SYNTHESIS, STRUCTURAL AND OPTICAL PROPERTIES OF MIXED HALOPHOSPHATE PHOSPHORS

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(R.R.Neurgaonkar)

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CHAPTER I

INTRODUCTION

GENERAL INTRODUCTION

The alkaline earth halophosphate phosphors of the apatite structure are being used extensively in fluorescent lamps because they enable a wide range of colours to be achieved by variations in their composition and in activator and sensitizer concentrations.

Among the halophosphates, the calcium halophosphate activated by antimony as the primary activator and manganese as secondary activator is the most important phosphor and is commonly used for general lighting purposes since its discovery in 1942 by A. H. Mckeag and P. W. Ranby. A unique feature of the calcium halophosphate phosphor 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 purpose.

Attempts have since been made by several workers to find better materials by a partial or total substitution of calcium in calcium halophosphate phosphors. The present investigation has been undertaken to synthesise a number of mixed phosphors by partially replacing the calcium in calcium halophosphate phosphors and to study the effect of such substitution on the crystal structure and the optical properties of these phosphors. Furthermore, the effect of sensitizer and activator on the fluorescent properties of these phosphors have also been studied.

HISTORICAL INTRODUCTION

A survey of the earlier work on halophosphate phosphors is given below under the following groups:

(I) Crystal structure of the halophosphate.

(II) Synthesis of the halophosphate phosphors.

The apatite structure[1]

The halophosphates $Ca_5F(PO_4)_3$, $Ca_5Cl(PO_4)_3$ and several other related compounds have the well-known apatite structure. The unit cell is hexagonal ~~axis~~ with Z = 2. For the fluoroapatite, the cell dimensions are a = 9.37, c = 6.88, c/a = 0.734.

The space group is $C^2_{6h} - C_{6_3/m}$ and the ions are located at

4CaI in (f) : $\pm \frac{1}{3},\frac{2}{3},Z;\ \frac{1}{3},\frac{2}{3},\frac{1}{2} - Z$, $Z_{ca} = 0$

6CaII in (h): $\pm X,Y,\frac{1}{4};\ \bar{Y}, X-Y,\frac{1}{4};\ Y-X, \bar{X},\frac{1}{4}$

$X_{ca} = 1/4;\ Y_{ca} = 0.$

6P in (h) : $X_p = \frac{5}{12}$; $Y_p = 13/36$

6'0'$_1$ in (h): $X_I = \frac{1}{3};\ Y_I = \frac{1}{2}$

6'0'$_{II}$in (h): $X_{II} = \frac{3}{5};\ Y_{II} = \frac{7}{12}$

12'0'$_{III}$in (i): $\pm (X,Y,Z;\ \bar{Y}, X-Y, Z;\ Y-X, \bar{X}, Z;$
$X,Y,\frac{1}{2} - Z;\ \bar{Y},X-Y,\frac{1}{2} - Z;\ Y-X,\bar{X},\frac{1}{2} - Z).$
$X_{III} = \frac{1}{3};\ Y_{III} = \frac{1}{4};\ Z_{III} = \frac{1}{16}$

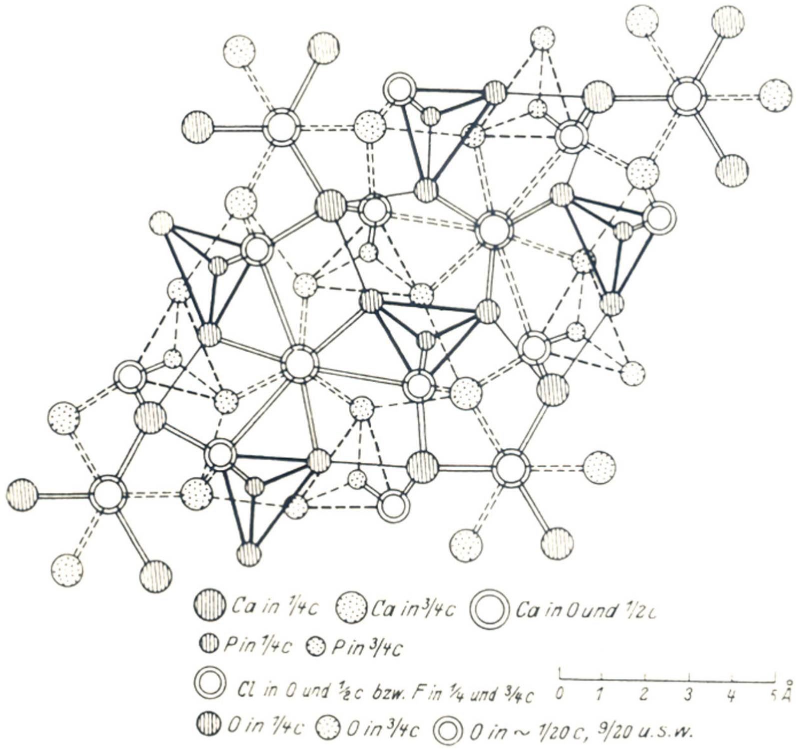


FIG : 1 : THE APATITE STRUCTURE

The fluorine atoms in fluoroapatite are situated at 2F in (a): $\pm (00\frac{1}{4})$; whereas the chlorine atoms in chloroapatite are situated at 2Cl in (b) = $(000;\ 00\frac{1}{2})$.

