calculated energy levels treating the crystalline field a perturbation. In another paper, Narita[47] has calculated the crystalline field of calcium fluorophosphate crystal at the position of the impurity Mn^{2+} ion and studied energy spectra of Mn^{2+} ion in this crystalline field, considering the influence of polarisation of oxygen ions on the crystalline field and taking the ionicity of phosphate ion as a parameter.

In our systems, we find that on substituting Th^{4+} or W^{6+} for Sr^{2+}, the lattice constants are changed, but we do not find a corresponding change in the position of the emission wavelength of either Mn^{2+} or Sb^{3+}. On the other hand, we find a substantial increase in the intensity which indicates clearly that the substitution affects the transition probabilities.

Mn^{2+} ion has d^5 configuration. In the transition groups, practically all of the d-d transitions appear to be electrical dipole. So in the free ion, direct inner-shell d-d transition is forbidden as the orbitals have same parity. However, when the ion is in a crystal this prohibition may be removed by the mixing of orbitals having opposite parity. So the combining states must differ in their symmetry properties by at least one component of a translational vector. This condition may be induced by (a) absence of center of symmetry of the crystal field, (b) destruction of the center of symmetry by vibrations.

The fact that substitution of Th^{4+} and W^{6+} increases the intensity of the phosphor, can be accounted for in the following way. Fig. 1.3 can be referred to for this purpose. When the phosphor is exposed to 2537Å UV radiation, Sb^{3+} ion gets excited by absorbing a photon having 41000cm^{-1}. The electrons return to another excited state of Sb^{3+} which is 21000 cm^{-1} above ground level, by a non-radiative process. At this stage, in normal course, some of the electrons are transferred to a manganese excited level which lies close to 21000 cm^{-1} level of Sb^{3+}. This is known as resonance transfer. Hereafter, there are two possibilities:

1) In presence of thorium, the number of electrons transferred to Mn^{2+} excited level by resonance transfer is increased so that the number of electrons coming to ground state from the antimony level (21000 cm^{-1}) decrease and correspondingly the intensity of antimony emission is decreased. The electrons which come to resonance level of manganese now lose certain energy by non-radiative transition as in the usual case and come to another excited level of Mn^{2+} which lies 17300 cm^{-1} above ground level. As the number of electrons is increased, the intensity of the manganese emission is correspondingly increased. So it can be concluded that the intensity of manganese increases at the cost

of intensity of antimony emission. However, this is contrary to our experimental findings. It is found that the intensities of both Mn^{2+} and Sb^{3+} emission are increased simultaneously.

2) Second possibility is that the increased intensity is due to the increased probability of a radiative transition at the cost of non-radiative transition. This will increase the intensity of the antimony emission. At the same time, the electrons which are transferred to excited level of Mn^{2+} by resonance transfer, come back to another excited level of Mn^{2+} which lies 17300 cm^{-1} above ground level, non-radiatively as usual. Here again, the probability of radiative transition from Mn^{2+} (17300 cm^{-1}) to ground level is increased and the ratio of radiative to non-radiative transition probabilities is increased. Thus, the intensity of Mn^{2+} emission is correspondingly increased.

From the results of our experiments, it is seen that the intensity of both, Sb^{3+} and Mn^{2+} emissions, is increased and hence the second mechanism is considered to be more plausible.

REFERENCES

1. Jenkins, H. G., McKeag, A. H., Ranby, P. W., J. Electrochem. Soc., 96 (1949), 1.

2. Struktur Bericht, Vol. 2, 1928-1932, p. 99.

3. Wollentine, R. W., Nagy, R., Lui, C. K., J. Electrochem. Soc., 95 (1949), 187.

4. McKeag, A. H., (To G.E.C.), U.S. Pat., 2,201,698, May, 21 (1940).

5. McKeag, A. H., Ranby, P. W., (To G.E.C.), U.S. Pat., 2,488,733, Nov., 22 (1949).

6. McKeag, A. H., Ranby, P.W., (To G.E.C.), U.S. Pat., 2,476,676, July, 19 (1949).

7. Bundel, A. A., Vainberg, B. I., Dobrolyubskaya T.S. and others, Izvest. Akad. Nauk. S.S.S.R. Ser.Fiz. 15, 815-23 (1951).

8. Anderson, J. T., Wells, R.S., J. Electrochem. Soc., 98 (1951), 414.

9. Fonda, G.R., (To G.E.C.), U.S. Pat., 2,592,261, April 8 (1952)."

10. Wallaeys, R., Ann. Chim. (Paris), 7, (1952), 808.

11. Wollentine, R. W., Nagy, R., Lui, C. K., J. Electrochem. Soc., 99 (1952), 187.

12. Aoki, Y., Hanno, M. (To Hitachi Manuf. Co.), Japan, 6272, Dec. 7 (1953).

13. Prener, J. S. (To G.E.C.), U.S. Pat., 2,636,010, April, 21 (1953).

14. Hinonishi, Y., Machida, J. (To Nippon Electro-Chem. Ind. Co.), Japan, 1972, Apr.14(1954).

15. Wanmaker, W.L., Ouweltjes, J. L., J. Electrochem. Soc., 103 (1956), 161.

16. Doherty, M. and Harrison, W., Brit. J. Appl. Phys. Suppl. No. 4 (1954), p. S11.

17. Wallentine, R. W., Nagy, R. (To Westinghouse Elec. Corp.), U.S.Pat. 2,672,451, March, 16 (1954).

18. Uhera, Y.
(To Tokyo Shibaura Elec. Co.) Japan, 4314, June,24 (1955).

19. Banno, M., Emoto, M., Sato, Y.,
(To Hitachi Manuf. Co.), Japan, 2765, April, 25, (1955).

20. Ranby, P. W., Henderson, S. T.
(To Thorn Elec. Ind. Ltd.), U.S. Pat.,2,726,214, Dec.6(1955).

21. Ouweltjes, J. L., Le J de Phys. Et Rad., 17, (1956), 641.

22. Wanmaker, W. L., Verheyke, M. L.,
Phillips Res. Rept., 11 (1956), 1.

23. Wollentine, R.W.,
J. Electrochem. Soc., 103 (1956), 17.

24. Henderson, S. T., Ranby, P. W.,
J. Electrochem. Soc., 104 (1957), 612.

25. McKeag, Hunt, B. E.,
(To G.E.C.), Brit., 877, 535, March, 11 (1957).

26. Wollentine, R. W.,
(To Westinghouse Elec. Corp), U.S.Pat., 2,780,600, Feb.5(1957).

27. Kamiya, S., Mizunu, H.,
Natl. Tech. Rept., 4 (1958), 1.

28. Wallaeys, R., Ali-Naghi Akhavan Naiki, Compt.Rend.,
246 (1958), 1556.

29. McKeag, A. H., Hunt, B.E.,
J. Electrochem. Soc., 106 (1959), 1032.

30. Butler, K. H.,
(To Sylvania Elec. Prod. Inc.), U.S.Pat., 2,898,302,
Aug. (1959).

31. Rimbach, H. W.,
(To Westinghouse Elec. Corp , U.S.Pat., 2,91912, Jan.19(1960).

32. Aia, M.A., Poss, S. M.,
(To Sylvania Elec. Prod. Inc.), U.S.Pat.,2965,786,
Dec. 20 (1960).

33. Rimbach, H. W.,
(To Westinghouse Elec. Corp.), U.S.Pat. ,2,968,626,Jan.17(1961)

34. Suchow, L.,
J. Electrochem. Soc., 108 (1961), 847.

35. Repsher, R. W.,
(To Westinghouse Elec. Corp), U.S.Pat., 3,023,340,
Feb., 27 (1962).

36. Apple, E. F.,
J. Electrochem. Soc., 110 (1963), 374.

37. Ouweltjes, J. L.,
cited in 'Modern Materials,' Edtd. by B.W.Gonser, Vol.5
(1965), 193.

38. Hoekestra, A. H.,
Phillips Res. Rept., Suppl. No. 2 (1968), 6.

39. Neurgaonkar, R. R. and Sinha, A. P. B.,
Ind. J. Pure and Appl. Phys., 7 (1969), 402.

40. Neurgaonkar, R. R.,
Ind. J. Pure and Appl. Phys., 7 (1969), 480.

41. International Tables for x-ray crystallography,
Vol. I (Kynoch Press), Birmingham, England (1952), 478.

42. International Tables for x-ray crystallography,
Vol. III, (Kynoch Press), Birmingham, England (1962), 211.

43. Ostaszewies, E.,
Acta. Phys. Polon, 19 (1960), 421.

44. Butler, K. H., Jerome, C. W.,
J. Electrochem. Soc., 97 (1950), 265.

45. Fonda, G. R.,
J. Opt. Soc. Am., 47 (1957), 877.

46. Narita, K.,
J. Phys. Soc. Japan, 16 (1961), 99.

47. Narita, K.,
J. Phys. Soc. Japan, 18 (1963), 79.

---000---

2. 1. : GENERAL INTRODUCTION

Alkaline earth sulphides have various commercial applications such as in cathode-ray tubes for televisions and radars, in electroluminescent panels, dyes, paints, etc. Sulphide phosphors surpass all other phosphors in the duration of their afterglow. The demand arising from the industrial uses has not only promoted experimental searches for new types of phosphors but has also been an important stimulus of basic research in this area.

The wealth of information that has been published concerning the properties of these phosphors is indeed enormous. A lot of work has been done in understanding and interpreting the luminescence processes and elucidating the nature of luminescence centres,especially in case of IInd group sulphide phosphors. Among these, ZnS and CdS have been most extensively studied and have become exceedingly important as the host materials. Recently, mixed phosphors such as (ZnCd)S have received close attention because of their response to infrared stimulation and also due to various other interesting properties. Many solid solutions of sulphides have been tried as host materials, in view of studying new phosphors, but in most cases the phases of the constituents have the same crystal symmetry. Relatively less attention has been paid to the possible mixed phosphor (Ca + Cd)S perhaps because the crystals of CaS and CdS belong to different classes of symmetry, the first being cubic and the second hexagonal.

Present work has been undertaken with a view of studying the effect of substitution of cadmium for calcium in calcium sulphide, on the structural properties and also the optical properties of this mixed sulphide phosphor when incorporated with suitable activators. A series of solid solutions having different proportions of calcium and cadmium have been studied. The effect of the concentration of activators on the luminescence of the mixed phosphor has also been studied. Some phosphors of this series show very bright yellow to orange luminescence.

2.2 : HISTORICAL INTRODUCTION

Levshin[1] has prepared mixed (Ca-Sr)S phosphor activated with three activators; Ce, Sm, La. These phosphors produce radiation by recombination of electrons without preliminary localisation. Phosphorescence has been found to play a secondary role, whereas fluorescence appears to be quite unimportant. Intensity of excitation has been kept about 1.5 x 10^{-4} w/sq. cm. and emission after excitation shows a very rapid rise, then a rapid decline after stoppage of excitation; phosphorescence is found to be very feeble, lasting some ten minutes. On excitation for 30 minutes the light summation of the flash reaches 96% of maximum magnitude but the process is not complete even in 5 minutes. The decline of emission after stoppage of excitation is stepwise. The results have been represented graphically.

Dreeben and Ward[2] have studied the system (Sr,Ca)S (solid) in equilibrium with (Sr^{2+} Cl^- O^{--} Ca^{2+}) (liquid phase) containing Eu^{3+} and Sm^{3+} activators. The distribution of activator between the solid and the liquid phase has been found to be controlled by the O^{2-} and Ca^{2+} ion concentration. It has been shown that the presence of calcium ions in the melt counteracts to some extent, the influence of the oxide ion which lowers the concentration of the activators in the solid phase. The effect is more pronounced with Sm^{3+}. This phenomenon has been explained on the assumption of the formation of ion-pairs or complex ions in the melt. The role played by these factors in the preparation of certain phosphors containing cations such as Li^{+}, Be^{2+}, Mg^{2+} with activators Ce^{3+}, Sm^{3+}, Bi^{3+} has been discussed.

Anikina[3] has done studies on (CaS.SrS); Ce, Sm phosphors. He has observed that a part of the energy of the exciting UV light is spent on liberation of electrons from the trapping levels and possibly also on raising electrons from the filled zone on to free levels of ionised centers. Alternatively, the exciting energy might be first absorbed by host lattice and then transmitted to electrons in traps. In either case, energy of exciting light has partly been wasted. This results in decreasing the yield. He has observed that in his experiments the yield increases by a factor of about 1.5 in the presence of a strong source of infrared. A possible mechanism has been suggested for this increase in the yield.

Gobrecht and Hahn[4] have reported luminescent Ba and Sr polysulphides. The materials have been prepared by holding the carbonates at 500° to 600° in presence of excess of S. Excited by Hg 366 mμ radiation, they emit yellow to orange-red luminescence. A red shift has been observed in the spectra at low temperature. The luminescence has, therefore, been ascribed to the polysulphide mole especially di- and tri-sulphide in analogy with the alkali polysulphide.

Wojtczak[5] has reported certain properties of calcium sulphide luminophors. The effect of type and proportion of reducing agent, of the ratio of melt constituents and of baking temperatures on the intensity of luminescence of CaS luminophors has been presented graphically. He has given a table presenting colours of luminophors and of emitted radiation and excitation time. Another table shows the luminescence intensity as a function of age of luminophor, time of excitation at 365 mμ and type and amount of reducing agent. An accuracy of 2-5% in the measurement of radiation intensity has been claimed for the technique employed.

Domange <u>et.al.</u>[6] have prepared solid solutions of sulphides by adding sulphides having NaCl type structure to yttrium sulphide. The systems such as MnS-Y_2S_3; CaS-Y_2S_3; PbS-Y_2S_3, are studied. The variation of the parameter 'a' in these mixed sulphides has been plotted as a function of the radius of the substituted ion. The work, however, does not draw any significant conclusions as regards the effect on structure but only offers some data about substitution of cations.

Patrovsky[7] has reported that the afterglow time of Ca-Sr sulphide activated with bismuth can be substantially prolonged by the addition of small amounts of lead. The optimum conditions for the preparation of this phosphor have been determined and its characteristic properties have been measured. The afterglow time of this phosphor has been shown to be many times longer than that of some well known substances with long lasting afterglow.

Wachtel[8] has prepared a red emitting CaS electroluminescent phosphor activated by Eu and Cu. The mole per cent of Eu has been kept from 0.01-1 and NH_4Br and $CaBr_2$ have been used as flux materials. The phosphor mixture has been washed with alcohol containing 0.5-5 mole per cent Cu compound and boiled. The precipitate has been washed, dried and fired at 960°. He has observed that the phosphor emission at 6540Å is fairly independent of excitation frequency.

Avinor[9] has prepared red-light emitting calcium-cadmium sulphide phosphor having decay time $<2 \times 10^{-6}$ sec. Antimony has been used as activator. The phosphor has been heated to 1100° for about 2 hours. It is observed that the best results are [redacted] obtained when the Cd content in the phosphor is 0.1-1.0 atom % and Sb is 0.001-1.00 atom %. He has also reported that strontium can be added in place of or in addition to calcium in the phosphor. Calcium sulphide and cadmium sulphide belong to different crystal symmetry, so that effect of this substitution on the crystal structure of the phosphor would have been worth studying.

A red light emitting calcium-cadmium sulphide luminescent material has been reported by Phillips Electronics and Associated Industries[10]. This material is excited by electron bombardment and has the decay time of $<2 \times 10^{-6}$ sec. The base material contains cadmium and calcium or strontium and it is activated by antimony. The phosphor has been fired in H_2S

atmosphere at about 1000° for 1 hour using CaF_2 as flux. The luminescent material has found use in cathode ray tubes.

Anderson[11] has studied the emission spectra of Nd^{3+}, Er^{3+}, Yb^{3+} activated cadmium sulphide crystals. These activators form the principal radiative recombination centers in selected crystals. The fluorescent life times have been found to be as follows: CdS: Yb~100 μ sec; for CdS:Nd~300 μ sec; for CdS:Er~ 3000 μ sec. Both the emission spectra and the life time measurements have shown that the rare-earth ions occupy more than one type of site in the CdS lattice. No emission has been observed from rare-earth ion metastable level greater than 1.53 ev above the ground state, even though the CdS band gap is 2.43 to 2.52 ev in the temperature range of the experiment. This has been taken as an evidence for rare earth-ion-acceptor type defect pairing.

Nizovtsev and others[12] have determined the excitation spectra for the phosphors CaS:Mn, Bi; CaS.SrS:Mn,Bi; CaS.SrS:Mn. The spectra show the maximum absorption at 250 mμ. The authors have attributed the decrease in the excitation for a further increase in the quantum energy to the surface character of the absorption of light. For the mixed phosphors the absorption shifts towards lower energy as the SrS concentration increases. They have studied the IR stimulation of flashes in CaS.SrS:Ce,Mn, at different temperatures. The sensitivity of the phosphor to the

IR radiation of a wavelength of $\sim 2\mu$ at low temperature has been attributed as, due to the electrons in small traps which give a maximum at -150°. The long wave boundary for the IR sensitivity has been shown to be $> 3\ \mu$. The brightness of the flashes due to IR radiation with a wavelength of $1.25\ \mu$ has been shown to be dependent on the temperature; it decreases as the temperature increases from -196° to -150°.