The neighbourhood of each ion is as follows:

Kind of atom	Atom symmetry	Number		Distance
Ca I	$C_3 - 3$	90	3I, 3II, 3III	2.32, 2.38, 2.85
Ca II	$C_s - m$	1F*		2.34
		2Cl		2.91 (2.93)
		6'0'	2III,2III,1II, 1I	2.29, 2.44, 2.67, 2.82
P	$C_s - m$	4'0'	1II, 2III, 1I	1.49, 1.60, 1.82
F*	$C_{3h} - 6$	3 Ca	II	2.34
		6'0'	III	3.10C
		2F		3.44
Cl**	$C_{3i} - \bar{3}$	6 Ca	II	2.91 (2.93)
		6 '0'	III	2.85^{c} (2.98)
		2 Cl		3.44^{c} (3.43)
0 I	$C_s - m$	110	1II,2III, 2I, 2III, 2II,2III	2.69^{a},2.67^{a},2.71^{bb} 2.98^{b}, 3.48^{b}, 3.55^{b}
0 II	$C_s - m$	110	2III, 1I, 2II, 2III, 2III, 2I	2.63^{ab}, 2.67^{b}, 2.86^{bb} 3.10^{c}, 3.21^{c}, 3.46^{b}.
0III	$C_i - 1$	1F*		3.10
		1 Cl*		2.85 (2.89)
		8'0'	III, II, I, III	2.58^{ac}, 2.63^{ab}, 2.67 , 2.94^{c}.
			I, II, II, I	2.98^{b}; 3.10^{bc}, 3.21^{c}, 3.55^{b}.

* for fluoroapatite only.
** for chloroapatite only.

It can be seen that the PO_4 groups form deformed tetrahedra. The four oxygen atoms of the PO_4 radicals form a regular tetrahedron but, the P- atom is displaced from the centre of the tetrahedron. The Ca I is surrounded by 6'O' atoms (I, II), near the corners of elongated triangular prism and 3'O'III in same similar C plane as the central Ca atom, Ca II is surrounded by 6'O' atoms and one fluorine atom in case of fluoroapatite and two chlorine atoms in case of chloroapatite.

A number of apatite-like minerals have chemical formulae which are not exactly in accordance with the structural requirement. It is not certain, then, in which way the atoms are distributed. Perhaps, there are chlorine, fluorine or metal vacancies, which are distributed in lattice.

The unit cell dimensions of some of the known apatites are given in table No. 1.

Table 1

Name	Formula	a	c	c/a	Type
Fluoro-apatite	$Ca_5F(PO_4)_3$	$9.3_{7\pm1}$	$6.8_{8\pm1}$	0.734	F
Chloro-apatite	$Ca_5Cl(PO_4)_3$	$9.5_{2\pm3}$	$6.8_{5\pm3}$	0.719	Cl
Pyromorphit	$Pb_5Cl(PO_4)_3$	$9.9_{5\pm2}$	$7.3_{1\pm2}$	0.735	Cl
Mimetesite	$Pb_5Cl(ASO_4)_3$	$10.2_{4\pm2}$	$7.4_{3\pm2}$	0.725	Cl
Vanadinite	$Pb_5Cl(VO_4)_3$	$10.3_{1\pm2}$	$7.4_{4\pm2}$	0.712	Cl
Hydroxyl-apatite	$Ca_5OH(PO_4)_3$	$9.4_{0\pm3}$	$6.9_{3\pm3}$	0.731	F
Tricalcium phosphate 2/3 hydrate	$Ca_9(H_2O)_2(PO_4)_6$	$9.2_{5\pm3}$	$6.8_{8\pm3}$	0.744	?
Oxy-apatite	$Ca_{10}O(PO_4)_6$	$9.3_{8\pm3}$	$6.9_{3\pm3}$	0.739	Cl
Carbonate-apatite	$Ca_{10}CaCO_3H_2O(PO_4)_6$	$9.2_{7\pm3}$	$6.9_{5\pm3}$	0.75	Cl

Synthesis of halophosphates

(1) Calcium halophosphate phosphors

Although many papers have been published on calcium halophosphate phosphors, a detailed description is available only for the preparation of antimony and manganese activated phosphors.

Jenkins, McKeag and Ranby[2] have shown that Sb^{3+} was necessary to induce the fluorescence in the calcium halophosphate phosphor and Mn^{2+} acted as a colour modifying agent. Calcium carbonate, diammonium phosphate, calcium fluoride, calcium chloride, antimony trioxide and manganese carbonate, were mixed in the appropriate proportion and fired at 1050-1150°C for about 1 hour. The emission peak was observed at 4800Å when it was activated by Sb^{3+} which shifted to 5800Å when Mn^{2+} was added. Furthermore, it was observed that emission peak changed from 5800Å to 5550Å when chlorine was replaced by fluorine. X-ray diffraction studies showed that the structure was similar to that of the mineral apatite.

Same results were observed when calcium in calcium halophosphate phosphors was replaced by strontium or barium partially or completely. Bismuth, tin, lead and arsenic were also reported as primary activator in place of antimony, but their efficiency was found to be very low as compared to that of antimony.

Nagy, Wollentin, and Lui[3] synthesized calcium halophosphate phosphors having different chlorine to fluorine ratios with antimony as primary activator and manganese as the secondary activator. It was found that the emission peak shifted from 5800Å for the chlorine compound to 5550Å for the fluorine one. It was shown that a trace of antimony was sufficient to induce the fluorescence while manganese was added up to 5 per cent by weight of the matrix. The blue emission was totally depressed by the addition of manganese.

McKeag and Ranby[4] studied the synthesis of calcium halophosphate phosphors by using bismuth as primary activator. It was observed that when calcium fluorophosphate was activated by 7.5% bismuth, white luminescent colour was observed; reddish light was obtained when calcium fluorophosphate was activated by 7.5% bismuth and 3% manganese and when calcium fluorophosphate was activated by 7.5% bismuth and 3% antimony, pale pink emission was observed.

Froelich[5] synthesized the calcium halophosphate phosphor by using antimony and manganese as activators. Colloidal calcium fluoride was obtained by adding hot solution of ammonium fluoride to the hot solution of calcium nitrate. To this solution antimony trioxide and manganese nitrate were added followed by a boiling aqueous solution of diammonium phosphate. Precipitate was then filtered and dried and heated at 1050-1150^{o}C for half an hour in an inert atmosphere. This phosphor was found to be very efficient for fluorescent lamps.

Studer and Rosenbaum[6] studied the decay of emission of calcium halophosphate phosphors activated by antimony and manganese. It was observed that in the first stage decay was the very rapid while in the second stage it was slow, but both followed the relationship $I_o = I_o \exp(- Kt)$. It was shown that the rapid decay was that of the antimony emission and the decay constant was about $K \quad 1500$ sec.$^{-1}$ and the slow decay was that of the manganese emission with $K \quad 75$ sec.$^{-1}$.

Butler and Jerome[7] determined the energy distribution of the emission spectra of calcium halophosphate phosphors activated by antimony and manganese. It was found that the spectrum was considerably affected by the crystal structure of the matrix and the sites at which activator ions were located in the matrix. Further, it was observed that increase in the activator concentrations did not affect the location of emission band in spectrum, but the relative intensity changed.

Fonda[8] studied the effect of activator concentrations and temperature on the location of the emission peak. The emission peak at room temperature for the halophosphate containing Sb but no Mn was at 4800Å. On increasing the temperature from 80°K to 475°K the peak position changed to nearly 4380Å. Furthermore, it was observed that the extent of shift was dependent on the concentration of antimony. Position of the manganese peak was independent of manganese concentration but shifted to shorter wave length on increase of temperature.

Ranby[9] studied the synthesis of calcium halophosphate phosphors using silver as the primary activator and manganese as secondary activator. Calcium monohydrogen phosphate, calcium carbonate, calcium fluoride, calcium chloride, silver phosphate and manganese phosphate were mixed in appropriate proportions and fired at 1150°C for about one hour in an inert atmosphere. It was observed that the emission due to silver ranged from 3200-4800Å with maximum intensity at 3800Å and on addition of manganese the emission shifted to yellow-orange range. Maximum intensity was obtained when the concentrations of silver and manganese ions were 0.4 per cent and 1.5 per cent by weight respectively.

X-ray analysis showed that the above phosphors have an apatite type of structure and that silver replaced calcium in position adjacent to halide ions in the crystal lattice.

Fortney and Moran[10] studied the calcium halophosphate phosphors activated with antimony and manganese. Calcium monohydrogen phosphate,3.00 moles; calcium carbonate,1.35 moles; calcium fluoride,0.76 moles; ammonium chloride, 0.35 moles; antimony trioxide, 0.12 moles and manganese carbonate, 0.12 moles; were used as starting materials in above proportion and the reaction was carried out at 1090°C for six hours. It was observed that emission curve of this phosphor corresponded to a colour temperature of 3500°C.

Butler, Bergin and Hannaford[11] studied the behaviour of the antimony in calcium halophosphate phosphors and showed that it is present in calcium halophosphate phosphor in trivalent form. It was found that during the firing of phosphors, antimony trioxide started to oxidise to tetraoxide at 450°C and was completely oxidised below 520°C. This tetraoxide reacted at 700-875°C with excess of calcium fluoride and calcium carbonate in phosphor mixture with formation of fluoromeite. Furthermore, it was shown that for good fluorescence certain amount of acid soluble antimony was needed, which was obtained from trivalent rather than pentavalent antimony.

Effects of activators on the optical properties of calcium halophosphate phosphors were studied by Fujimori and Maekawa[12]. Salts or oxides of lead, antimony, bismuth, magnesium and tungsten were used as primary activators and manganese, cerium, magnesium, molybdenum were used as secondary activators. It was shown that the mixtures of above compounds gave very good fluorescence when heated at 1100°C in inert atmosphere for 1-3 hours and these fluorescent substances were found very useful in the mercury vapor electric lamps.

Doherty and Harrison[13] studied the synthesis of calcium halophosphate phosphors using antimony and manganese as activators. Tricalcium orthophosphate, calcium chloride, calcium fluoride, antimony trioxide and manganese carbonate were used as the starting materials. In place of calcium monohydrogen phosphate and calcium carbonate, they directly employed the tricalcium orthophosphate, which was obtained by either wet synthesis or dry synthesis and reaction was carried out at 1060°C for about one hour. Concentrations of antimony and manganese were changed from 0 to 10 per cent and 0 to 5 per cent respectively and they showed that even traces of antimony were sufficient to induce the fluorescence in the calcium halophosphate phosphor and maximum intensity was observed when the concentration of antimony was 1.8 per cent of the basic raw material. Furthermore, it was shown that antimony is present in the phosphor in trivalent and manganese in divalent state.

They have also studied the effect of varying the chlorine to fluorine ratio on the fluorescence properties of calcium halophosphate phosphors and have shown that 1:1 ratio gave peak at 5750Å.

Fortney and Moran[14] synthesized calcium halophosphate phosphors using antimony as primary activator and manganese as secondary activator. They prepared the phosphors by using activators other than oxide, phosphate or carbonate. Good results were obtained even by using activators in the form of calcium-antimonate, manganese-antimonate or even antimonic acid. Calcium monohydrogen phosphate, calcium oxide, calcium fluoride and ammonium chloride were fired with the above activators at 1090°C for about six hours in a nitrogen atmosphere.

Wanmaker[15] studied the effect of temperature and halogen on the properties of calcium halophosphate phosphors, activated with antimony and manganese. The halophosphate phosphors prepared from calcium monohydrogen phosphate, calcium carbonate, calcium fluoride, antimony trioxide, showed that below 900°C all antimony was present in the form of calcium-antimonate and due to the presence of halide ions Sb^{+++} got incorporated and at ratio F/PO_4 of 2.64, a maximum percentage of antimony was incorporated. A similar maximum was also obtained when fluorine was replaced by chlorine. Further, he showed that the peak of emission band of antimony activated fluorophosphate was at 4750Å and when it was replaced by the chlorine the peak was shifted to 4950Å; with incorporation of manganese in the form of manganese carbonate, the peak was shifted towards the longer wave lengths, when it was fired at 1050°C for about one hour.