Levshin and others[13] have studied the absorption spectra of thin films of CaS.SrS system. The absorption spectra of CaS film deposited on a cold substrate have shown that annealing produces a higher crystallinity of the film, making the absorption edge sharper and decreasing the long wavelength absorption. With introduction of Mn and Bi as impurities new maxima are found to appear. The maxima of the glow of the sublimate phosphors SrS.CaS:Bi (3×10^{-4} g/g); CaS.SrS:Mn (10^{-3} g/g) have been found to shift to long wavelength region compared with powder-like phosphors CaS-Bi, CaS-Mn. The maximum of the emission band in CaS.SrS:Bi has been observed at 5000Å. In CaS.SrS:Mn the emission band consists of overlapping narrow bands. The excitation spectrum of Mn in the region of long-wave drop is found to coincide with the spectrum of the ground absorption of CaS. In CaS:Bi, besides the maximum of ground absorption, intense maximum of activator excitation has been observed.

Mathur and Razdan[14] have tried to correlate the electron trap depths as computed from the experimental decay and thermo-luminescence curves of sulphide phosphors. They have studied the decay of phosphorescence and thermo-luminescence of SrS:Bi and BaS:Cu phosphors. The curves are broken into exponentials by using the method of 'successive substraction'. Trap depths have been calculated by using the exponential constants α's and the thermoluminescence curve peaks. It has been found that the trap depths calculated by using α of the slowest exponential and the low temperature peak of the thermoluminescence curve of SrS:Bi (Na_2SO_4) phosphor are in good agreement. Same has been found to be true for BaS:Cu (borax) phosphor. They have concluded that in determining trap-depths, a careful analysis of decay curves is as useful as the study of thermoluminescence.

Ranade and Thakar[15] have done magnetic susceptibility measurements of CaS:Zr phosphors. They have observed that at low concentration of zirconium the material is diamagnetic, whereas the higher concentration of zirconium leads to paramagnetism of the phosphor. The observed dependence of the magnetic nature on the concentration of zirconium has been explained in terms of the change of ionic state of the activator at high concentration.

Malhotra and Bhawalkar[16] have reported that fluorescence spectra of CaS:Zr, Di phosphors show two bands (at 5800 and 4600 Å) due to Zr and a number of lines due to didinium. They have observed that the activators show a strong interaction and the intensity of both Zr bands and Di lines increases with the increase in concentration of Di upto 0.006% by wt. for different concentrations of Zr. At higher concentrations of Di, Zr bands are found to be suppressed, showing transfer of energy from Zr to Di atoms by quantum mechanical resonance.

Amar Singh[17] has done studies on phosphorescence decay and thermoluminescence of CaS(Cu,Zr) and SrS(Cu,Zr) phosphors for different percentages of copper. He has observed that copper acts as the principal activator and the variation of the percentages of copper has no effect upon the distribution of trap levels and the value of 'S' ('attempt to escape') frequency. He has found that all the qualitative results obtained in the case of the single activator (Cu) have also been observed in the case of doubly activated phosphors such as CaS (Cu,Zr).

2.3 : EXPERIMENTAL TECHNIQUE

Synthesis

Calcium sulphide and cadmium sulphide were taken as the starting materials for the synthesis of the mixed sulphide phosphor. Calcium sulphide was prepared by the method described by Burr[18]. Purified sulphuretted hydrogen gas was passed over calcium carbonate which was heated to about 900°. Calcium sulphide was prepared freshly for every lot of the phosphor mixture as it shows a tendency to get oxidised on storage. Cadmium sulphide was prepared by passing purified sulphuretted hydrogen gas in cadmium chloride solution, the precipitate washed several times with distilled water and alcohol and finally dried at low temperatures (50-60°C) in an oven.

Appropriate amounts of calcium and cadmium sulphides were intimately mixed by grinding them in alcohol for about two hours in an agate mortar and pestle. The mixtures were air dried. They were then heated in a silica boat to about 800° in H_2S atmosphere, in a specially prepared furnace, for about 1&1/2 hours. These sulphide mixtures, when allowed to cool at room temperature, show a tendency to get hydrolysed. Hence they were removed from the furnace to a desiccator when slightly hot and allowed to cool there.

In the next stage, copper and manganese were introduced in this basic matrix, independently as well as in presence of each other as activators. The concentration of copper was varied from 0 to 1% by weight, with an interval of 0.1%. The concentration of manganese was varied from 0 to 5 per cent by weight with an interval of 0.5%. As the amounts of activator were small and as it is known that oxides show good solubility in sulphide matrix, the activators were introduced in the form of oxides. The compounds actually used were carbonates of copper and manganese. The phosphor mixtures were prepared by grinding appropriate amounts of these materials in alcohol in agate mortar and pestle for about two hours. They were then air dried. Mixtures prepared in this way were found to be homogeneous. A lot of 2-3 g. of such a phosphor mixture was heated in an alumina crucible, at about 800°C for one hour. As the sulphur in the basic matrix as well as the activator manganese show a tendency to react with oxygen from air, the phosphor mixtures were heated in nitrogen gas atmosphere. The nitrogen gas was purified by passing it through several traps. Special furnace was devised for the heat treatment of these phosphors as described on page 27. Different zones of the furnace were calibrated with a standard chromel-alumel thermocouple. The mixtures were heated in the zone showing maximum temperature.

X-ray diffraction studies

X-ray diffraction technique was employed to check the formation of solid solutions of the sulphide phosphors. X-ray spectrograms giving directly the intensity of the diffracted beam were taken at the Bhabha Atomic Research Centre, Trombay. The x-ray diffractometer has a Geiger counter for directly measuring the intensity of the diffracted beam for different values of 2θ, using copper target. The 'd' values were obtained from the diffraction data. The diffraction lines were indexed and 'a' values were calculated for the compositions 1 and 2 which were cubic. The other compositions were mixtures but the lines due to the two phases could be indexed separately and the 'a' values for the cubic phase and the 'c' and 'a' values for the hexagonal phase were calculated. The hexagonal lines were indexed with the help of a standard c/a vs log d chart.

Measurement of spectral energy distribution and intensity of emission

The fluorescence time constant of these phosphors was found to be very short. Fluorescence emission spectra were recorded at the Bhabha Atomic Research Center, Trombay. A pen ray UV lamp (3650Å) with long wave filter was used as the excitation source. A Kiethley 610B electrometer and photomultiplier tube (IP 21) was used for recording the spectrum. Graphs were plotted for relative intensity which was expressed in arbitrary units as a function of emission wave lengths, after making the necessary correction for the response of the photomultiplier tube.

2.4 : RESULTS AND DISCUSSION

X-ray diffraction studies

Pure cadmium sulphide shows hexagonal structure, whereas pure calcium sulphide shows cubic structure. An attempt has been made here to prepare a series of solid solutions of these compounds which belong to different crystal symmetry. Following compounds have been prepared to see the solubility of one compound in the other.

1 : $(Ca_{90\%} + Cd_{10\%})S$
2 : $(Ca_{80\%} + Cd_{20\%})S$
3 : $(Ca_{70\%} + Cd_{30\%})S$
4 : $(Ca_{60\%} + Cd_{40\%})S$
5 : $(Ca_{50\%} + Cd_{50\%})S$
6 : $(Ca_{40\%} + Cd_{60\%})S$
7 : $(Ca_{30\%} + Cd_{70\%})S$
8 : $(Ca_{20\%} + Cd_{80\%})S$
9 : $(Ca_{10\%} + Cd_{90\%})S$

Preliminary checkings of the formation of solid solutions were done by taking Debye-Scherrer patterns using Cu-$K\alpha$ radiation for the above compounds. It was found that compounds from 3 to 9 were pure mixtures of the two compounds. Compounds 1 and 2 showed cubic structure. This showed that calcium could not be incorporated in CdS matrix, whereas cadmium can be replaced for calcium in calcium sulphide upto 20 per cent.

The x-ray patterns were indexed as described on page 33 The method of successive refinement was then employed to get constant values of 'a' for these cubic systems. The observed and calculated 'd' values together with intensities of observed reflections and 'a' value for a typical composition are recorded in Table No. 2.1.

Table No. 2.1

X-ray diffraction data and 'd' values for
$(Ca_{80\%} + Cd_{20\%})S$
a = 5.630

Intensity	hkil	$d_{obs.}$	$d_{cal.}$
m	$11\bar{2}1$	3.25	3.25
vs	$20\bar{2}0$	2.81	2.82
s	$22\bar{4}0$	1.99	1.99
w	$31\bar{4}1$	1.70	1.70
m	$22\bar{4}2$	1.63	1.63

Emission spectrum studies

In the present work, an attempt has been made to study the spectral energy distribution of (Ca + Cd)S phosphors activated with copper and manganese. Nine compositions of the mixed sulphide matrix have been prepared. From each basic composition different phosphors have been prepared by varying the concentration of copper and manganese as described earlier. The phosphors activated with copper alone show bright fluorescence in yellow region, whereas those activated with manganese alone, emit nearly in the orange region. The optimum concentration of each activator has been found out. Phosphors containing both these activators together in optimum concentrations have also been studied. They emit in orange region. The experimental results are presented in a series of graphs in Figures 2.1 to 2.6. The graphs have been resolved in various gaussion curves. The peak wavelengths and intensities have been tabulated and are presented in Table No. 2.2.

Table No. 2.2

Peak wavelengths and intensities of emission

	Composition	Emission wavelength in Å	Intensity peak height (in arbitrary units)
1:	$(Ca_{90\%} + Cd_{10\%})S$ with 0.4% Cu	5940 5560 5280 5000	51 20 14 10
2:	$(Ca_{90\%} + Cd_{10\%})S$ with 2% Mn	5980 5700 5400	50 19 13
3:	$(Ca_{90\%} + Cd_{10\%})S$ with 0.4% Cu + 2% Mn.	5980	100
4:	$(Ca_{80\%} + Cd_{20\%})S$ with 0.4% Cu	5940 5560	14 5
5:	$(Ca_{80\%} + Cd_{20\%})S$ with 2% Mn	5980 5700	58 15
6:	$(Ca_{80\%} + Cd_{20\%})S$ with 0.4% Cu + 2% Mn	6050	96

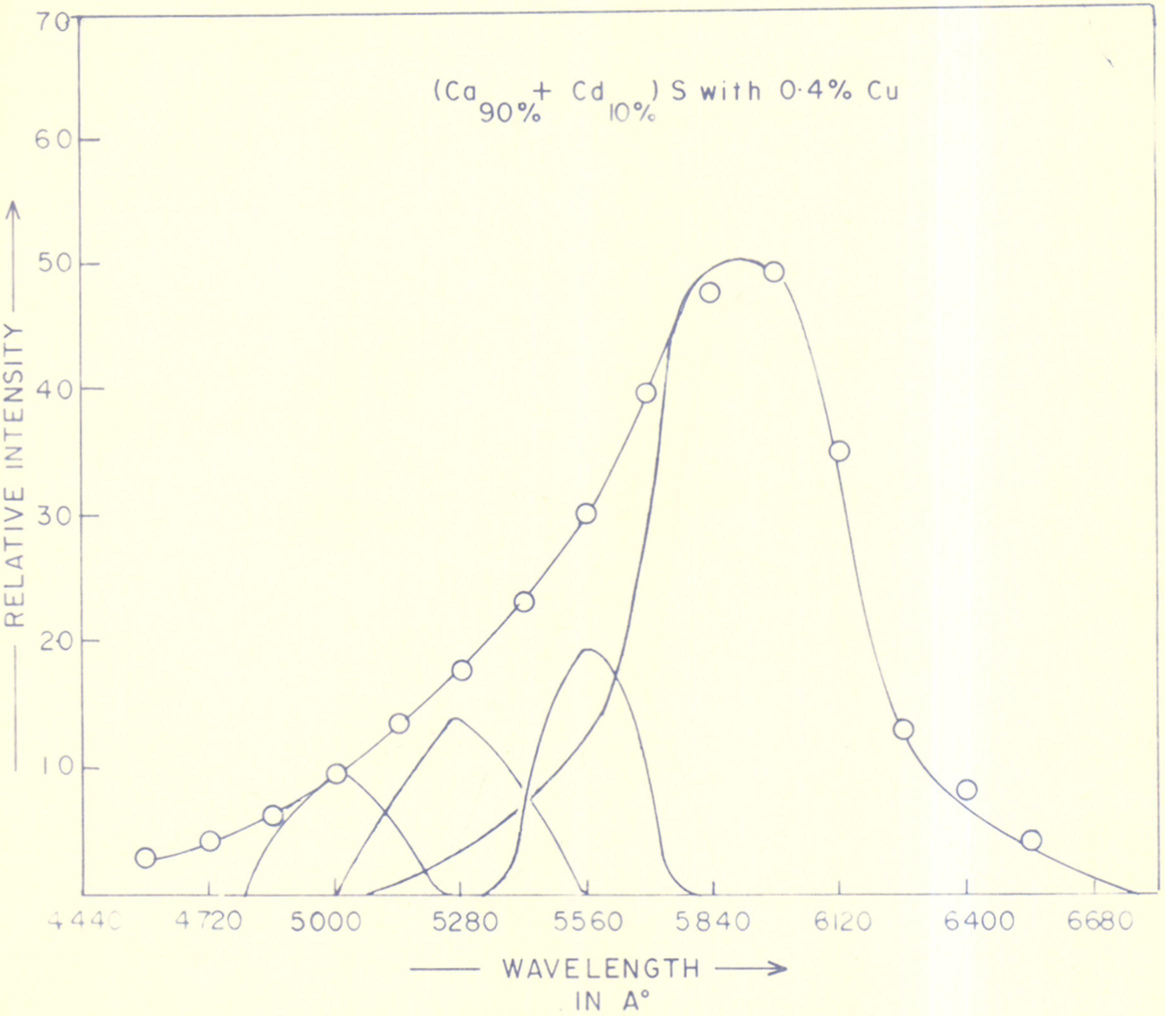

(Ca$_{90\%}$ + Cd$_{10\%}$) S with 0·4% Cu
RELATIVE INTENSITY
70
60
50
40
30
20
10
4440
4720
5000
5280
5560
5840
6120
6400
6680
WAVELENGTH IN A°

FIG. 2·1

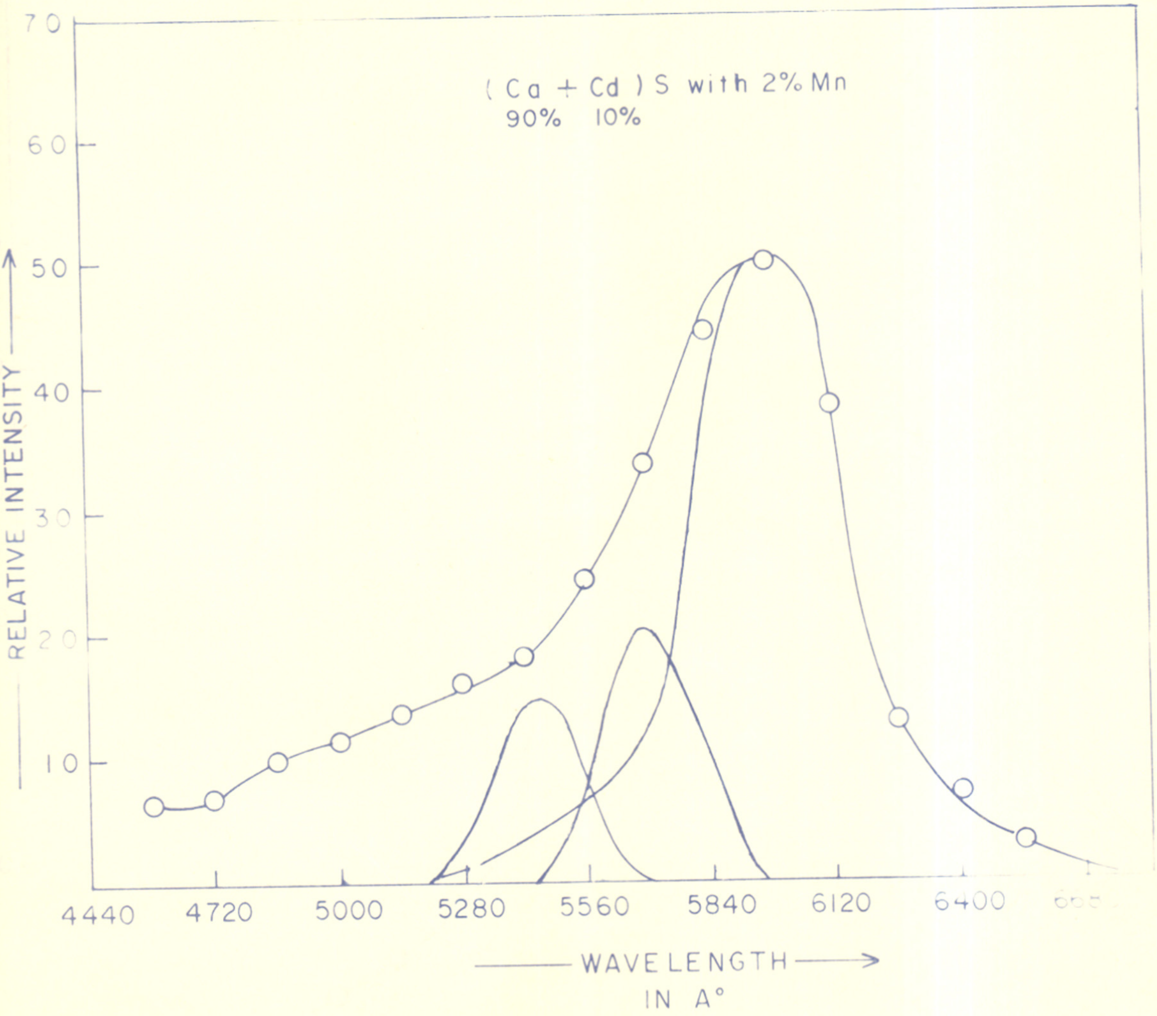

(Ca + Cd) S with 2% Mn
90% 10%
70
60
50
40
30
20
10
RELATIVE INTENSITY
4440
4720
5000
5280
5560
5840
6120
6400
WAVELENGTH
IN A°

FIG. 2·2

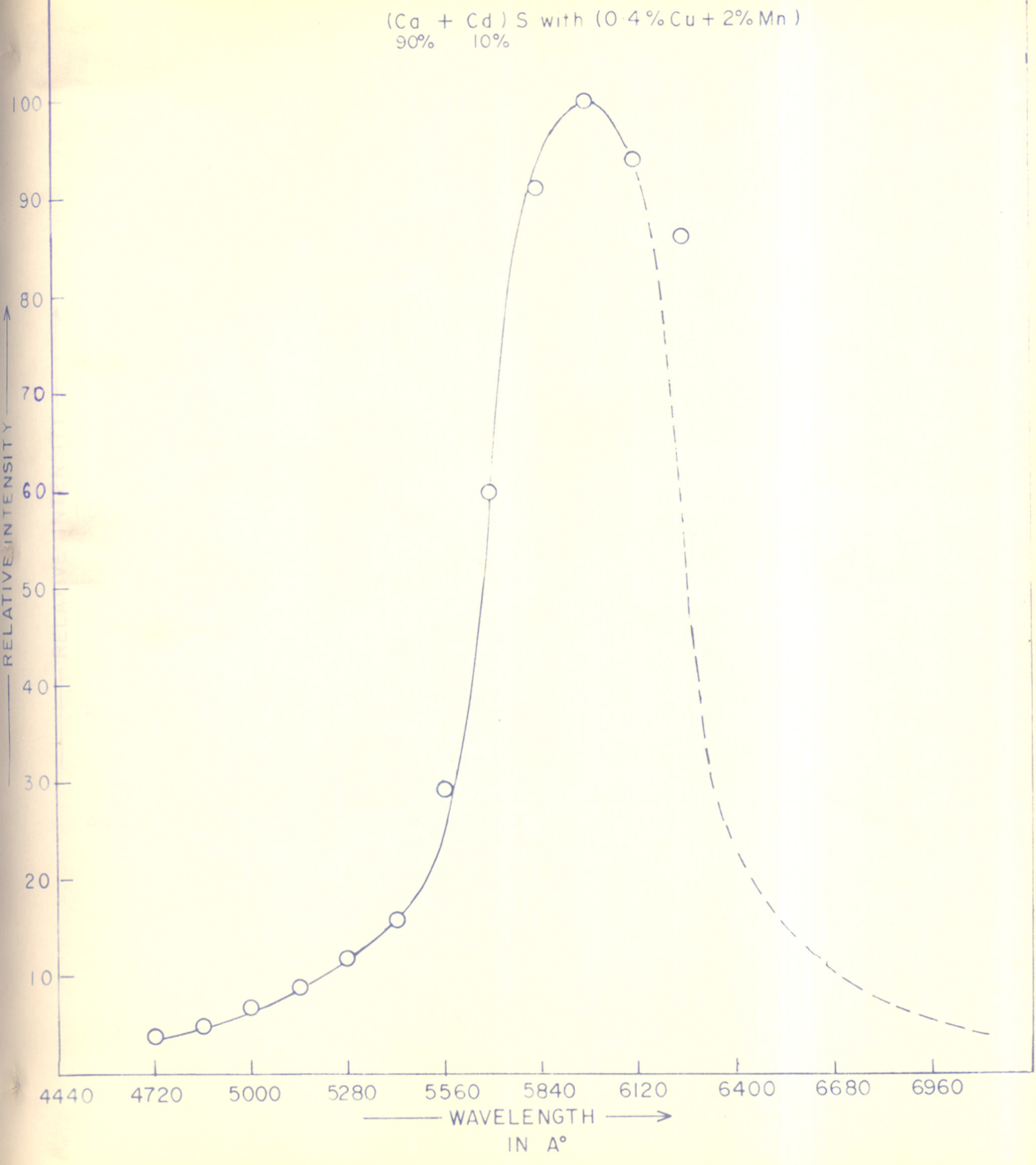

(Ca + Cd) S with (0·4% Cu + 2% Mn)
90% 10%
RELATIVE INTENSITY
100
90
80
70
60
50
40
30
20
10
4440
4720
5000
5280
5560
5840
6120
6400
6680
6960
WAVELENGTH
IN A°

FIG. 2·3

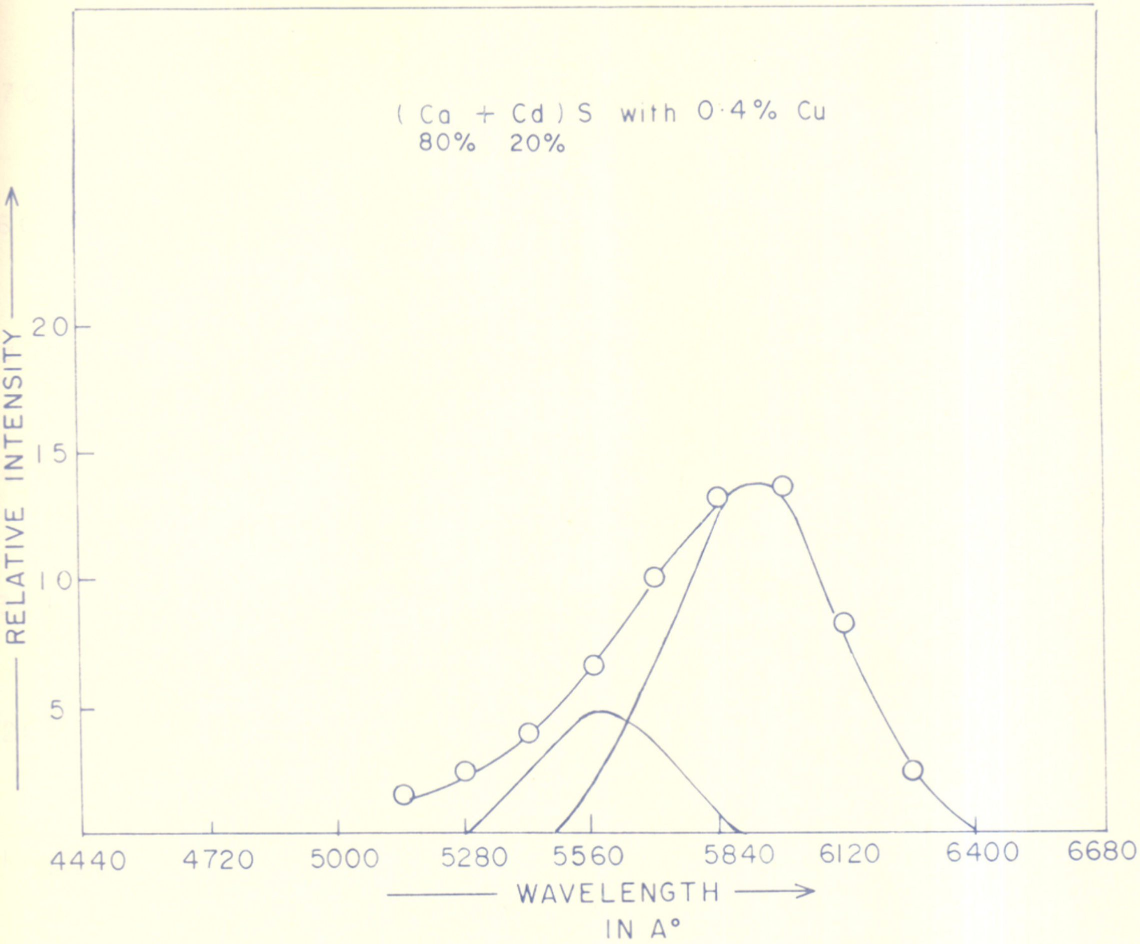

(Ca + Cd) S with 0·4% Cu
80% 20%
RELATIVE INTENSITY
20
15
10
5
4440
4720
5000
5280
5560
5840
6120
6400
6680
WAVELENGTH
IN A°

FIG. 2·4

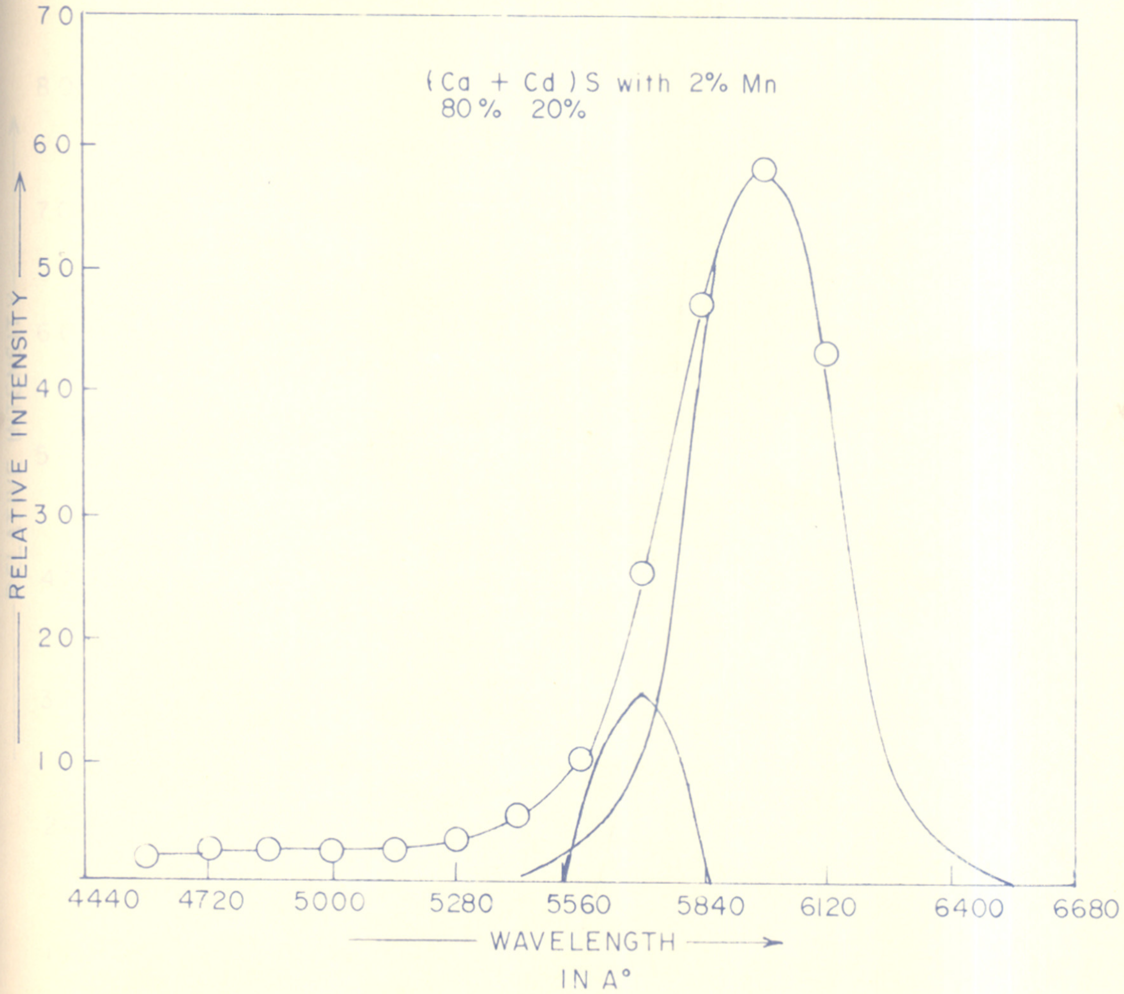

(Ca + Cd) S with 2% Mn
80 % 20%
70
60
50
40
30
20
10
RELATIVE INTENSITY
4440
4720
5000
5280
5560
5840
6120
6400
6680
WAVELENGTH
IN A°

FIG 2·5

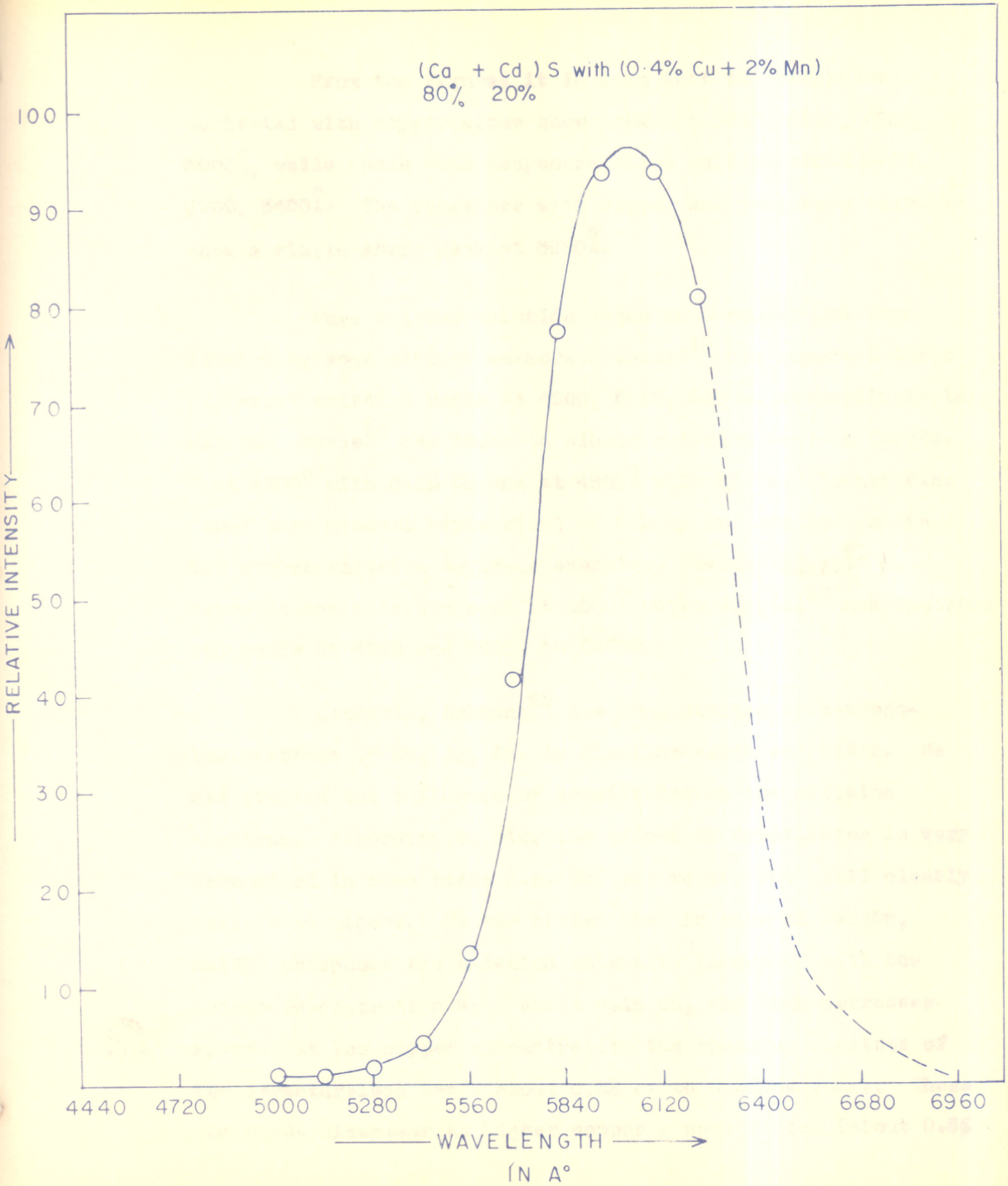

(Ca + Cd) S with (0·4% Cu + 2% Mn)
80% 20%
100
90
80
70
60
50
40
30
20
10
RELATIVE INTENSITY
4440
4720
5000
5280
5560
5840
6120
6400
6680
6960
WAVELENGTH
IN A°

FIG. 2·6

From the figures it is seen that the phosphors activated with copper alone show peaks at 5940, 5560, 5280, 5000Å, while those with manganese alone emit at about 5980, 5700, 5400Å. The phosphors with copper and manganese together show a single sharp peak at 5980Å.

Pure calcium sulphide doped with copper has been studied by some earlier workers. Lenard[19] has reported three different emission bands at 4200, 5120, 6000Å, respectively in CaS:Cu. Sorge[20] has observed single emission band in CaS:Cu, F at 4300Å with 0.1% Cu and at 4800Å with 1% Cu. He has also found that gradual replacement of CaS by SrS and BaS shifts the copper emission to lower energies. Avinor <u>et.al.</u>[21] have reported one emission band at 4600Å while Wachtel[22] has reported two bands at 4350 and 5000Å in CaS:Cu.