Thurnau[16] studied the quantum efficiency of calcium halophosphate phosphors activated by antimony and manganese, using grazing incidence vacuum grating monochromator with hydrogen arc, in the wave lengths range of 275Å to 1715Å under the excitation in extreme ultra violet, using sodium salicylate as standard phosphor. It was found that the excitation spectra for calcium halophosphate phosphors were limited to a range from 1026Å to 1640Å. A decline of quantum efficiency below 1026Å was observed in each spectrum.

Wanmaker and Verheyke[17] made thermogravimetric measurements on the calcium halophosphate phosphors, activated by antimony and manganese. These studies showed that calcium monohydrogen phosphate was converted to $Ca_4H_2O_7$ between 430°C and 500°C and calcium carbonate was dissolved between 600 to 910°C. Antimony trioxide was partially oxidised to Sb_2O_4 between 540-600°C and decomposition of Sb_2O_4 to Sb_2O_3 occurred at 1000°C. Manganese carbonate converted to Mn_3O_4 at 650°C and MnO was obtained at 960°C. The dissolution temperature of calcium carbonate was lowered by the presence of calcium monohydrogen phosphate. Further, they showed that in the mixture of calcium halophosphate phosphors, the loss of antimony, chlorine or fluorine occurred only after the reaction with calcium carbonate was complete.

Tokyo[18] synthesized an efficient calcium halophosphate phosphors activated by antimony and manganese. He employed the manganese in the form of orthophosphate in place of carbonate and the other starting materials were mixed in the following proportions: Calcium monohydrogen phosphate 27.00 g.; calcium fluoride, 1.7 g.; antimony trioxide, 1.09 and manganese orthophosphate, 1.19; and were fired for 45 minutes at 1160°C. It was shown that unlike other phosphors, shorter firing gave better results because otherwise antimony and chlorine were lost partially.

Kodera, Yonemura and Sekine[19] synthesized a highly fluorescent calcium halophosphate phosphor using antimony and manganese activators. The starting materials were mixed in the following proportions. Calcium monohydrogen phosphate, 27.01; calcium carbonate, 8.6-8.8 g.; calcium chloride, 1.89 g.; calcium fluoride, 1.7 g.; manganese phosphate, 1.9 g. and antimony trioxide, 1.18 g.; and were fired at 1160°C for about 45 minutes. Excessive heating was avoided as it volatalised antimony and chlorine. It was observed that the fluorescence was obtained in the range of 4000-6200Å with wide maxima at approximately 4700Å and 5900Å.

Henderson and Ranby[20] synthesized calcium and calcium-strontium halophosphates using cerium and manganese as activators. The phosphors were fired at 1100°C to 1200°C in mildly reducing atmosphere, such as, mixture of nitrogen and hydrogen.

For the calcium halophosphate phosphors the maximum intensity was observed when concentrations of cerium and manganese were 6×10^{-2} and .039 per atom of phosphors respectively, while in calcium-strontium a halophosphates, the maximum intensity was observed when the proportion of calcium to strontium was 4:1 and the concentrations of the activators were the same as above. The fluorescent emission when only cerium was present was at about 3400Å and it moved in the visible region at about 6000-7000Å when manganese was also incorporated. Addition of Sr was found to shift the Mn emission to a longer wave length. X-ray diffraction studies showed that both these phosphors have the apatite structure.

Fonda[21] studied the influence of activator environment on the spectral emission of calcium halophosphate phosphors activated by antimony and manganese. It was observed that the substitution of chlorine for fluorine produced a shift towards the longer wave lengths. As the size of the chlorine ion is larger than the fluorine ion, its field strength, the quotient of its ionic charge by its ionic radius, is therefore less. This results in a lower electronic attraction between the chlorine ion and its neighbouring calcium ion, so that the spacing between such a calcium ion is increased. The spacing between such a calcium ion and its neighbouring three oxygen ions, is correspondingly reduced. When a manganese ion is substituted for such calcium ion, its levels are depressed and its emission shifts towards longer-wave lengths.

Mizuno and Kamiya[22] studied the effect of anion addition on the efficiency of calcium halophosphate phosphors activated by antimony and manganese activators. Effect of addition of BO_3 on the synthesis of calcium halophosphate phosphors were studied and it was found that the luminescent intensity was decreased on addition of BO_3 ions, while the addition of SiO_2 had no effect on the after-glow of calcium halophosphate phosphors.

McKeage and Hunt[23] synthesized calcium halophosphate phosphors containing copper, tin and manganese as activators. Copper and tin were used in the cuprous and stannous state and their concentrations were varied from 0.1 to 1.0 per cent and 0.5 to 5.0 per cent by weight of the matrix. The phosphors were usually fired in the range of 900-1200°C in a mildly reducing atmosphere of nitrogen containing a little hydrogen. High chlorine content gave good results. Moderate blue fluorescence was observed when only copper was used and orange fluorescence was obtained when manganese was added to it. Strongest emission was observed when chlorine to fluorine ratio was 0.7 to 0.3. Tin gave a weak blue fluorescence and orange-pink fluorescence was observed when manganese was incorporated with tin. X-ray examination confirmed that the phosphors had an apatite structure.

Fortney[24] synthesized the calcium halophosphate phosphors using antimony and manganese as a activators. Calcium monohydrogen phosphate was obtained by mixing calcium carbonate and H_3PO_4 and to their suspension, Calcium carbonate, calcium fluoride, manganese carbonate, antimony trioxide and ammonium chloride, were added. The mixture was dried and fired at 1130°C for six hours. It was observed that best results were obtained when the calcium to phosphorus ratio was between 4.7:3 and 4.9:3.