Recently, Lehmann[23] has done studies on cathodoluminescence of Cu, Ag, Au, in alkaline earth sulphides. He has studied the influence of coactivator on the emission spectrum. According to him, the effect of coactivator is very pronounced in some cases e.g. SrS:Au; weaker but still clearly visible in others. He has stated that in case of CaS:Cu, Na(3%) phosphors the emission intensity increases with the copper concentration upto about 0.1% Cu, and then decreases again. At low copper concentration the spectrum consists of two structureless bands about 0.28 ev to 0.30 ev apart. These two bands disappear at higher copper concentration (about 0.5%

and more) and instead, a very broad and irregularly shaped band with the peak at about 5170 to 5390Å appears. The spectra observed at low concentration apparently are due to isolated luminescent centers and the broad bands, observed at high concentrations to interaction between adjacent centers. He has observed the emissions at 4200Å for CaS:Cu (0.1%) without coactivator as well as with F, Li, K, Rb, P, As, coactivators; at 4350Å with Na coactivator; at about 4770Å with F, Li, Na, K, Rb, P, As, coactivators.

The reason for the variation between different samples is not clear but it is likely that our samples which are solid solutions of CaS and CdS have lower band gap and hence the longer emission wavelengths. We find that in our samples the energy levels appear to be systematically shifted by 0.5 ev, when compared to Lehmann's results. This shift can be attributed to the lowering of the band gap of CaS by CdS.

The emission levels in CaS phosphors have not been identified, but there is a more systematic study in case of ZnS doped with copper. Bowers and Melamed[24] have reported five principal emissions of the ZnS:Cu, Cl-system. The addition of small impurities of copper together with Cl produces a strong green emission with peaks at 5200 and 5400Å for the hexagonal and cubic forms respectively. At low copper concentrations, the blue and green peaks are both present, the higher concentration of Cu favouring the green emission, while at the same time diminishing the intensity of the blue. The green emission reaches its maximum intensity at 0.009 to 0.01 mole per cent copper and at this concentration the blue emission is virtually absent under ordinary conditions of excitation. With the addition of Cu beyond 0.01 mole per cent the green emission reaches its maximum intensity and a blue emission reappears. This blue emission reaches its maximum intensity at 0.06% Cu and diminishes at higher concentration. At a concentration of 0.3% Cu, Bube[25] has reported a new green emission having a maximum at 5200Å but of a considerable broad band width. The foregoing emissions are all presumed to occur in presence of an excess of chloride. Froelich[26,27] has described a broad red emission produced when copper is added to ZnS and prepared in absence of any additional impurity such as chloride.

Impurity	Emission colour	Wave-length	Proposed centers
Cl	Blue I	4400	Interstetial Zn^{+}, Zn vacancies.
Cu(0.01%) : Cl	Green I	5200	Cu^{+} interstetial or substitutional.
Cu(0.06%) : Cl	Blue II	4400	Cu^{2+} Cl.
Cu(0.3%) : Cl	Green II	5200	Substitutional Cu^{+}.
Cu	Red	6700	? Cu^{++}.

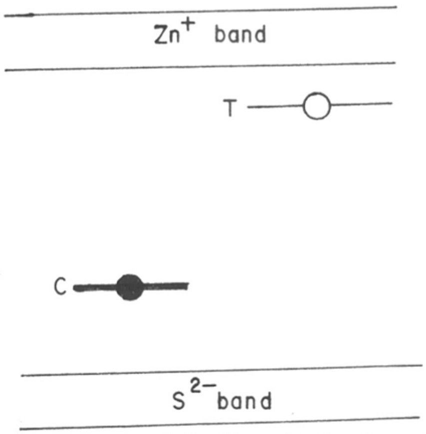
The origin of the blue emission appearing at 0.06% Cu is not well established. It has been suggested that this blue emission is due to a complex of the form $(Cu^{2+}:Cl^{-})$. A lack of knowledge exists as regards the red emission which appears when no chloride is present. Because of the absence of a charge compensating ion such as Cl^-, one might be led to expect Cu^{2+} as the responsible center.

The authors have said, the situation regarding the green and red emissions is somewhat less apparent. Because of the difference in charge between Zn^{2+} and Cu^+, the incorporation of Cu^+ substitutionally in the lattice such as ZnS requires simultaneous substitution of monovalent negative ion such as Cl^-, Br^-, I^- or a tripositive ion such as Al^{3+} or sulphur vacancy. Since one of these impurities must be present with Cu in order to produce green emission they conclude that in this case, Cu is present substitutionally. As the emission is the same, for any one of the above impurities, direct association between them and copper, has been ruled out and the green emission has been proposed to arise from the copper in a substitutional site having a normal or nearly normal Zn and S environment, a conclusion in agreement with Kröger. This being the case, the red emission can arise from Cu in a substitutional site whose environment differs from a normal substitutional position or from interstetial Cu. In the former case, since the charge compensating impurities are absent, sulphur vacancies would be required. For interstetial Cu, however, Zn vacancies are necessary. As they have always observed a blue emission associated with the red emission, similar to the blue emission obtained with ZnS:Cl they have concluded that Zn vacancies are produced and that therefore the red emission due to copper without Cl has resulted from interstetial Cu ions.

Crosnier and Curie[28] have reported that for (65% ZnS + 35% CdS) (1.4×10^{-4} g. Cu) samples, the short wavelength band peaks in the green at 5400Å and the long wavelength band in the red at 6450Å. For this sample, the intensity for the short wavelength band rises suddenly and the result is a non-monotonic variation of emission colour. They have also prepared series of (ZnS + CdS):Cu samples with a smaller concentration of copper and observed that the long wavelength emission band dominates in all phosphors and such series do not show any colour inversion.

In our samples copper has been added as CuO and three possible modes of incorporation of copper appear to be feasible (i) Cu^{2+} goes in solid solution substutionally and an equivalent amount of O^{2-} ions replace S^{2-} ions, (ii) CuO reacts with CaS to form free CaO and incorporating Cu^{2+} in place of Ca^{2+} in the sulphide matrix. The anion lattice in this case would be entirely of S^{2-} ions. (iii) CuO reacts with CaS to produce CuS which being unstable at high temperature decomposes to give Cu_2S so that Cu is incorporated as Cu^{+}. In that case as there is no charge compensating impurity present, there would be either sulphur vacancies or Cu^{+} is incorporated partially at the interstetial sites. Ignoring for the time being, the variation in the anion lattice broadly speaking we have three distinct cases (i) Cu^{2+} substitutional, (ii) Cu^{+} substitutional, (iii) Cu^{+} interstetial. On the basis of above results of ZnS:Cu phosphors and keeping in mind the higher band gap of (Ca+Cd)S phosphor which is expected to lead to an overall increase in the emission frequency (decrease in emission wavelength), we tentatively conclude that the 5940Å emission is due to Cu^{2+} substitutional and the lower wavelength emissions are due to Cu^{+}.

As far as the mechanism of emission is concerned two possible models have been suggested in literature



Klasens[29] has given a model for ZnS phosphor as follows: Between the uppermost occupied or S^{2-} band and the next occupied or Zn^{+} band there are localised levels. The levels C near the full band which are normally occupied by electrons are usually attributed to luminescent centers while the levels T, which are normally empty, are responsible for trapping of the electrons. Excitation of the phosphor with 3650Å radiation then lifts an electron from the occupied level C into the conduction band. These electrons, moving freely through the lattice may be captured by empty T levels or they may recombine with empty C levels under emission of light. The C levels are associated with the presence of activators and have, therefore, often been considered as ground states of these activators. Luminescence then is a direct property of the activator.

Klasens has suggested that C levels may also arise from S^{2-} ions disturbed by adjacent activator ions. This theory of indirect activation has already been applied by Kröger in discussing the properties of many ZnS phosphors. Earlier work of Kröger has indicated that the spectral distribution of Ag, Zn and Cu activated phosphors are independent on the nature of coactivator.

Prener and Williams[30] have suggested a model treating ZnS as a covalent molecule. Here the electronic states of the valence band are those of the least tightly bound electrons in the zinc to sulphur bond. The impurity such as copper as a substitutional zinc site gives rise to a localised level above the valence band, the level is unfilled and cannot give rise to luminescence when excited by 3650Å radiation. The coactivator such as chloride ion creates a filled localised level below the conduction band. In addition, there are a series of excited hydrogen-like levels below the conduction band. In an actual phosphor the activator and coactivator are both needed to produce luminescence. At equilibrium, the electron trapped in the field of the coactivator will be transferred to the low-lying empty level due to the presence of activator.

However, our results cannot be explained on the basis of the model proposed by Prener and Williams simply because there is no coactivator present. The model proposed by Klasens does not necessarily involve coactivator and hence can be used to explain our results. Further, this conclusion is also supported from the results on phosphors containing both Mn and Cu as would be discussed later.

The role of Mn^{2+} as an activator is well-established. Particularly much work has been done on the phosphors in which manganese ion is surrounded by oxygen ions. There appear to be two sets of Mn activated phosphors; one in which the principal emission is in the orange region and in the other, it is in the green region. Some typical well-known orange emitting phosphors are listed below:

Phosphor	Colour of emission	Emission wave-length in A°	Excitation
1: CaS:Mn	Orange	6000	Near UV to 4200Å.
2: ZnS:Mn	Orange	5850	Near UV to 4600Å.
3: (Zn+Cd)S:Mn	Orange	5900	Near UV to 4600Å.
4: $CdSiO_3$:Mn	Pinkish yellow	5950	Below 3200Å.
5: $(ZnBe)SiO_4$:Mn	Yellow white	5950	Below 3000Å.
6: CdB_2O_4:Mn	Pink	6150	Below 3600Å.
7: $Sr_2P_2O_7$: Mn		About 5900	-
8: $3Ca_3(PO_4)_2(F:Cl)$:Sb,Mn	-	Between 5750-5900 depending on ratio F:Cl.	2537Å.

Recently, Brown et.al.[31] have studied some green emitting phosphors. Their results are presented below:

Phosphor	Colour of emission	Emission wavelength
$MgGa_2O_4$:Mn	Green	5080Å.
Zn_2SiO_4:Mn	Green	5180,5220Å.
$ZnAl_2O_4$:Mn	Green	5320Å.
Zn_2GeO_4:Mn	Green	5240Å.
$Li_2ZnGe_3O_8$:Mn	Green	5280Å.

It is now more or less established that the emission in Mn-activated phosphor arises from the electronic transition between Mn levels.

In certain Mn-activated phosphors it has been observed that there is a long temperature independent decay of luminescence from divalent manganese centers and that this luminescence is not associated with photoconductivity. These facts, along with the poor optical absorption in the manganese ions, have led to the general conclusion that the optical transition leading to luminescence is a forbidden one. From considerations of the energy involved in the emission spectrum Kröger[32] has concluded that the energy levels involved in absorption and emission must have the same principal quantum number. He has further concluded that the ground state in case of divalent manganese is ^6S term and the excited states are ^4G, ^4D, ^4P, ^4F terms. Johnson and Williams[33] measured the magnetic moment of Mn^{2+} activated ZnF_2

and found that it is decreased when the phosphor was excited. This was interpreted as being due to a change in multiplicity of the luminescent center and is in agreement with the suggestion of Kröger that the ground state is six-fold degenerate and the excited state four-fold degenerate. Ginther[34] studied a detailed excitation spectrum for divalent manganese in K_4MnCl_6 and Klick and Schulman[35] found very similar spectra in absorption and excitation measurements on $MnCl_2$. The presence of as many as nine absorption bands for divalent manganese is an indication that in solids the manganese ion retains many of the characteristics of its atomic spectrum. Further, it has been suggested that the lowest excited levels of manganese ions have their orbital angular momentum quenched since both theory and experiment on magnetic ion salts indicate this to be the case.

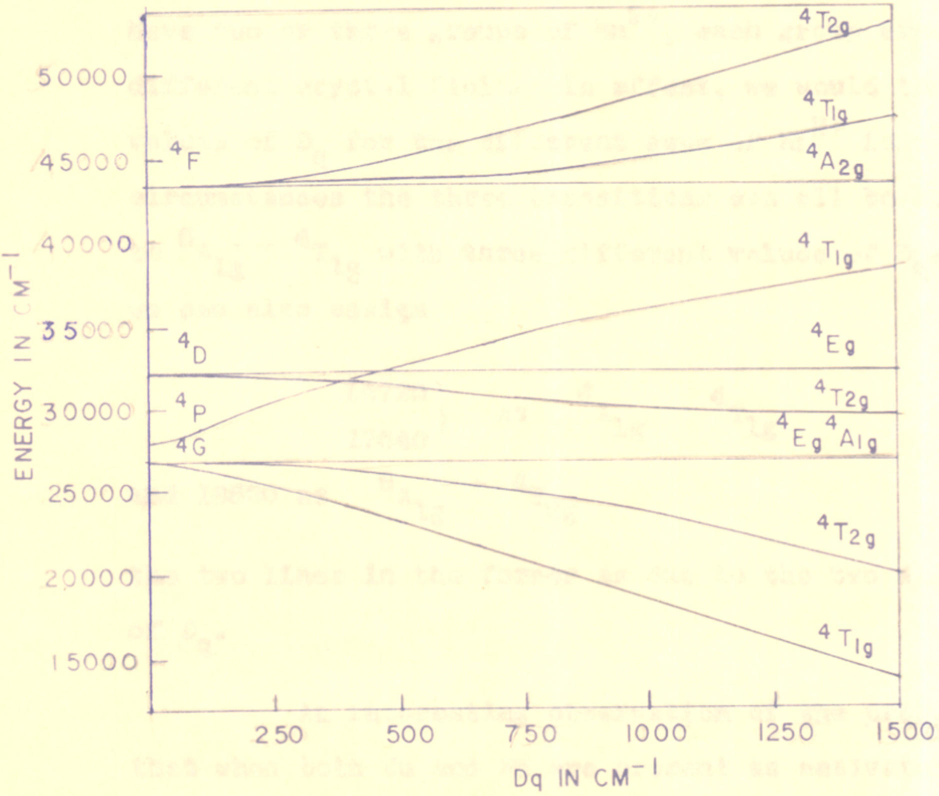
The energy levels are dependent, to some extent, on the surroundings as can be seen from the different emissions due to variation of host. However, the dependence is much less then what is observed for Cu doped phosphors where the levels responsible for emission are crystal levels which are strongly dependent on the matrix. On the other hand, the Mn transitions are essentially between the atomic levels slightly perturbed by the crystal field.

Brown *et.al.* have derived the electronic states of Mn^{2+} from excitation spectra for five green emitting phosphors as referred to earlier. According to him only $MgGa_2O_4$:Mn is found to give a spectrum consistent with octahedral (or tetrahedral) symmetry of Mn^{2+}; the other four phosphors show spectra typical of Mn^{2+} ion in symmetry lower than octahedral. Solutions of the Tanabe and Sugano[36] energy matrices using the $MgGa_2O_4$:Mn levels as input give Racah parameters of $B=624\ cm^{-1}$ and $c=3468\ cm^{-1}$. They have concluded that the complete splitting of at least one of the ^4T levels in all the remaining compounds requires distortion of the expected octahedral (or tetrahedral) symmetry down to C_{2v}, C_{2h}, C_2 or D_{2h} symmetry. Following discussion of our results has been done on similar lines.

As can be seen from Table 2.2 that the emission due to manganese alone from the present phosphor can be resolved in three distinct peaks

	$\lambda(\mathring{A})$	$\nu(cm^{-1})$
A:	5980	16720
B:	5700	17540
C:	5400	18520.

The observed spectrum was compared with the calculated energy values given by Tanabe and Sugano[36], to see if the two could be made to match at a suitable value of D_q and the Racah parameters B and C. However, no good agreement could be found for all the three lines at the same time. The diagram given by Orgel[37] has been reproduced here for reference in Fig. 2.7.



ENERGY LEVEL DIAGRAM FOR THE Mn^{++} ION

Fig. 2·7

The descrepancy may be due to one of the following possibilities: (1) the local site symmetry around the Mn^{2+} is not purely octahedral but is distorted to a lower symmetry group. Brown et.al. have suggested a similar lowering of symmetry to C_{2v}, C_{2h}, C_2 or D_{2h} as said above.

(2) In view of the fact that the host matrix is a solid solution, the surroundings of all the Mn^{2+} ions are not identical and we have two or three groups of Mn^{2+}, each group experiencing a different crystal field. In effect, we would then have different values of D_q for the different sets of Mn^{2+} ions. Under these circumstances the three transitions can all be assigned as due to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ with three different values of D_q. Alternatively, we can also assign

$$\left.\begin{matrix}16720\\17540\end{matrix}\right\} \text{ as } {}^6A_{1g} \rightarrow {}^4T_{1g}$$

and 18520 as ${}^6A_{1g} \rightarrow {}^4T_{2g}$

the two lines in the former as due to the two different values of D_q.

An interesting observation of the present work is that when both Cu and Mn are present as activators, there is only one emission peak at 5980Å. The Cu emissions at 5560, 5280, 5000Å are entirely suppressed as also the 5700 and 5400Å emissions from the Mn level. It appears that the entire energy is funneled to the 5980Å manganese transition.

Earlier, Pringsheim and Vogel[38] have observed that if a phosphor contains a more than one activator, the corresponding emission bands are sometimes superimposed in the luminescence spectrum as in the case of CaS activated with manganese and bismuth or the emission bands of one are suppressed by the emission band of the other, as for instance, the Cu band by the addition of Bi or the Sm bands by the addition of Pr to a CaS phosphor.

Our results can possibly be explained with the help of the concept of resonance transfer. In doubly activated phosphors, one of the activators, sometimes acts as a sensitiser. The sensitiser generally serves to introduce either an absorption band or an excited level at the desired location for the other activator. Some of the excitation energy absorbed by the sensitiser is transferred to the activator and reappears in an emission band characteristic of the latter. In the present case, it can, therefore, be suggested that copper introduces certain levels which lie close to manganese levels and the transfer of energy takes place from copper to manganese levels, resulting in an emission only from manganese activator at about 5980Å.

Furthermore, the suppression of copper emission is accompanied by the enhancement of manganese emission which suggests that the resonance energy transfer from copper to manganese is more efficient than the radiative decay direct from the copper level. The fact that all the original emissions from copper are equally suppressed, suggests that they arise from the same initial state. If the initial states were different then, only one which matches close with the manganese level would decrease. However, the observed facts show that green and red both emissions due to copper are completely suppressed which leads to the conclusion that the emission arises from the same initial level but to two different states. This would support that all the transitions originate from the bottom of the conduction band.

Furthermore, from our results, it appears that cadmium does not act as an activating impurity but merely modifies the host lattice. Similar conclusion has been drawn by Pringsheim and Vogel[39] for ZnS and CdS solid solutions. They have stated that if such mixed crystals are activated with Ag or Cu the luminescence bands and the corresponding excitation bands are steadily displaced towards the red end of the spectrum with increasing cadmium content. Manganese differs as an activator from Cu and Ag. The manganese emission bands remain unaltered when a part of Zn is replaced by Cd in the fundamental lattice in view of the fact that these arise from the transitions between atomic levels unlike the case of copper doped phosphors where the transitions are between crystal levels and hence depend upon the band gap. The different emission wavelengths arise from the fact that the final levels (e.g. due to Cu^{+} and Cu^{2+}) are at different locations near the valence band. The selective absorption bands on the long wavelength end of the absorption spectrum which are characteristic of Mn remain unaltered also with increasing concentration of Cd.

REFERENCES

1. Levshin, V. L.,
Doklady. Akad. Nauk. S.S.S.R., 58 (1947), 779.

2. Dreeben, A. D., Ward, R.,
J. Amer. Chem. Soc., 73 (1951), 4679.

3. Anikina, L. I.,
Doklady. Akad. Nauk. S.S.S.R., 88 (1953), 41.

4. Gobrecht, H., Hahn D.,
Z. Physik., 135 (1953), 523.

5. Wojtczak, J.,
Przmyst Chem., 38 (1959), 690.

6. Domange, L., Flahaut, J., Patrie, M.,
Compt. Rend., 253 (1961), 1454.

7. Patrovsky, V.,
Collection Czechoslov. Chem. Communs., 26 (1961),1799.

8. Wachtel, A.
(To Westinghouse Elec. Corp.), U.S.Pat. 2,988,515,
June 13 (1961).

9. Avinor, M.
(To North American Phillips Inc. Co.), U.S. Pat.,3,053,772,
Sept. 11 (1962).

10. Phillips Electronics and Associated Industries Ltd.,
Brit. 928,615, June 12 (1963).

11. Anderson, W. W.,
J. Chem. Phys., 44 (1966), 3283.

12. Nizovtsev, V. V., Levshin, V. L., Mikhailin, V. V.,
Izv. Akad. Nauk. S.S.S.R. Ser.Fiz. 30 (1966), 1552.

13. Levshin, B. L., Mikhailin V. V., Dianova, I. M.,
Kulman, L. K., Opt. Spektroskop, 22 (1967), 90.

14. Mathur, V. K., Razdan, K. N.,
Ind. J. Pure and Appl. Phys., 6 (1968), 260.

15. Ranade, J. D., Thakar, J.,
Ind. J. Pure and Appl. Phys., 6 (1968), 209.

16. Malhotra, B. R., Bhawalkar, D. R.,
Ind. J. Pure and Appl. Phys., 7 (1969), 573.

17. Amar Singh,
Ind. J. Pure and Appl. Phys., 7 (1969), 367.

18. Burra, M. S.,
A Text Book of Inorg. Chem.; Vol.III, Part I, p.59.
Edited by J. N. Friend, Charles Griffin and Co. Ltd.,
Exeter Street, Strand, W.C. 2, London (1925).

19. Lenard, P., Schmidt, F., Tomaschek, R.,
Handb. d. Exp. Phys. Vol. 23 (1928).

20. Sorge, O.,
'Undersuchungen über die Erdalkalisulphid phosphor',
Thesis, Tech. Univ., Berlin (1959).

21. Avinor, M., Carmi A., Weinberger, Z.,
J. Chem. Phys., 35 (1961), 1978.

22. Wachtel, A.,
J. Electrochem. Soc., 107 (1960), 199.

23. Lehmann, W.,
J. Electrochem. Soc., 117 (1970), 1389.

24. Bowers, R., Melamed, N. T.,
Phys. Rev., 99 (1955), 1781.

25. Bube, R. H.,
Phys. Rev., 80 (1950), 655.

26. Froelich, H.,
J. Opt. Soc. Amer. 42 (1952),982.

27. Froelich, H.,
J. Electrochem. Soc., 100 (1953), 496.

28. Crosnier, A., Curie, G.,
Luminesc. Org. and Inorg. Materls., International
Conf., New York (1961), 418.

29. Klasens, H. A.,
J. Electrochem. Soc., 100 (1953), 72.

30. Prener, J. S., Williams, F. E.,
J. Electrochem. Soc., 103 (1956), 342.

31. Brown, J. J., Palumbo, D.T.,
J. Electrochem. Soc., 117 (1970), 1184.

32. Kröger, F. A.,
'Luminesc. in Solids containing manganese'
(Amsterdam Van.Compen), 1940.

33. Johnson, P. D., Williams, F. E.,
J. Chem. Phys., 17 (1949), 435.

34. Ginther, R. J.,
J. Electrochem. Soc., 98 (1951), 74.

35. Klick, C.C., Schulman, J. H.,
J. Opt. Soc. Amer., 42 (1952), 910.

36. Tanabe, Y., Sugano, S.,
J. Phys. Soc. Japan, 9 (1954),753.

37. Orgel, L. E.,
J. Chem. Phys., 23 (1955), 1004.

38. Pringsheim, P., Vogel, M.,
Luminescence, Page 88, Intersc. Publishers Inc.,
New York (1946).

39. Pringsheim, P., Vogel, M.,
Luminescence, page 84, Intersc. Publishers Inc.,
New York (1946).

---000---

3.1 : GENERAL INTRODUCTION

Although the history of fluorescence started from investigation of fluospar which provided the name of the phenomenon, even today, our understanding of the fluorescence of fluorite minerals appears to be far from complete.

After many systematic investigations, it has only been shown that natural fluorites are activated by a great variety of admixtures. Numerous attempts have since then been made to prepare synthetic luminescent fluorides which may resemble the natural ones. These attempts have thrown some light on the mechanisms involved in the luminescence of fluorides. However, the great complexity of behaviour shown by these materials has still kept the field for investigation wide open. At the same time, recent technical applications of these materials in diversified fields have increased the demand of new and better synthetic fluoride materials. However, the work done so far in this field appears to be restricted to simple fluorides. Although some complex-fluorides have been reported recently, the data regarding their properties are still insufficient.

It is a widely accepted fact today that various impurities are the carriers of luminescence in crystals. Rare earth ions embedded in some simple fluorides have previously been studied. In the present work, the Ca^{2+} ions in CaF_2 have been completely replaced by a monovalent ion Na^+ and trivalent ion Y^{3+} to form a mixed fluoride $NaYF_4$ and the structural and optical properties of this mixed fluoride, when activated with suitable activators, have been studied. Sodium yttrium fluoride is still expected to have fluorite structure, the parent compound being CaF_2. X-ray analysis method has been used to verify the crystal structure. The mixed fluoride has been activated with two rare earths namely europium and terbium. The fluorescence spectrum of these two ions in the phosphor has been studied. The effect of the variation of the concentration of activators on the fluorescence spectrum has also been studied. An attempt has been made to see whether terbium, when added to the phosphor in presence of europium, serves as a sensitiser to the other activator.

3.2 : HISTORICAL INTRODUCTION

Leverenz[1] has studied the decay characteristics of the fluoride phosphors which are used in cathode-ray beam tubes. He has found that these characteristics are varied by substituting ZnF_2 in the phosphor by CdF_2. The phosphors are prepared either by adding CdF_2 to ZnF_2(I) or to zinc Mg fluoride (II) and crystallising after adding 0.001 to 0.1 mole Mn per mole of I and II. Alternatively, the material may be mixed as oxides of Zn and Cd or the oxides of Zn, Cd and Mg and then converted to fluoride by adding HF. Manganese is added as $Mn(NO_3)_2$, the mixture stirred and evaporated to dryness in a water bath. The dried mixture is then crystallized in a furnace at about 800°C, cooled and ground.

Hund[2] has prepared $NaYF_4$ crystals and studied its crystal structure. He has described two methods of preparation: (1) by heating the two solid components NaF and YF_3 at high temperatures, and (2) by precipitation method in which hot NaF solution is added in excess to YCl_3 solution. He has reported that the compound exists in dimorphic forms. Although most of the properties of these two forms are the same, the crystal structure differs markedly. The two components NaF and YF_3 when heated to high temperature and cooled rapidly to room temperature then the solid $NaYF_4$ shows the cubic structure. However, the same solid solution when cooled slowly to room temperature shows a different structure having some new lattice. The first one, having the cubic structure, has been called as β-form while the second having the unknown structure, has been called as α-form. The compound obtained by precipitation method also shows cubic structure. He has given the x-ray diffraction diagrams of the α- and β-forms and has also reported the lattice parameters of β-form.

Smith[3] has studied the cathodoluminescence of several mixed fluoride phosphors. He has found that manganese activated $NaZnF_3$, $KZnF_3$, K_2ZnF_4, $NaMgF_3$, $KMgF_3$, K_2MgF_4, CaF_2, $KCaF_3$, $KCdF_3$ and the solid solutions between CaF_2 and AlF_3 exhibit efficient cathodoluminescence. With MgF_2 and ZnF_2, AlF_3 has been found to be only diluent; with CaF_2, however, three compounds, $2CaF_2.AlF_3$, $CaF_2.AlF_3$ and $CaF_2.2AlF_3$, were discovered, the first having a peak of emission at 5380Å and the latter two at 5250Å. Emission of Mg and Zn compounds containing K or Na has been found to be almost identical with that of the original MgF_2 and ZnF_2. Although CaF_2:Mn has an efficient green and CdF_2:Mn a weak green emission, their K perovskites show strong yellow-orange emission. From the above results he has put forth a hypothesis relating a coordination number of six for the divalent cation in fluorides to orange emission and a coordination number of eight to green emission.

Feofilov[4] has determined the direction of orientation of europium ions in the calcium fluoride crystal lattice, by means of the luminescence polarization method. The CaF_2 crystals contain 10^{-2} per cent EuF_3. The lines for luminescence of Eu^{3+} are partially polarized, the degree of polarization depending upon the position of electrical vector of the excited light in relation to the axis of symmetry of the crystal. The data lead to the conclusion that the Eu^{3+} replaces the Ca^{2+} isomorphically.

Lind[5] has reported blue emitting fluoride phosphors with long exponential decay of phosphorescence suitable for use in cathod ray tubes. The phosphor can be represented by a general formula $aCaF_2.bMF_2.cBeF_2.dMn$, where $(a + b) = 1, 0.75 \leqslant a \leqslant 1; 0.01 \leqslant c \leqslant 9; 0.0006 \leqslant d \leqslant 0.12$ and M is Mg, Zn, Sr, Cd, Ba, Hg or Ra. In a typical preparation 10.0 gm. $CaCO_3$, 2.5 gm. BeO, and 0.033 gm. Mn (as MnF_2) are allowed to react with excess 50% aqueous HF. The solution is rapidly dried at 125° to 150°. After drying, additional HF is added to transform any hydrolysis products. The resultant dried residue is fired in a covered C crucible for 1 hour at 750° and then cooled, ground and refired for thirty minutes at 700°C. The final material corresponds to $CaF_2:BeF_2:0.006\ Mn$ and possesses the tetragonal zircon structure. He has reported the peak emission under cathod ray excitation at 4750Å.

Feofilov[6] has investigated the absorption and luminescence of bivalent ions of rare-earth elements in natural and synthetic fluorite crystals. He has found that the absorption spectrum of synthetic $CaF_2:Sm^{2+}$(I) consists of a series of wide bands, which become narrow on cooling the crystal to -160°. At this temperature the maxima of the bands are located at 690.2, 632, 535, 507, 495, 445, 425, 307, 288, 256 and 240 mμ. The presence of intense absorption near 632 and 425 mμ causes the green colour of fluorite containing traces of Sm^{++}. Excitation with a source corresponding to the wavelengths of the absorption region causes luminescence, in the near infrared. At room temperature the luminescence spectrum appears as a non-structural wide band with the maximum at 735 mμ. With a decrease in the temperature, the intensity of the luminescence increases and the spectrum is characterised by a weak resonance line near 690.2 mμ; an intense narrow band at 708.2 mμ and several weak lines near 715, 720.2, 724, 727.8 mμ. An identical spectrum is obtained with the natural green fluorite. The green colour has been shown to be definitely due to the presence of Sm^{2+} and not to the mixture of blue and violet coloured colloidal particles as previously explained by K. Prizibram. The absorption spectrum of $CaF_2:Eu^{2+}$(II) at room temperature, had a weakly developed structure and is located in the near ultra violet with a maximum at 338 mμ and another maximum at 222 mμ in the short wave region. On cooling to -160° the absorption spectrum is modified by the appearance of several narrow bands: 413, 389, 378, 366 mμ and others. Dark blue luminescence of (II) is evident at room temperature. The luminescence spectrum has one maximum near 426 mμ at 20° and several narrow intense bands at 4.2°K; 4128.8, 4130.0, 4131.1, 4131.4, 4133.7, 4134.4Å and a group of wider bands at 4160, 4162, 4168, 4169, 4181, 4190, 4197Å. The remaining lines more than 175 cm^{-1} away from the resonance line 4130Å are probably caused by the overlapping of crystal lattice vibrations with purely electronic transitions (24213 cm^{-1}). Natural CaF_2(II) gives identical results. The spectrum of synthetic $CaF_2:Yb^{2+}$ (III)at -160° is characterised by absorption at 365, 308, 273, 262, 247 mμ. The crystals are non-luminescent at room temperature; however, at -160° yellow-green luminescence is very intense, the spectrum of which has no definite structure.

Datta and Ghosh[7] have studied the thermoluminescence of NaCl, NaF, NaI, KI, LiCl and also those of thallium activated NaCl, NaBr, KI. The measurements are confined in the spectral range 330 to 650 mμ. All alkali halides have visible thermoluminescence emission. They have found that there may be different spectral bands in the same glow peak. On incorporation of impurities into the host crystal lattice there is generally an increase in the luminescence intensity; trapping and luminescence centers are perturbed or destroyed and new centers are created. They have assumed the observed emission for the pure sample due to release of trapped electrons (holes) and its recombination with holes(electrons). In some cases, there may be tunneling of trapped electrons to trapped holes. Excitons probably play an intermediate role in the luminescence emission process. NaF shows the maximum of emission at 403 mμ at 185°K and at 415 mμ at 290°K.

Adler and Kveta[8] have studied the effect of thermal treatment on $CaF_2:Eu^{3+}$. They have found that reduction of Eu^{3+} to Eu^{2+} takes place when CaF_2 containing 10^{-3} to 0.1 mole trapped Eu^{3+} is heated to 950° for one hour in vacuuo. Similar heat treatment in H atmosphere also results in this reduction. A quantitative reduction of Eu^{3+} to Eu^{2+} by W X-rays in dosages of 220 rad./sec. for 1/2 hour has been observed, if all traces of oxygen ions are excluded from the lattice to prevent the formation of 'G' centers. Attempts to prepare CaF_2 containing trapped Eu^{2+} by crystallising from hot solutions were unsuccessful, this suggests that Eu^{2+} in naturally occurring specimen of CaF_2 is due to radiation and not chemical processes. They have also found that various thermal treatments of the $CaF_2:Eu$ phosphor result in different ultraviolet and x-ray line emission spectra owing to the different coordination of the light emitting center effected by this treatment.

Thoma _et al._[9] have reported phase equilibrium diagram of the condensed system $LiF-YF_3$. They have reported some data from thermal analysis of heating and cooling curves and by identifying the phases present in small samples which have been quenched after equilibration at higher temperatures. According to them a single compound $LiF-YF_3$ is formed. It melts incongruently to YF_3 and liquid at 819° and is tetragonal $a_o = 5.26 \pm 0.03$Å and $C_o = 10.94 \pm 0.03$Å; space group $^{I}4_{1/a}$. Dergunov has reported the formation of complex compounds between alkali fluoride and YF_3; $KF-YF_3$, $RbF-YF_3$, $CsF-YF_3$. In these three cases the single compound formed is of the cryolite type having the general formula 3MF.YF_3. In the system NaF-YF_3 he found evidence only of solid solution with a pronounced minimum in the liquidus. Further, he has stated that although the single intermediate compound in each of the systems LiF-YF_3 and NaF-YF_3 is of 1:1 ratio, the compounds are not isostructural. The occurrence of scheelite structure for the compound LiF-YF_3 is unique in the fluoride systems.