Repsher[25] synthesized calcium halophosphate phosphors using antimony and manganese as activators and showed that the efficiency of phosphors were increased by appropriate grinding and wash treatment. The phosphors after grinding to $< 20\mu$ diameter were given wash treatment first with 0.01 to 0.3 N nitric acid and then with water to remove acid and then dried. Calcium oxide, phosphorus pentoxide, manganese carbonate, antimony trioxide, calcium fluoride and strontium chloride, were used as the starting materials and were fired at 1190°C for about three hours, cooled and refired at 1120°C for about 2.5 hours. It was found that the final product had a colour temperature of 4500°K.

Ostaszewiez[26] synthesized calcium halophosphate phosphors using antimony and manganese as activators. Calcium monohydrogen phosphate, calcium carbonate, diammonium phosphate, calcium fluoride, calcium chloride, manganese orthophosphate and antimony trioxide, were used as starting materials. He found that the manganese emission varied from 5764Å to 5935Å.

Aia and Poss[27] studied the synthesis of calcium halophosphate phosphors activated by antimony and manganese by adding small quantity of cadmium for calcium in the matrix. It was found that the intensity of calcium halophosphate phosphors increased when the cadmium concentration in the matrix was 0.03 to 0.5 g. atom cadmium per three mole of phosphate. Calcium monohydrogen phosphate, calcium carbonate, calcium fluoride, calcium chloride, manganese carbonate, antimony trioxide and $CdNHPO_4$ were used as starting materials and fired at 1090°C for about one hour in an nitrogen atmosphere.

McKeag and Hunt[28] synthesized calcium halophosphate phosphors using copper as primary activator. Copper was used in the cuprous state and its concentration was varied from 0.1 - 1.0 per cent by weight of the matrix. A strong red component of emission was observed when manganese was incorporated with copper.

Johnson[29] determined the diffuse reflectivity and excitation spectra of calcium halophosphate phosphor powder and the optical absorption of its single crystal in the spectral region of 1100-3000Å. It was found that intrinsic optical absorption of the host lattice started at approximately 1500Å in fluorophosphate and 1570Å in the chlorophosphate and absorption in manganese bands in the fluoroapatite at 1600, 1750 and 2150Å resulted in luminescence in absence of antimony.

It was observed that the host lattice had the forbidden energy gaps of approximately 8 e.v. Divalent manganese showed strong absorption from 5.5 to 8 e.v. and tetravalent antimony from about 4.5 to 8 e.v.

Suchow[30] studied the colour centres produced in calcium halophosphate phosphors by short wave ultra-violet radiations, and it was observed that the optically bleachable colour centres consisted of trapped electrons which could be returned to their original states on proper irradiation or heating. It was also observed that halophosphate base materials are photoconducting during the irradiation with 1849Å ultra-violet. It was found that this radiation promoted electrons to the conduction band from which they fell into a trap. Therefore, it was found that employing the trap with 3650Å radiation gave the reverse process and photoconductivity occurred again.

Narita[31] studied theoretically the effect of changes in the lattice constant of the host crystal on the energy levels of the activator ion, in calcium fluorophosphate phosphors activated by Mn^{++} only. On the assumption that the emission of this fluorescent body was due to the transition of Mn^{++} ions from the lowest excited state to ground state, the calculation led to shift of the emission peak by about 200Å to longer wave lengths side for one per cent decrease in the lattice constant.

Johnson[32] investigated the location of Mn^{2+} and Sb^{3+} ions in calcium halophosphate phosphors by studying the polarisation of the emitted radiation and also the electron spin resonance of synthetic single crystal. It was concluded that the luminescent Mn^{2+} was at the CaI position in the fluorophosphate and at the CaII in the chlorophosphate. Polarisation studies showed that Sb^{3+} was predominently present at CaII position in fluorophosphate but the position of Sb^{3+} in chlorophosphate was uncertain, although it was believed to be mainly at CaI position.

Apple and Isher[33] studied the effect of very rapid cooling (quenching effect) of (1) calcium fluorophosphate, (2) calcium chlorophosphate, and (3) calcium chlorofluorophosphate phosphors, containing antimony and manganese as activators from 600-1200°C to room temperature. It was observed that there was no effect of rapid cooling on the spectral energy distribution in case of fluorophosphate while in case of chlorophosphate and chlorofluorophosphate emission peaks were shifted towards shorter wave lengths. However, there was no change in the antimony band. Further, it was observed that there was a considerable change in the crystal structure due to rapid cooling from the elevated temperature and it was found that structure of chlorophosphate closely approached to that of fluorophosphate phosphors.

Hoekstra and Wanmaker[34] studied the synthesis of calcium halophosphate phosphors and increased the efficiency of these halophosphate phosphors by giving a wash treatment. The calcium halophosphate phosphors activated with antimony and manganese as activators were first treated with reducing agents like H_2SO_3 and H_3PO_4 to reduce the higher valent manganese and antimony present on the surface. Dilute hydrochloric acid was used to dissolve any $Ca(SO_3)_2$ which formed during the first wash treatment. Then this residue was passed through a hydrocyclone and finally washed with water and dried.

Apple[35] studied the formation of colour centres in calcium halophosphate phosphors and it was found that an irradiation of unactivated calcium halophosphate phosphor with 1800Å radiation led to the formation of three absorbing colour centres in 2500-7000Å region and whose spectral distribution and relative intensity dependent upon the chlorine to fluorine ratio. The magnitudes of the colour centres were reduced when the samples were prepared with excess of calcium oxide or calcium fluoride which decrease when the sample was quenched. Incorporation of impurities such as antimony, manganese and cadmium led to a change in both the numbers of colour centres and the spectral distribution of the induced absorption.