Kariss and Feofilov[10] have investigated absorption and emission of holmium and erbium bivalent ions in crystals of the fluorite type. They have studied CaF_2 and SrF_2 activated with Ho^{2+} and Er^{2+} in concentrations from 0.05 to 1.0 mole per cent of the corresponding fluorides. These phosphors have been grown in a reducing atmosphere and then subjected to γ-rays to change the activator into the bivalent state. Luminescence has been excited with the aid of Hg lamp. Cyrstal containing Ho^{2+} (electronic configuration $4f^{11}$, ground state $^4I_{15/2}$) are pale-green in colour. At 300°K, the absorption spectrum consists of a series of broad bands in the ultraviolet, visible and near infrared region. The maxima in CaF_2-Ho^{2+} lie at 897, 680, 512 mu, in SrF_2:Ho^{2+} near 855, 655, 495 mμ. On cooling to 77°K, crystals show intense infrared luminescence (narrow lines at 1.821 and 1.832 and 1.825 and 1.834 for CaF_2:Ho and SrF_2:Ho respectively). The luminescence period is 3×10^{-2} sec. The spectra, according to the authors, could be interpreted as the allowed transition of Ho^{2+} ion from $4f^{11}$ to $4f^{10}5d$ configuration.

Rabbiner[11] has stated that fluorescent line spectra of trivalent rare earth doped fluorite crystal fall into two distinct types, 'I' and 'II', according to the method of crystal preparation. According to him, the theoretical bases for spectra 'I' and 'II' are not completely understood. A preliminary analysis of spectra I and II of Sm^{3+} in CaF_2 has indicated that in this case the fluorescent lines can be accounted for largely as transitions between the crystal field split levels of the upper fluorescent and lower ground multiplet Russel-Saunders states of the free Sm^{3+} ion. Based on a frequency shift between corresponding subgroups of 'spectra I and II,' these two spectra have been identified as originating from two different upper fluorescent states of Sm^{3+}. However, there are spectra of several other trivalent rare earth doped fluorites for which the approximate spectral location of the subgroups are the same for type I and II; and the analysis of the spectra I and II of one such crystal such as Dy^{3+} in CaF_2 could be helpful in this regard. This has been carried out by Rabbiner. He has found that fluorescent 'spectra I' of Dy^{3+} in CaF_2 consists of approximately 45 lines which originate from the crystal field split levels of the ${}^4F_{11/2}$ and ${}^6H_{15/2}$; ${}^6H_{13/2}$ and ${}^6H_{11/2}$; free ion states in accord with energy level schemes which indicate the crystal field symmetry for 'spectra I' about the Dy ion to be of the type of O_h group.

When trivalent rare earth ions are introduced into the CaF_2 lattice they occupy Ca^{2+} sites, the valency mismatch being compensated in a variety of ways. When the charge compensation is remote from the rare-earth ion the O_h cubic symmetry of the crystalline field is preserved but if it is sufficiently close, the symmetry of the electric field can be reduced from cubic to tetragonal, trigonal or even rhombic. Weber and Bierig[12] have determined the energy levels arising from the crystal field splitting of the free ion ground states of trivalent rare-earth ion in CaF_2 from the survey of the optical and electron paramagnetic resonance spectra. The predicted ground states are in agreement with existing paramagnetic resonance data. They have estimated the magnitude of the cubic crystal field parameters and their variation throughout the rare-earth series. Axial crystal fields of tetragonal and trigonal symmetries, due to nearest-neighbour charge compensation, are found to cause large perturbations on the cubic field energy levels. The paramagnetic resonance spectra of all rare earth ions have been reviewed and new resonances for Ce^{3+}, Sm^{3+}, Er^{3+} and Yb^{3+} have been reported.

Taylor[13] has studied fluorescence of CaF_2:Tb,Dy. He has found that the fluorescence of Tb^{3+} ions in CaF_2 is enhanced in the presence of Dy^{3+} ions, by 5 times at room temperature when the crystals are excited by high pressure mercury arc. He has given the energy diagram of these ions. He has further suggested that energy transfer takes place between the metastable levels of Dy^{3+} as $^4F_{9/2}$ and Tb^{3+} as $^5D_4$. Owing to the greater strength of the Dy^{3+} absorption lines between 3000 and 4000Å, the transfer process leads to an enhancement of the Tb^{3+} emission from $^5D_4$ level. Emission from $^5D_3$ of Tb^{3+} remains unchanged while emission from $^4F_{9/2}$ level of Dy^{3+} in the doubly doped crystal decreased to one half that of the singly doped crystal. A non-radiative energy transfer is thought to occur between $^4F_{9/2}$ level of Dy^{3+} and the $^5D_4$ level of Tb^{3+}. A possible mechanism for the energy transfer has been suggested as an ion-ion interaction through their dipole or quadrupole fields. No stimulated emission has been detected from the $^5D_3$ level of Tb^{3+} in the doubly doped crystal with pumping energies upto 1300 j and cooling to 4.2°K.

Danielson[14] has reported some properties of single crystals of CaF_2:Ce,Mn. He has referred to the earlier work done by Ginther and Leach who have studied the non-photoconducting phosphor CaF_2:Ce,Mn. These authors have shown that radiation in some UV absorption bands of Ce^{3+} produces a green Mn^{2+} emission ($^4G \rightarrow {}^6S$) in addition to the usual allowed blue Ce^{3+} emission ($^2D \rightarrow {}^2F$). This resonant transfer of energy, from the Ce^{3+} sensitizer S to the Mn^{2+} activator A, is thought to occur by a spin-exchange mechanism and can occur with high efficiency. Danielson has irradiated CaF_2:Ce,Mn with UV light sufficiently intense to significantly alter the A ground state populations. Under these conditions there is no longer a simple proportionality between the UV radiation and the S and

A fluorescence. The relative quantum efficiency of sensitisation decreases at the higher irradiation intensities apparently because an appreciable number of A ions are in the metastable excited state where transfer of energy from S is no longer possible. This effect leads to a saturation of the sensitisation process which is accompanied by a perceptible increase in the S quantum efficiency. The A saturation emission has been determined and from these measurements he has estimated the number of lattice sites surrounding S which can be sensitized. The reason for the rather large number of such sites obtained by this method has been briefly discussed.

Krotova *et al.*[15] have investigated the structure of CaF_2 crystal with Sc, Y and La additions, by observing the optical and physico-chemical properties of these crystals as a function of impurity concentration and the method of reduction. The nature of optical centers in these crystals, as well as the processes occurring during irradiation and additive reduction have been investigated in a similar manner. CaF_2-ScF_3, CaF_2-LaF_3, have the same structure as CaF_2-YF_3, namely a structure with interstetial F^- ions. A radial heterogeneity in distribution of Sc and La in CaF_2 has been observed. By the concentration series method, absorption spectra of γ-irradiated and additively coloured CaF_2-Sc, CaF_2-Y and CaF_2-La crystals have been investigated. Absorption spectra do not depend on the method of reduction and they are determined entirely by specific impurity. The oscillator force is determined for the 17600 cm^{-1}

band for the ${}^2D_{3/2} \rightarrow {}^2D_{5/2}$ Y^{2+} transition in CaF_2 and the portion of Y going over to the bivalent state during γ-irradiation. Optical properties of twice activated CaF_2-Y,La crystals are non-radiative and depend on the method of reduction of the impurity.

Kirton and McLaughlan[16] have given an account of a combined optical and paramagnetic resonance investigation of trivalent Yb ions in ten different sites in calcium fluoride. They have attempted a correlation between site geometry and optical absorption for six of these ten sites. A single optical absorption line is observed for all but one of these sites so that it is impossible to deduce the magnitude of the Stark splitting. However, they have found that there is some evidence to indicate that they are large (of the order of hundreds of cm^{-1}), rather than small as suggested by Low. They have also reported a new rhombic paramagnetic resonance which they have thought to arise from pairs of Na^+ and Yb^{3+} ions on adjacent Ca^{2+} sites.

Shore and Wanklyn[17] studied the systems PbF_2-AlF_3, CaF_2-AlF_3. They have presented a phase diagram on the basis of DTA and X-ray powder patterns. According to them the compound PbF_2-AlF_3, melts incongruently at 649°C. Solid solubility of AlF_3 in PbF_2 occurs with upto 15 mole per cent AlF_3. In case of the system CaF_2-AlF_3, their results agree with those of Holm who has established the existence of $CaAlF_5$ which melts incongruently and has high β and low α temperature forms.

3.3 : EXPERIMENTAL TECHNIQUE

The double fluoride, sodium-yttrium fluoride was prepared by the precipitation method. First yttrium-oxide was dissolved in a small amount of concentrated HCl. The solution was then neutralised with NH_4OH till the gelatinous hydroxide just appeared. A few drops of HCl were again added so that the solution again became clear. To this yttrium chloride solution, excess of hot solution of sodium fluoride was added so that a white precipitate of sodium yttrium fluoride was obtained:

$$YCl_3 + 4NaF \rightarrow NaYF_4 + 3NaCl.$$

This precipitate was digested on a hot water bath for few hours. The precipitate was filtered and washed several times with distilled water so that the soluble NaCl and NaF salts were removed. It was further kept for air-drying for 24 hours so that it was obtained in the form of homogeneous white powder.

To this basic matrix $NaYF_4$, europium and terbium were added as the activators separately as well as together. The activators were introduced in the form of their fluorides. For this purpose, europium and terbium trifluorides were prepared. The spec pure oxides of these rare earths were dissolved in AR grade HCl so that they were converted to chlorides. This solution was evaporated to dryness on a hot water bath in a platinum dish. To this dried mass excess of HF solution was added and the solution was again evaporated to dryness. This procedure was repeated a number of times which resulted in complete conversion to the rare-earth fluorides.

Appropriate amounts of $NaYF_4$, EuF_3, TbF_3, were mixed together and homogeneous mixtures were prepared in the same way as described for halophosphate and sulphide phosphors earlier. The concentration of europium was varied from 1 to 12 per cent by weight of matrix, with an interval of one per cent. The optimum concentration of europium was determined. Six concentrations of terbium 0.2, 0.5, 1, 3, 5, 10 per cent by weight of matrix were attempted. Another sample with the two activators in their optimum concentrations was also prepared. These samples were heated in purified nitrogen gas atmosphere at about 1000°C for about 5 to 6 hours, in a Okay furnace. The samples were slowly cooled in the furnace itself. These phosphors after cooling to room temperature were removed from the furnace, ground and tested for fluorescence and x-ray diffraction studies.

X-ray diffraction studies

X-ray diffraction technique was used to see whether the mixed fluoride shows only one phase. X-ray spectrogram giving directly the intensity of the diffracted beam were taken at Regional Rezearch Laboratory, Hyderabad. The x-ray machine utilized the copper target. The 'd' values were obtained from this diffraction data. The unit cell is found to be cubic. The diffraction lines were indexed and the 'a' value was calculated.

Measurement of spectral energy distribution and intensity of emission

The microphotometer tracings of the fluorescence spectra of the fluoride phosphors were recorded at Bhabha Atomic Research Center, Trombay, India. The tracings were taken in the wavelength range 5800-6600Å because the region between 4300 to 5800Å did not include any fluorescence lines. The exciting radiation from the Xenon arc lamp was also recorded after passing it through the filters for reference. These tracings showing the relative intensity as a function of emission wavelength have been reproduced elsewhere.

3.4: RESULTS AND DISCUSSION

X-ray diffraction studies

Calcium fluoride shows the well-known fluorite structure in which each calcium ion is surrounded by eight fluoride ions and there is an octahedral symmetry of the crystal field around the Ca^{2+} ions. Calcium ions in calcium fluoride can be substituted partially or completely by other metal ions. In the present work calcium ions have been completely substituted by two different ions, a trivalent yttrium ion Y^{3+} and a monovalent sodium ion Na^{+}, so that the charge compensation has been taken care of. The trivalent yttrium ion has the same ionic radius as that of divalent calcium ion viz. 1.06Å while, the ionic radius of monovalent sodium ion is 0.98Å. Taking into consideration the ionic radii of the substituted cations we expect that the cubic symmetry can still be retained with a slight variation in the lattice parameter.

Hund[2] has done studies on the structure of $NaYF_4$. He has found that $NaYF_4$ shows two forms which depend upon the method of preparation and temperature. He has reported that the β-form which is formed by heating NaF and YF_3 at 1100°C, shows cubic structure, the a_0 value being 5.448Å.

However, we have prepared $NaYF_4$ by precipitation method and have also observed that the compound shows the cubic structure with a slight change in the lattice parameter. The a_o value obtained here is 5.662Å which is higher than that reported by Hund. The difference can, probably, be attributed to the method of preparation of the compound. The x-ray data showing the observed and calculated 'd' values with their intensities has been recorded in Table 3.1.

Table No. 3.1

X-ray diffraction data and 'd' values for $NaYF_4$
$a_o = 5.662$

Intensity	hkil	$d_{obs.}$	$d_{cal.}$
w	-	3.48	-
w	$11\bar{2}1$	3.28	3.27
vs	$20\bar{2}0$	2.83	2.83
s	$22\bar{4}0$	2.00	2.00
m	$22\bar{4}2$	1.63	1.63
m	$40\bar{4}0$	1.41	1.42
m	-	1.41	-
ms	$42\bar{6}0$	1.27	1.27

Emission spectrum studies

During last few decades rare-earths and in particular europium and terbium have been extensively used as the activators in luminescent materials. Some simple fluorides activated by these rare-earths have already been studied[18,19]. In the present work, we have activated the mixed fluoride $NaYF_4$ by europium and terbium. The concentration of europium has been varied from 1 to 12 per cent as described earlier. We have observed that the compound does not show appreciable fluorescence upto 6 per cent europium. After 6 per cent, the fluorescence intensity goes on increasing with the activator percentage. At 10 per cent, it shows the maximum intensity which falls down again with any further increase in activator percentage. Six compounds with different percentages of terbium have been prepared as said earlier. However, it has been found that, terbium shows only very weak green fluorescence. An attempt has also been made here to see whether terbium serves as sensitiser to europium activator. For this purpose, the optimum concentration of europium viz. 10 per cent, has been kept fixed and three concentrations of terbium viz. 0.2, 1.0, 5.0 per cent have been tried. It has been found that these compounds show very weak fluorescence (much weaker than those containing only Eu activator). Hence, it can be said that terbium serves neither as an efficient activator nor as a sensitiser for europium in $NaYF_4$. In fact, it quenches the fluorescence of europium. This is contrary to the general observation that terbium serves as a sensitiser to europium activator.

The experimental results are presented in a series of figures 3.1 to 3.3 which show a plot of relative intensity as a function of emission wavelength. The peak wavelengths, expressed in wave numbers and peak heights in arbitrary units have been recorded in Table 3.2.

Table No. 3.2.

Peak wavelength (in wave numbers cm^{-1})	Peak height (in arbitrary units)				
	6% Eu	7% Eu	8%Eu	9%Eu	10%Eu
17080	-	5	2	2	4
16910	4.5	7.5	8.5	7	13
16800	-	4	4	4	7
16470	10.5	15	30	19	26
16340	4	17	22	17	22
16190	1	12	11	11	15
16050	-	10	15	8	19
15990	7.5	11	17	11	21
15550	4	5.5	10	7	8
15350	2.5	5	-	4	10
15130	2	2	2	1.5	1
15010	1	1	-	1	1

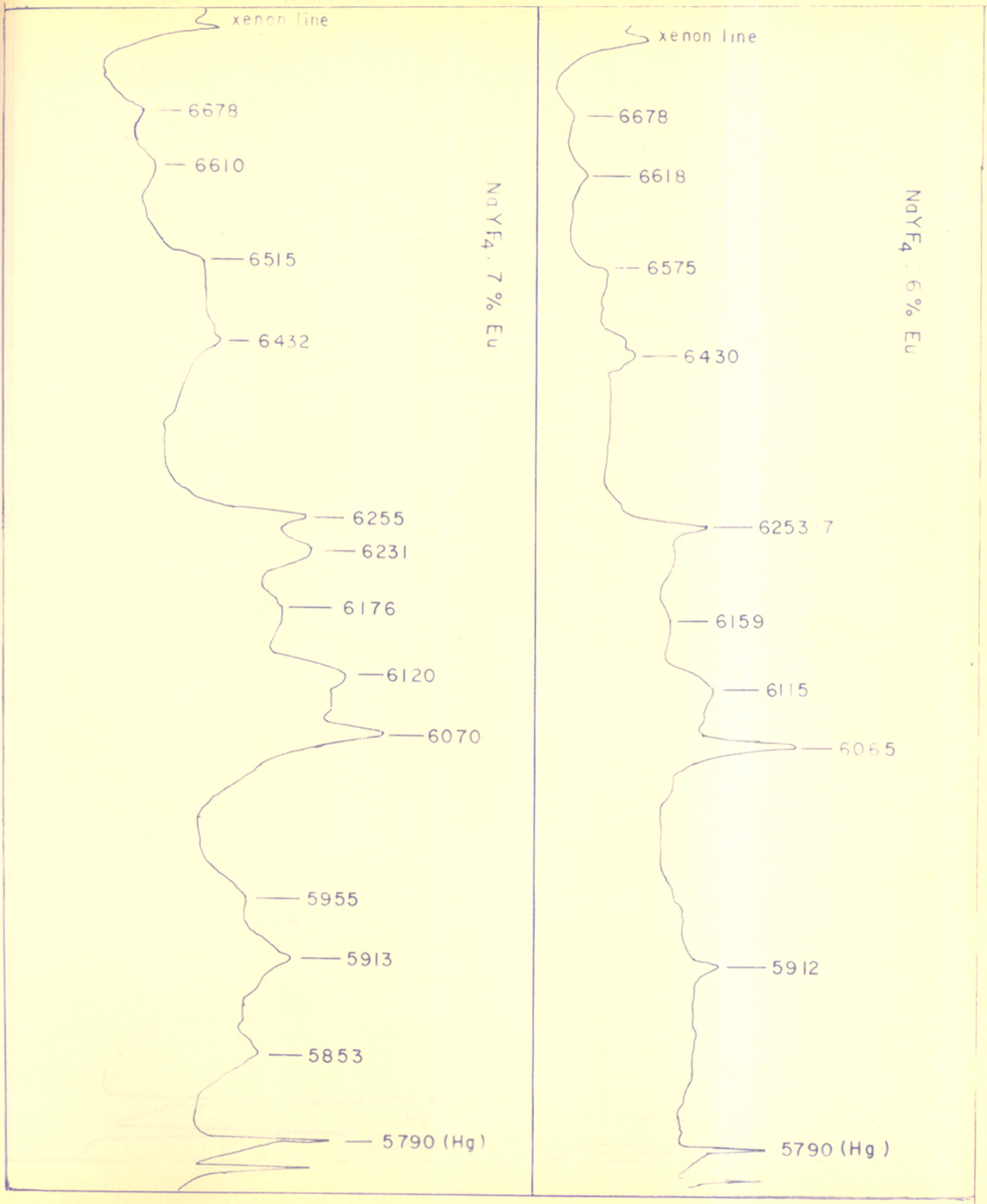

xenon line
6678
6610
6515
6432
NaYF4. 7% Eu
6255
6231
6176
6120
6070
5955
5913
5853
5790 (Hg)
xenon line
6678
6618
6575
6430
NaYF4 : 6% Eu
6253·7
6159
6115
6065
5912
5790 (Hg)

FIG 3.1

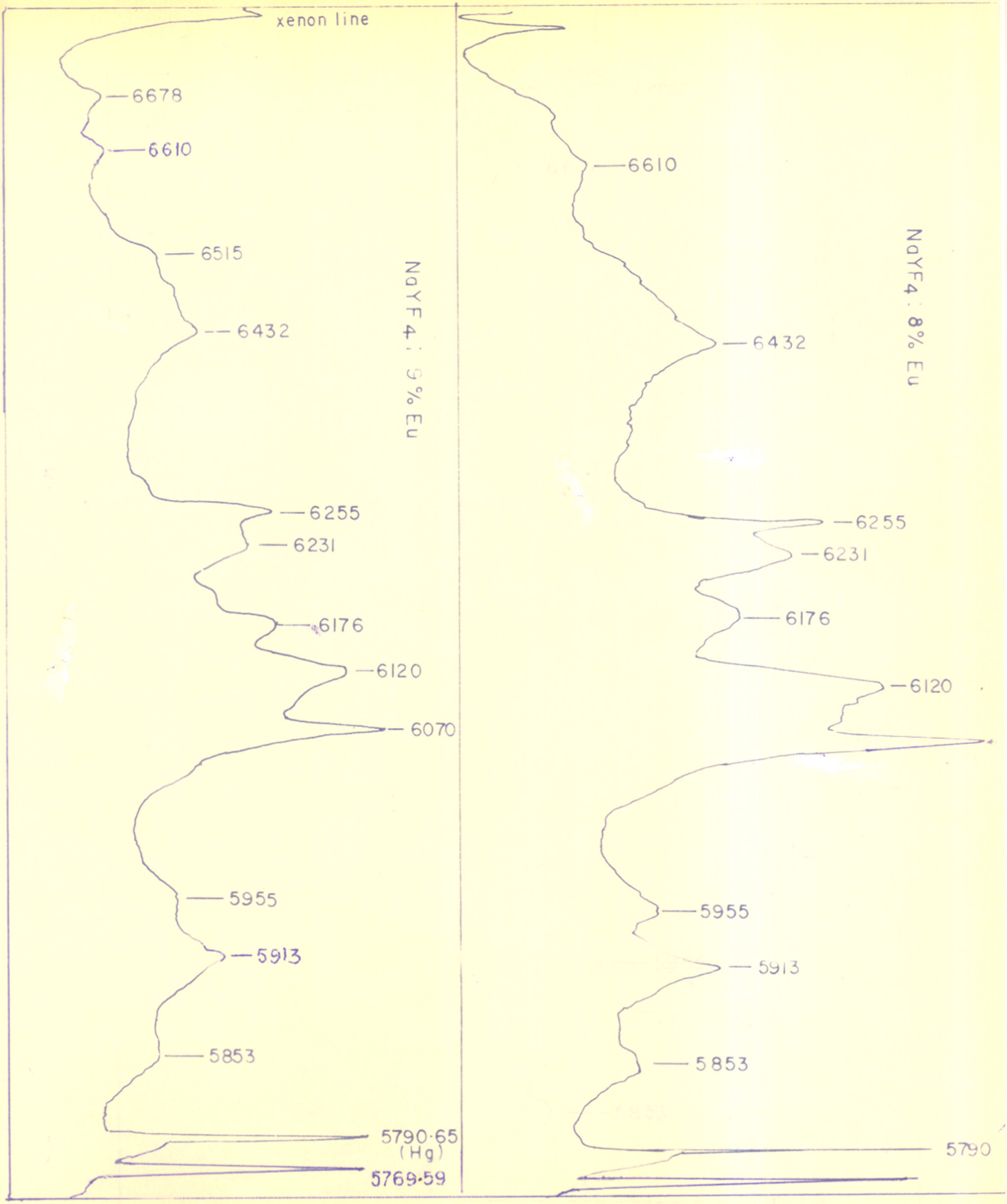

xenon line
6678
6610
6515
6432
6255
6231
6176
6120
6070
5955
5913
5853
5790·65
(Hg)
5769·59
NaYF4 : 9% Eu
6610
6432
6255
6231
6176
6120
5955
5913
5853
5790
NaYF4 : 8% Eu

FIG. 3.2

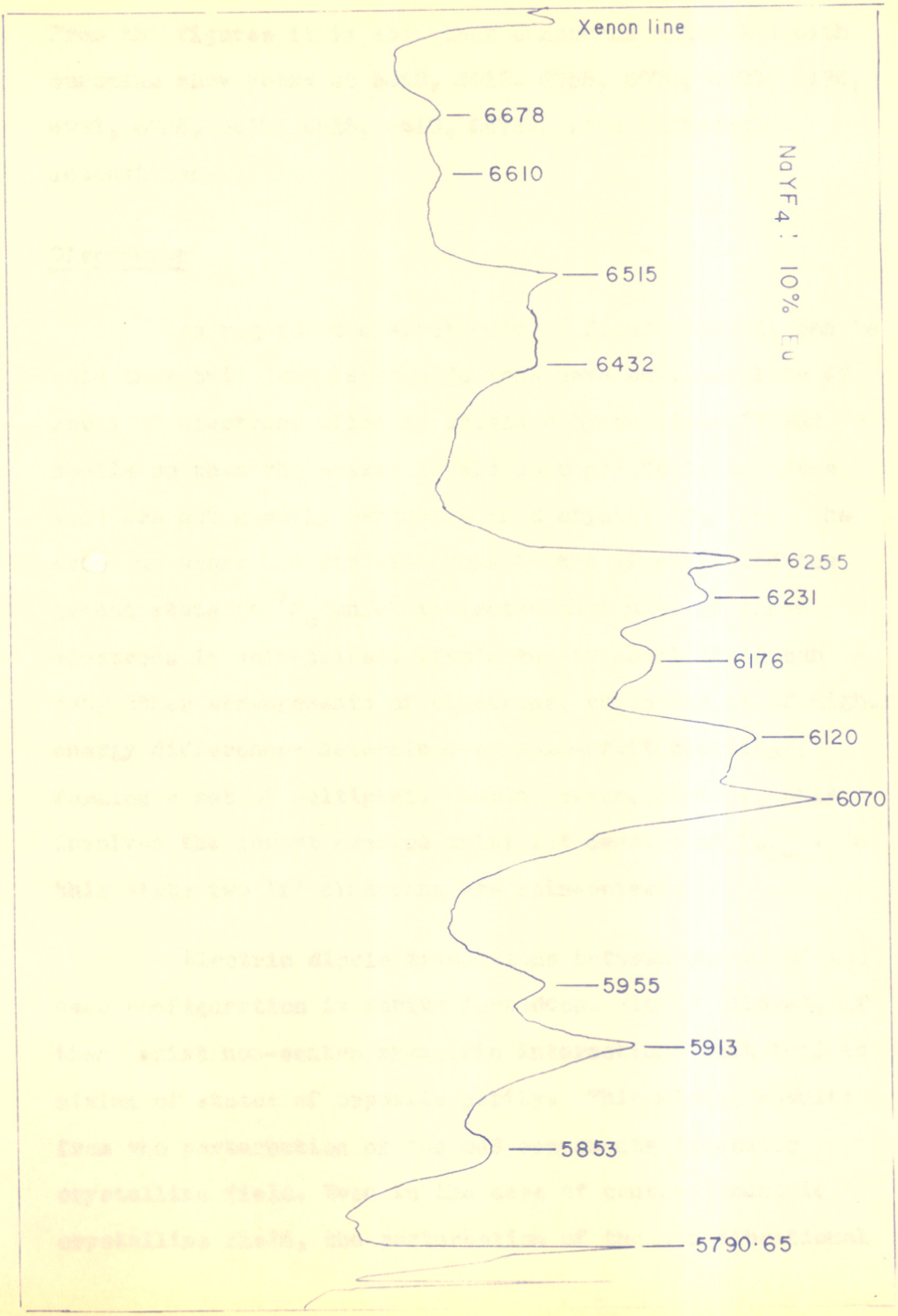

Xenon line
6678
6610
6515
6432
6255
6231
6176
6120
6070
5955
5913
5853
5790·65
NaYF$_4$: 10% Eu

FIG. 3 3

From the figures it is seen that compounds activated with europium show peaks at 5853, 5913, 5955, 6070, 6120, 6176, 6231, 6255, 6432, 6515, 6610, 6678Å, with different intensities.

Discussion

As regards the electronic configuration, it can be said that trivalent lanthanide ions have an incomplete 4f shell of electrons which is shielded by complete 5S and 5p shells so that the energy levels appropriate to the free ions are not greatly perturbed in a crystal lattice. The europium atoms has six electrons in the 4f shell and the ground state is $^7F_0$ which indicates that none of these electrons is spin-paired. Within the 4f shell there can be many other arrangements of electrons, these may be of higher energy differences determined by spin-orbit couplings, forming a set of multiplet. Luminescence, however, only involves the lowest excited multiplet denoted as $^5D_{0-4}$. In this state two 'f' electrons are spin-paired.

Electric dipole transitions between states of the same configuration is parity forbidden. It is allowed, if there exist non-centro symmetric interactions that lead to mixing of states of opposite parity. This mixing results from the perturbation of the odd components in static crystalline field. Even in the case of centro-symmetric crystalline field, the perturbation of the odd vibrational modes of the lattice surroundings rare-earth ions can cause this mixing. The transitions thus induced by vibration is usually called forced electric dipole transition. In addition to such lines, sometimes extra lines are observed in the spectra which are called as due to 'vibronic-electronic transitions' to distinguish them from 'pure electronic transitions'. These are due to electron-phonon interactions. Vibronic transition arises from an emission or absorption of a photon accompanied by a phonon.

As regards the luminescence of rare earth ions, it is known that all salts of rare earths do not show photoluminescence; for instance, the fluoride and dehydrated chloride of europium are not fluorescent and the fluorescence yield of the oxide is very small. This seems to be due to the very narrow spacing of the ions in the lattices of these compounds which favour internal conversion. If $EuCl_3$ is hydrated it becomes strongly fluorescent. The fluorescence of the rare earth sulphate with eight molecules of water is especially easy to observe.

Although the absorption and emission spectra are determined, in the main, by the nature of the rare earth ions, they are influenced in several respects by the symmetry of the crystal lattice and by the nature of the anion. The lines are all forbidden but not all to the same degree. The Eu^{3+} line $0' \rightarrow 0''$ ($\Delta J = 0$, $J = 0$) is missing in cubic or hexagonal crystals; ($EuBr_3 + 9H_2O$, europium ethyl sulphate + $9H_2O$) but it appears in triclinic crystals (europium acetate + $8H_2O$).

When Eu^{3+} ions are imbedded in crystals of CaF_2 or SrF_2 the intensity distribution in the fluorescence spectra is anomalous, in that, the generally strong line group near 5900Å, corresponding to the transition ($J' = 0 \rightarrow J'' = 1$) is very weak, while the forbidden yellow line ($J' = 0 \rightarrow J'' = 0$) is extremely strong and is shifted from 5790 to 5725Å when $BaCl_2$ is the base material, the relative intensities of these line groups are normal in the fluorescence spectrum at room temperature but show the same anomaly as in CaF_2 and SrF_2 at the temperature of liquid air.

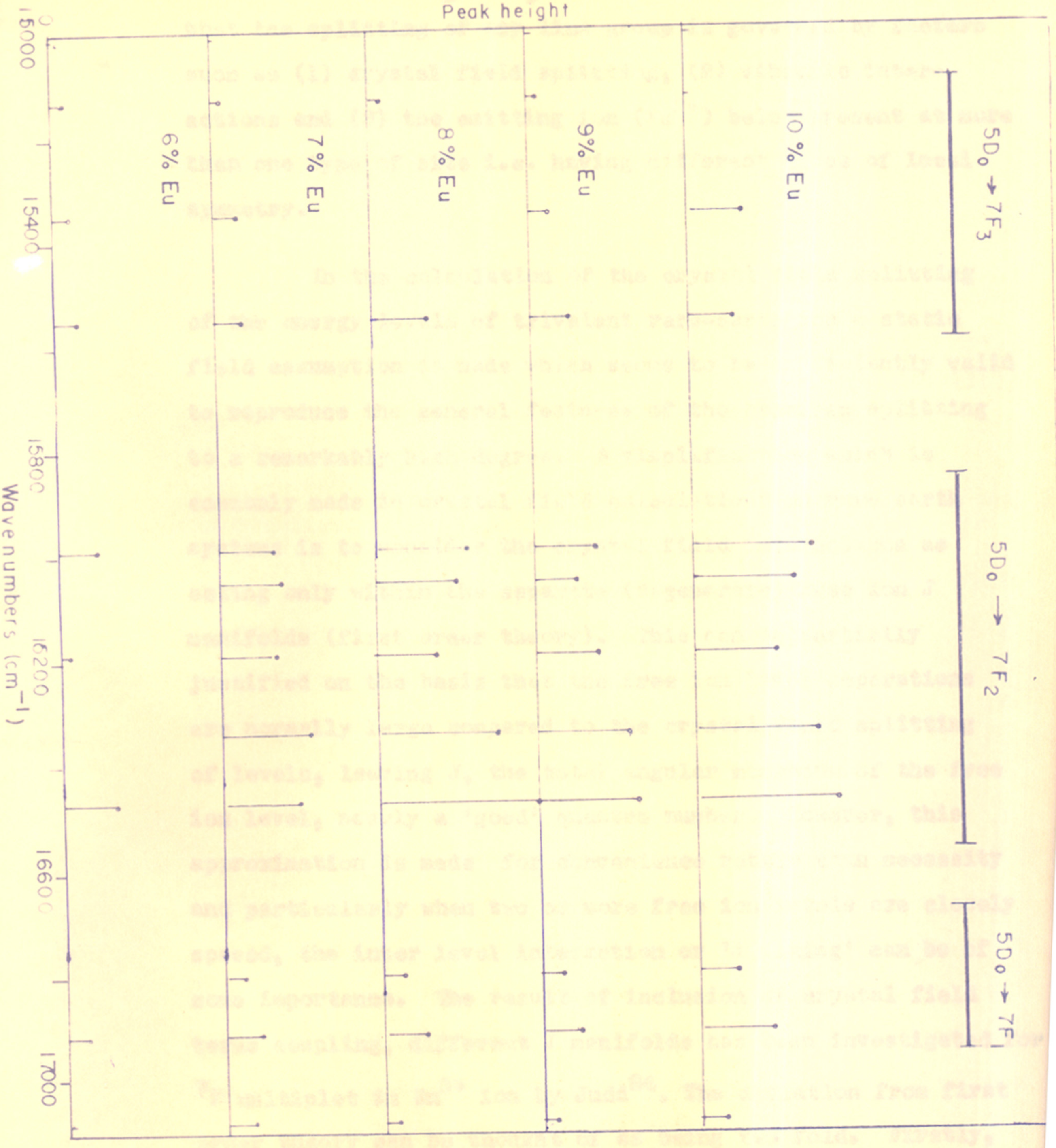
In the fluorescence spectrum of europium sulphate and similarly in the spectra of other rare earth salts, the lines corresponding to the transitions between two electronic levels are split into a number of components. This is due to the Stark effect caused by the electric field of the surrounding ions. According to the theory which is developed by Bethe[20], the number of expected components can be derived from the symmetry of the electric field. The number of sub-levels into which each electronic level is resolved increases from 1 for $J = 0$ or $J = 1/2$ with increasing J values and reaches 13 for $J = 6$, in electric fields of lowest symmetry. If the values of J' are known the symmetry of the field can be derived from the observed number of components. The calculation is unequivocal, however, only if one of the two combining terms is not split up by the action of the field (as for J = 0 or 1/2 or generally for S-terms). This condition is fulfilled for the europium septet originating at J = 0 as is shown by the fact that the line at 5791 Å (0'→0") is simple. If only the stronger lines are taken into account the spectrum of europium oxalate is in satisfactory agreement with a field of cubic symmetry. In the spectrum of europium sulphate, the splitting of the line J" = 1 into a complex group shows that the field symmetry cannot be cubic, while the group J" = 3 with five components of equal strength and the group J" = 4 with six components prove the electric field to be of hexagonal symmetry.