Kamiya and Masuda[36] studied the emission characteristics of calcium halophosphate phosphors activated by antimony and it was observed that the emission properties dependent on the concentration of activator and on the ambient temperature of firing. Calcium fluorophosphate phosphors prepared with antimony as activator had the main peak at 5000Å at liquid nitrogen temperature. This was displaced to shorter wave lengths on increasing the temperature, while there was little change on second peak which was at 3900Å. The activation energies for the radiationless transition of the main band was found to be 0.5 - 0.6 e.v.

Kamiya[37] studied the effects of changing the fluorine to chlorine ratio on crystal growth and on fluorescent characteristics of calcium halophosphate phosphor activated with antimony and manganese. Fluorine to chlorine ratio was 1:0, 2:1 and 1:2 respectively and these compounds were prepared by firing at 900-1100°C for about 15-60 minutes. The activation energies of crystal growth for the fluorophosphate and chlorophosphate were 30 Kcal./mole and 20 Kcal./mole respectively,and further it was shown that the particle size of compounds grew with reaction temperature. The average particle size of fluorophosphate and chlorophosphate prepared at 1000°C were 9-10 mμ and 12-13.5 mμ respectively.

(2) Synthesis of cadmium halophosphate

Although many papers have been published on cadmium halophosphate phosphors since its discovery by A. H. McKeag and Randall[38], there are only a few wherein a detailed description of the method of preparation of phosphor has been given. McKeag and Randall studied the synthesis of cadmium chlorophosphate phosphors using only manganese as activator. Two methods were developed to prepare the cadmium chlorophosphate. In the first method, cadmium sulphate, diammonium phosphate and manganese chloride, were used as the starting materials and fired at 925°C for about 30 minutes, whereas in the second method, cadmium sulphate, diammonium phosphate, manganese sulphate and cadmium chloride, were used as the starting materials and fired at 800°C for about 30 minutes. X-ray diffraction studies showed that they have a structure similar to apatite and in which unit cell is hexagonal having axes $a_o = 9.7\text{Å}$ and $c_o = 6.4\text{Å}$. Emission peak due to manganese was observed at 5900Å.

McKeag[39] synthesized cadmium halophosphate phosphors by using manganese as activator; cadmium sulphate, diammonium phosphate, manganese sulphate and magnesium chloride, were used as the starting materials. In this case magnesium chloride was used in the place of cadmium chloride and fired in the range of 700-900°C for about 30 minutes.

McKeag[40] synthesized cadmium halophosphate phosphors using only manganese activator. Cadmium sulphate, diammonium phosphate, manganese sulphate and sodium chloride, were used as the starting materials. X-ray diffraction studies showed that the compound has structure similar to apatite and emission due to manganese was observed at 5900Å.

McKeag and Ranby[41] synthesized the cadmium halophosphate phosphors using lead as primary activator and manganese as the secondary activator. Luminescent grade cadmium orthophosphate, cadmium fluoride, lead carbonate and manganese sulphate, were used as the starting materials and fired at 700-1000°C for about 30 minutes in the nitrogen atmosphere. The compound showed an emission peak at 5900Å.

Prener[42] studied cadmium halophosphate phosphors activated with manganese in which cadmium fluoride was partially replaced by zinc fluoride. Concentrations of zinc fluoride varied from 5 to 20 per cent in the matrix. The luminescent grade cadmium orthophosphate, cadmium fluoride, zinc fluoride and manganese phosphate, were used as the starting materials and fired at 950°C for about one hour. The phosphor emitted a red light under ultraviolet and cathode-ray excitations.

Wollentin, Lui and Nagi[43] synthesized cadmium chlorophosphate phosphors using manganese activator and replacing partially cadmium chloride by the chlorides of magnesium, calcium, zinc, barium, strontium, in various molar ratios. Cadmium oxide, diammonium phosphate, manganese chloride and chlorides of one or more of the elements, magnesium, zinc, calcium, barium and strontium, were used as the starting materials and fired in the range of 650-950°C for about 45 minutes. Concentration of manganese was varied from 0.2 to 1% by the weight of the matrix and with increasing concentration of manganese the emission shifted towards the longer wave-lengths.

Wollentin[44] synthesized cadmium halophosphate phosphors using lead and manganese as activators and partially replacing cadmium fluoride by the other fluorides like aluminium, calcium, zinc, strontium, barium and magnesium and sodium and potassium. The spectral emission of these phosphors were varied by changing the concentrations of activators and halides. The substitution of halides of sodium, potassium and zinc in place of cadmium fluoride shifted the emission and excitation spectra towards longer wave-lengths. A double band emission was observed with peak at 4500Å and 5900Å and at higher concentrations of manganese, the blue peak was completely supressed.

McKeag and Ranby[45] synthesized the cadmium fluorophosphate phosphors using lead and manganese as activators. The luminescent grade orthophosphate, cadmium fluoride, lead carbonate and manganese phosphate, were used as the starting materials and were fired at 700-1000°C for about 30 minutes.

(3) Synthesis of magnesium halophosphate

Anderson and Wells[46] studied the synthesis of magnesium halophosphate phosphors using uranium as activator. Magnesium orthophosphate, magnesium fluoride and uranium oxide,were used as starting materials and fired at 900-1100°C for about 20-25 minutes in an inert atmosphere. Concentration of uranium was varied from 0 to 5 per cent wt. of the matrix, the maximum intensity was observed when the concentration of uranium was 2 to 2.5 per cent wt. of the matrix. The replacement of fluorine by chlorine did not produce any photoluminescence. The emission due to uranium was observed in green region. Further studies showed that the same results were obtained when uranium was replaced by silver and thallium.

The position of the emission peak is strongly dependent on the crystal field to which the emitting ion is subjected. Substitutions in the crystal lattice, therefore, have an important influence on the colour of the emission mainly because they affect the crystal field through the changes in lattice constant which result in the change of Me-anion distance. In addition, the polarizability of the metal ion, ability to form covalent bonds, etc. also vary with substitution and thus the total effect on the energy separation between the ground and excited state changes, becomes a complicated function of various parameters.

Some work has already been done experimentally to see the effect of substitution in various phosphors. Gobracht and G. Heinsohn[47] have studied the vanadates of Na, K, Rb and Cs and have found that the wave length of emitted radiation increases as one goes from the bigger to smaller ions. However, Butler[48] has observed to the contrary in the case of Ba or calcium orthophosphates substituted with various other alkali earth ions. He finds that the wavelength increases as one goes from smaller to bigger. Recently, Fonda[49] and Klasen, Zalm and Hyysman[50] have done a rather extensive work on compounds of the type ABF_3 (where A and B = K, Rb, Cs and Mg, Zn, Cd, Ca respectively), AF_2 (where A = Mg, Zn, Cd, Ca) and AS (where A = Ca, Sr and Ba). They found in all cases an agreement with Gobracht and Heinsohn's work of MVO_3, that the wave length increases as one goes from big to small ions. Ouwettjes[51] has reported that Sr halophosphate (MN) emits at a shorter wave length as compared to Ca halophosphate. On the other hand, Henderson and Ranby have shown that the replacement of Ca by Sr in calcium halophosphate causes a slight shift to longer wave length.

Recent calculations by Narita[52] have shown that a contraction in the Me-O distance shifts the emission to higher wave length. A 2% contraction causes a shift by 300 cm^{-1} to lower energy i.e. about 75Å increase in wave length of Mn emission.

From this it appears that the problem of the effect of substitution on the emission has not yet been well understood. It is also clear that the correlation so far attempted has been only on the basis of the radii of the substituents and no attempt has been made to correlate with the actually measured values of the lattice constants on the inter-atomic distances. We have, therefore, prepared solid solutions of calcium halophosphates containing various ions, actually determined the lattice constant and the inter-atomic distance and simultaneously studied the effect of substitution on the emission wave length and intensity. We have also attempted to determine the distribution of the ions, at least approximately, from the intensity of the diffraction lines.

CHAPTER II

EXPERIMENTAL TECHNIQUES

EXPERIMENTAL TECHNIQUES

Preparation of the basic materials

Calcium carbonate, cadmium carbonate, magnesium carbonate, beryllium oxide, thorium oxide, ammonium phosphate, etc. were the starting materials used in the synthesis of mixed halophosphate phosphors. Out of these starting materials, calcium carbonate was common in all the halophosphates and was prepared by the following process.

(1) Preparation of pure $CaCO_3$

Pure calcium carbonate was prepared from the commercial grade calcium carbonate, containing iron as the major impurity, by the partial precipitation method.

Commercial or c.p. grade calcium carbonate and c.p. grade hydrochloric acid were used as the starting materials.

1.25 kg. of c.p. grade calcium carbonate was dissolved in 2.5 litres of dilute hydrochloric acid, by adding small portion each time and was continuously stirred by a mechanical stirrer. It was found that the solution which had originally a pale yellow colour, changed to deep yellow colour on the addition of calcium carbonate in hydrochloric acid. Further, it was found that the deep yellow colour completely disappeared at the neutralisation point obtained on addition of excess of calcium carbonate to the solution. The excess of calcium carbonate in suspension adsorbed the major portion of the iron impurities and other impurities present in the solution. The excess of calcium carbonate was then filtered off on a Büchner funnel and calcium chloride solution was then transferred to a four-litre beaker and a few c.c. of liquid bromine water was added to this solution to oxidise the $Fe^{(+2)}$ to $Fe^{(+3)}$, which was finally precipitated as hydroxide and was filtered off.

Further purification and the removal of the impurities from the calcium chloride solution was done by a partial precipitation of calcium carbonate at 70-80°C by using pure concentrated ammonium carbonate which was obtained by distillation of ammonical commercial ammonium carbonate in water.

The calcium chloride solution was first heated to 70-80°C and then 30 cc. of pure ammonium carbonate was added and the solution was stirred vigorously. The precipitate was then allowed to settle and was filtered through a Büchner funnel. The calcium carbonate-precipitate adsorbed the remaining impurities, from the solution. The clear solution was then again heated to 70-80°C and precipitated as calcium carbonate by adding the ammonium carbonate. The precipitation was over in two hours. The precipitate was allowed to settle and was filtered through a Büchner funnel and was washed with hot distilled water till it was completely free from chloride. The precipitate was finally washed with absolute alcohol. Calcium carbonate was then dried in an electrical furnace at 110°C for about 12 hours. The dry material was crushed, finely ground and sieved.

A spectroscopic analysis showed the following foreign elements present in calcium carbonate prepared above.

Elements detected	in %
Fe	Less than 0.008
Pb	Less than 0.001
Chloride	Less than 0.01
Aluminium	Less than 0.05

(2) Synthesis of mixed halophosphates

The mixed halophosphate phosphors; represented by the general formula $3(Ca,M)_3(PO_4)_2:(Ca,M)X_2$, where

M represents cadmium, magnesium, beryllium and thorium and X represents fluorine, chlorine or both, were prepared by the following method.

The preparation of these halophosphates was carried out in the two stages. The first was the preparation of a halophosphate of suitable purity and physical conditions without addition of sensitizer and activator, according to the following equation:

$$9(Ca,M)CO_3 + 6(NH_4)_2HPO_4 + 1(Ca,M)X_2 =$$
$$3(Ca,M)_3(PO_4)_2 \cdot (Ca,M)X_2 + 12NH_3 + 9CO_2 + 9H_2O$$

In all the systems except calcium-thorium, the proportion of calcium to cadmium, calcium to magnesium and calcium to beryllium, were kept constant. In all our experiments we used carbonates or oxides of the respective metals, fluorides or chlorides of these metals and ammonium phosphate as starting materials. These materials were intimately mixed in the required molecular proportions by grinding in alcohol in a mortared and pestle. These mixtures were dried in a oven at 70°C and transferred into silica-crucible. The crucible containing the phosphor mixture was heated in air at the required temperature for about one hour. The mixture was then cooled to the room temperature. Heating and cooling were done at slow rates. These halophosphates were again ground in alcohol in mortar and pestle and it was observed that the pure mixed halophosphate were non-luminescent.