The analysis of the groups in the fluorescence spectra of other rare earth salts is less complete. From the number of components in the group J" = 1 of the terbium sulphate fluorescence spectrum, it can be concluded only that the electric field has neither cubic nor hexagonal symmetry. The same is true for the fluorescence spectrum of samarium sulphate, in which every group consists of two subgroups in this case the excited electronic state is also split into two sub-levels by the molecular Stark effect and therefore all lines are split into doublets.

Furthermore, the frequencies of individual lines are influenced to a certain extent by the structure of the crystal. Thus the line 0'→0" of europium sulphate coincides almost exactly with the mercury line 5791Å but is shifted in the direction of greater wavelength in the spectrum of oxalate and lies at 5780Å in the fluoride, it is even shifted to 5723Å in a europium activated SrF$_2$. Effects of this type have been investigated more thoroughly in the spectra of rare earth imbedded in crystals of another compound such as CaS or MgO etc.

Figure No.3.4 shows the plot of energy (expressed in wave numbers) against intensity of our samples. In the fluorescence spectra of Eu^{3+} the transitions originate from the excited ^5D levels. Blasse *et al.*[21] have studied the europium activated perovskites. It is seen from their results that the transitions originating from $^5D_0$ are very strong. Sinha[22] has also reported, while studying the fluorescence spectrum of europium chelates, that the transitions from $^5D_0$ are much stronger than those from $^5D_1$ or $^5D_2$ etc. Chang and Gruber[23] have also got similar results for Y_2O_3:Eu^{3+} systems. This is attributed to the obvious fact that from $^5D_{1-2}$ to $^5D_0$ a rapid radiationless decay takes place, reducing the population in the upper D levels considerably. We have also observed that the transitions mainly originate from $^5D_0$ level.

The lines in Figure 3.4 can be divided into three line groups and can be ascribed the transitions $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$. The first transition $^5D_0 \rightarrow {}^7F_1$ gives rise to three lines while $^5D_0 \rightarrow {}^7F_2$ gives rise to five lines


Peak height
0
15000
15400
15800
16200
16600
17000
Wavenumbers (cm^{-1})
6% Eu
7% Eu
8% Eu
9% Eu
10% Eu
5D$_0$ → 7F$_3$
5D$_0$ → 7F$_2$
5D$_0$ → 7F$_1$

and the last one $^5D_0 \rightarrow {}^7F_3$ to three lines. It is well known that the splitting of any line group is governed by factors such as (1) crystal field splitting, (2) vibronic interactions and (3) the emitting ion (Eu^{3+}) being present at more than one type of site i.e. having different types of local symmetry.

In the calculation of the crystal field splitting of the energy levels of trivalent rare-earth ion a static field assumption is made which seems to be sufficiently valid to reproduce the general features of the observed splitting to a remarkably high degree. A simplification which is commonly made in crystal field calculations on rare earth systems is to consider the crystal field interactions as acting only within the separate (degenerate) free ion J manifolds (first order theory). This can be partially justified on the basis that the free ion level separations are normally large compared to the crystal field splitting of levels, leaving J, the total angular momentum of the free ion level, nearly a 'good' quantum number. However, this approximation is made for convenience rather than necessity and particularly when two or more free ion levels are closely spaced, the inter level interaction or 'J mixing' can be of some importance. The result of inclusion of crystal field terms coupling, different J manifolds has been investigated for ^7F multiplet in Eu^{3+} ion by Judd[24]. The deviation from first order theory can be thought of as being two fold. Firstly, there may be modifications in the separations of the Stark components within a level and secondly a general elevation or depression of the level as a whole, which causes an apparent shift in the center of gravity of the free-ion levels. Hence, in general it can be said, there are two factors which should be taken into consideration while deciding the crystal field effect (1) strength of the crystal field which governs the separation of the Stark component, (2) site symmetry which governs the number of lines. However, here the crystal field is assumed to be weak. At the same time, the observed lines cannot be accounted for, by the O_h symmetry. So it seems that the O_h symmetry in the usual fluorite structure is changed to some other symmetry in the $NaYF_4$:Eu system. This aspect is discussed later.

In addition to the electronic lines originating from the crystal field perturbations, lines with some structure, so called vibronic structure, due to electron-phonon interactions, are sometimes involved in the optical spectra of rare earth ions. Vibronic transition arises from simultaneous emission or absorption of a photon and phonon. So in the luminescence process there may be two competing processes: (1) radiative decay due to photons only, (2) decay due to some photons and some phonons. In the first case, the intensity of emission of the fluorescence process, will be fairly strong while in the second case, it will be greatly reduced. However, our results show that the observed fluorescence lines are quite intense and sharp with definite frequencies, which can be ascribed to definite electronic transitions. This rules out the possibility of the vibronic interactions.

The observed number of lines in a fluorescent spectrum gives some idea about the site symmetry of the ions. In this respect, Blasse and Bril[25] have studied the fluorescence spectrum of Eu^{3+} in several hosts. They have tabulated their results giving number of lines observed for different symmetries. This table has been reproduced below:

Number of lines expected for certain symmetries

Site symmetry	Transitions		
	$^5D_o \rightarrow {}^7F_o$	$^5D_o \rightarrow {}^7F_1$	$^5D_o \rightarrow {}^7F_2$
O_h	0	1	0
D_{3d}	0	2	0
D_{3h}	0	2	1
D_3	0	2	2
C_{2v}	1	3	4
C_2	1	3	5

From the table it is seen that the O_h symmetry gives rise to only one line due to $^5D_o \rightarrow {}^7F_1$ transition while no line is expected due to $^5D_o \rightarrow {}^7F_2$ transition. However, we have observed three lines due to $^5D_o \rightarrow {}^7F_1$ transition and five lines due to $^5D_o \rightarrow {}^7F_2$ transition. This clearly indicates that the O_h

symmetry in the usual fluorite structure is destroyed in $NaYF_4$:Eu system and it is reduced to some lower symmetry. From the table it is seen that the C_2 symmetry gives rise to three and five lines respectively for ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ transitions which is in accordance with our observation.

Hund has compared the CaF_2 and $NaYF_4$ crystal structures and has proposed that each Ca^{2+} ion is replaced by 1/2 (Na + Y) ions so that the O_h symmetry is still retained in $NaYF_4$ host. In our system europium ions replace the yttrium ions. As the ionic radii of europium and yttrium are different, this will cause a slight distortion of the surrounding of the europium ion or in other words, the point group symmetry will change. Thus, somehow, all the symmetry elements except C_2 are destroyed. So from the observed facts we propose here that the O_h symmetry in $NaYF_4$ is lowered to C_2 by the substitution of europium ions. Chang[26] has reported the absorption and emission spectra of $Y_2O_3:Eu^{3+}$. While interpreting the results he has also suggested that the normal symmetry of the crystal is mostly reduced to C_2 by the substitution of Eu^{3+} ions.

---000---

REFERENCES

1. Leverenz, H. W.,
   (To Radio Corp. America), U.S. Pat., 2,470,627,
   May 17 (1949).

2. Hund, F.,
   Z. Anorg. Chem.,261 (1950), 106.

3. Smith, A. L.,
   J. Electrochem. Soc., 101 (1954), 189.

4. Feofilov, P. P.,
   Doklady. Akad. Nauk, S.S.S.R., 99 (1954), 731.

5. Lind, E. L.,
   (To Radio Corp. America), U.S.Pat., 2,757,144,
   July 31 (1956).

6. Feofilov, P. P.,
   Optika i Spektroskopiya, 1 (1956), 992.

7. Datta, B.C. and Ghosh, A. K.,
   Ind. J. Phys., 32 (1958), 578.

8. Adler H. and Kveta, I.,
   Osterr. Akad. Wiss. Math. naturw. Kl. Sitzber. Abt.II,
   167 (1958), 213.

9. Thoma, R. E., Weaver, C. F., Friedman, H. A., Insley, H.,
   Harris, L. A., Yakel, H. A.,
   J. Phys. Chem., 65 (1961), 1096.

10. Kariss, Ya. E. and Feofilov, P. P.,
    Optika i Spektroskopiya, 15 (1963), 572.

11. Rabbiner, N.,
    Phys. Rev., 132 (1963), 224.

12. Weber, M. J. and Bierig, R. W.,
    Phys. Rev., 134 (1964), A 1492.

13. Taylor M. J.,
    Proc. Phys. Soc., 87 (1966), 281.

14. Danielson, B. L.,
    Phys. Rev., 142 (1966), 228.

15. Krotova, L. V., Mikaelyan, R. G., Osiko V. V.(USSR),
    Izv. Akad. Nauk. S.S.S.R., Neorg. Mater. 3 (1967),1123.

16. Kirton, J. and McLaughlan, S. D.,
Phys. Rev., 155 (1967), 279.

17. Shore, R. G. and Wanklyn, B. M.,
J. Amer. Ceram. Soc., 52 (1969), 79.

18. Arkhangelskaya, V. A.,
Optika i Spektroskopiya, 18 (1965), 92.

19. Brown, M. R., Whiting, J.S.S., Shand, W. A.,
J. Chem. Phys. 43 (1965), 1.

20. Bethe, H.,
Ann. Phys. 5 (1929), 133.

21. Blasse, G., Bril, A., Nieuwpoort, W. C.,
J. Phys. Chem. Solids, 27 (1966), 1587.

22. Sinha, A. P. B.,
"Inorganic Chemistry, Vol. II, edited by Rao C.N.R.
and Ferraro, J. R., Academic Press, p. 255 (1971).

23. Chang, N.C. and Gruber, J. B.,
J. Chem. Phys., 41 (1964), 3227.

24. Judd, B. R.,
Proc. Roy. Soc. London, A 228 (1955), 120.

25. Blasse, G. and Bril, A.,
Phillips Res. Repts., 22 (1967), 46.

26. Chang, N. C.,
J. Appl. Phys., 34 (1963), 3500.

SUMMARY

SUMMARY

Part I - Halophosphate phosphors

The most widely used phosphor in fluorescent lamps, to day, is the halophosphate. Halophosphates have the general formula $M_{10}(PO_4)_6X_2$, where M is alkaline earth metal and X is halogen and they crystallize in the apatite structure. The apatite structure tolerates extensive substitution for metal ion, phosphorus and halogen, permitting the preparation of a considerable number of chemical combinations.

In the present work, thorium and tungsten have been substituted for strontium, in strontium halophosphate and the effect of this substitution on the crystal structure and optical properties of the phosphors has been studied. Further, the effect of sensitizer and activator on the fluorescent emission of these phosphors has also been studied.

The basic halophosphate matrix has been prepared by heating appropriate mixtures of the constituents at 1100°C according to the following equation

$$9(Sr,M)CO_3 + 6(NH_4)_2HPO_4 + SrF_2 \rightarrow$$
$$3(Sr,M)_3(PO_4)_2.SrF_2 + 12NH_3 + 9CO_2 + 9H_2O$$

where M = Th or W. In the second stage, antimony and manganese have been introduced in the basic matrix as sensitizer and activator respectively.

In strontium-thorium fluorophosphate $(Sr_{1-x}Th_{x/2}\square_{x/2})_{10}(PO_4)_6F_2$ system, nine compositions in the range $0 < x < 0.18$ and in strontium-tungsten fluorophosphate $(Sr_{1-x}W_{x/3}\square_{2x/3})_{10}(PO_4)_6F_2$ system, seven compositions in the range $0 < x < 0.11$ have been studied where $\square$ represents the metal vacancy. The concentration of antimony has been kept constant at 3 per cent whereas the concentration of manganese has been varied from 0.5 to 4 per cent.

The x-ray powder diffraction technique has been employed to see the completion of the reaction and to determine the extent of substitution in the mixed halophosphate matrix. The 'd' values and lattice parameters have been reported. The visually estimated intensities of different diffraction lines have been compared with the calculated intensities for different planes, using different models. With the help of this comparison, the distribution of the substituted cations on the two sites in the apatite structure has been determined. The measurement of spectral energy distribution and intensity of emission has been done with the following assembly: A UV lamp providing 2537Å wavelength as excitation source, phosphoroscope, constant deviation spectrometer, photomultiplier tube, spot galvanometer. Graphs have been plotted for relative intensity as a function of emission wavelength.

From the x-ray diffraction results, it has been concluded that thorium and tungsten ions are substituted for strontium at site(I) leaving a metal vacancy at site(II).

From the results of spectral energy distribution studies, it has been found that substitution of thorium and tungsten, for strontium, in the Sr halophosphate activated with Sb and Mn, does not shift the emission peaks of the phosphors but increases the intensity to a considerable extent, at the optimum concentration of the substituted ions. A plausible mechanism for this has been proposed.

Part II - Sulphide phosphors

Lately, some mixed sulphides have received close attention, because of their interesting properties. Work done so far in this field concerns mostly with substitution of alkaline earths having the same crystal symmetry as the host lattice.

In the present work, a mixed phosphor (Ca + Cd)S has been studied in which the crystals of CaS and CdS belong to different classes of symmetry. The effect of substitution of one cation for the other in the host matrix, on the structural and optical properties of the phosphor has been studied. The effect of concentration of activators on the luminescence of this mixed phosphor has also been studied.

Synthesis of mixed sulphide phosphor has been done in two stages. In the first stage, appropriate mixtures of CaS and CdS have been fired in H_2S atmosphere at about 850°C.

CaS has been prepared by passing H_2S over heated $CaCO_3$ while CdS has been prepared by usual precipitation method. In the second stage, copper and manganese, have been introduced independently as well as in presence of each other, as activators. About nine compositions of the host matrix, having different proportions of calcium and cadmium have been prepared. Copper percentage has been varied from 0.1 to 0.5 whereas manganese percentage has been varied from 0.5 to 2.5.

The completion of the reaction and extent of substitution has been checked by x-ray diffraction method. The 'd' values and lattice parameters of the phosphor have been reported. It has been shown that cubic CaS tolerates the substitution of Cd upto 20 per cent but hexagonal CdS does not tolerate the substitution of Ca for Cd.

It has been found that the activators, copper and manganese, show bright yellow and orange-red fluorescence respectively, when excited by UV source having 3650Å radiation. When copper and manganese both are present together, an orange-red fluorescence is observed. From the spectral energy distribution studies, graphs showing the relative intensity against emission wavelength have been plotted. The graphs have been resolved into various gaussian curves.

With the help of previously reported data, the different peaks, due to the activators have been identified, the mode of substitution of the activator has been proposed.

In case of copper alone the peak at 5940Å has been attributed to the Cu^{2+} at substitutional site while the emission peaks at lower wavelengths are attributed either to Cu^+ substitutional or Cu^+ interstetial. A model for the mechanism of emission has been proposed. In case of manganese alone, definite energy transitions have been assigned to the peaks of emission. In case of phosphors, containing copper and manganese together, the concept of resonance transfer, from sensitizer to activator, has been proposed to explain the observed sharp and single peak of emission. Furthermore, it has been proposed that cadmium does not act as an activator impurity but merely modifies the host lattice.

Part III - Fluoride phosphors

Fluoride compounds have been known to show fluorescence since a very long time. However, the systematic study of the luminescent fluoride has been started quite recently. Some simple fluorides have already been used as fluorescent host materials.

In the present work, attempt has been made to prepare a mixed fluoride $NaYF_4$ phosphor activated with rare earth ions particularly europium and terbium. The host $NaYF_4$ has been prepared by the precipitation method. A solution of hot NaF has been added to a solution of YCl_3 to precipitate $NaYF_4$. Later, the activators Eu^{3+} and Tb^{3+} have been added independently as well as in presence of each other. The mixtures have been fired at 1000°C for about four to six hours in N_2 atmosphere. The effect of the concentration of the activators has also been studied.

The structure of $NaYF_4$ has been determined by x-ray diffraction method. There are two structures proposed for $NaYF_4$ in literature. The two forms are temperature dependent. The one formed at higher temperature is cubic while the other one formed at low temperature has unknown structure. It has been found that the $NaYF_4$ prepared by precipitation method also shows the cubic structure. The 'd' values, intensities of the diffracted lines and lattice parameters have been reported.

In the spectral energy distribution studies, the microphotometer tracings have been recorded for the fluorescence spectra of the samples. It has been found that only europium serves as a good activator. Terbium does not serve as an activator nor does it act as a sensitizer to europium, on the contrary it is found to quench the fluorescence of eurupium. The spectra have been analysed and the energy transitions have been assigned to the various peak wavelengths observed in the fluorescence spectra. Crystal field effect on the energy levels of Eu^{3+} ion in $NaYF_4$ has been considered and it has been proposed that the substitution of europium ions in the $NaYF_4$ crystal distorts the octahedral symmetry and gives rise to a lower symmetry C_2. The observed lines in the fluorescence spectra have been accounted for as due to C_2 symmetry.

ACKNOWLEDGEMENT

ACKNOWLEDGEMENT

I wish to express my sincere gratitude to Dr. A. P. B. Sinha, for his inspiring guidance during the persuit of this work.

I am also thankful to Dr. R. R. Neurgaonkar for some of the suggestions and discussions made during the course of the work.

Thanks are due to Director, Bhabha Atomic Research Centre, Bombay, for taking the spectra of the samples.

Finally, thanks are also due to the Director, National Chemical Laboratory, Poona-8, for allowing to carry out this work and submit it in the form of a thesis.

P. G. Pol.

(P. G. Pol)