In the second stage, the halophosphates were intimately mixed with a suitable sensitizer and a suitable activator. They acquired luminescent property only after they were properly activated by incorporating sensitizer and activator. The choice and quantity of these activators determined the spectral energy distribution of emitted light and its luminous efficiency. We used lead or antimony as primary activator or sensitizer and manganese as a secondary activator in our synthesis.

It was found that almost any compound of lead, antimony and manganese could be used. In all our experiments, we used lead oxide, antimony trioxide and manganese carbonate as the source of these ions. Since the amount of additives, required to obtain good luminescence, was very small, doping materials of c.p. grade purity could have been employed. We actually used all materials of the AR grade purity.

Appropriate amounts of these materials were intimately mixed together with basic materials (usually 5-7 g. lot) by grinding in alcohol in agate mortar and pestle. Homogeneous mixture was obtained after 3-4 hours grinding in alcohol. The mixtures were dried in an oven at 70°C to remove the alcohol and again ground for some time and transferred into the silica crucible of 10-20 cc. capacity. These crucibles containing the phosphor mixture were kept in the silica furnace having the gas regulating arrangement.

As manganese has a tendency of oxidising to higher valency in air at elevated temperatures in which form it reduces the intensity of the phosphors, the halophosphate mixtures were heated in nitrogen gas atmosphere. We passed the nitrogen gas through various traps, because nitrogen from cylinder contains some oxygen, traces of water, etc. We passed the nitrogen gas through concentrated sulphuric acid, sodium-potassium alloy (40:60%) and then through potassium hydroxide and phosphorus pentoxide, to remove water, oxygen and last traces of water or carbon dioxide. It is found that sodium-potassium alloy gave satisfactory results. The mixtures were heated in a specially designed silica furnace.

The Kanthal wire (A grade, 18 SWG) was wound over the central part of a long silica tube (transluscent) of 3" internal diameter and 30" length and covered by applying a special cement (9 parts kaolin plus 1 part borax, c.f. John Strong and Collaborators, Modern Physical Laboratory Practice, Blackie and Sons Ltd., 562, 1945).

The wound portion of the tube was enclosed within a box made up of asbestos cement sheets. The end portions (about 8" long) of the tube and two leads of the wire were taken outside the box, the box was packed with magnesia asbestos powder. This type of fabrication minimized the heat losses; moreover, it gave a long zone of constant temperature in the centre of the tube. During the firing the ends of the tube were continuously cooled by a water circulation system.

Another silica tube of 2" diameter (internal), of which one end was closed and about 25" long, was inserted in the furnace in such a way that about 8" of the closed side of the tube remained in centre of hot zone of the furnace. Be-60 female joint was fixed to the other end of the tube, where from the mixture was inserted into the silica tube. B-60 male had the arrangement of inlet and outlet for the nitrogen gas under circulation.

From the other end of the furnace a calibrated chromel-alumel thermocouple covered by a protective silica tube (about 1 cm. internal diameter) was introduced in such a way that the measuring junction of thermocouple was at the centre of the furnace where the phosphor mixtures in silica crucibles were kept for heating.

Thus the mixtures in silica crucibles covered with lids were heated at different temperatures for about one hour in the nitrogen gas (free from oxygen) atmosphere. The rate of flow of nitrogen gas was regulated to 1 lit/min.

Phosphors were then cooled to room temperatures under the same gas atmosphere and were then taken out of the furnace. They were crushed to a fine powder by grinding under alcohol in a mortar. These phosphors were then transferred in sample bottles and preserved in a dessicators to avoid the oxidation of the phosphors.

Effect of annealing and quenching

The effect of annealing and quenching after the final firing was also studied and it was found that the results in two cases were significantly different. In both, annealing and quenching experiments, the samples were brought gradually to the desired temperatures. However, in the annealing experiments, the sample was cooled from firing temperatures to 300°C very slowly in about 5-7 hours in the nitrogen gas atmosphere, while in the quenching experiments, the sample was cooled to 300°C in less than five minutes by taking out the heating tube from furnace into the open air.

Measurement of spectral energy distribution and intensity of emission under UV excitation

For the measurements of spectral energy distribution and intensities of the mixed halophosphate phosphors, we have constructed the following type of instrument. This consists of the following equipments:

i) The ultra-violet lamp as the source of irradiation of the sample.

ii) Sample holder and the beam chopping arrangement.

iii) Constant deviation spectrometer as the dispersing unit.

iv) Photomultiplier tube as the detector.

For the excitation of the mixed halophosphate phosphors, short-wave ultra-violet of about 2537Å is necessary. For this purpose, we used the low pressure mercury vapor discharge ultra-violet lamp (Mineralight C50-60 Cyc. Model R51, Ultra-violet Prod. Inc., South Pasadona, Calif.,220V).

The lamp was covered with thick black paper having small hole at centre. The sample was placed on a glass slide and was clamped in front of UV lamp. The holder was placed in such a way that the phosphor layer faced the UV radiations and the glass backing was opposite to it. This was done because glass is not completely transparent in the UV region.

It could therefore absorb the exciting UV radiations but not the visible emitted radiations.

In order to stop the direct radiations of the ultra-violet source from entering the spectrometer, we introduced a 'chopper', which is also commonly known as 'Phosphoroscope' (first it was introduced by E. Bacquerel[53] in measurements of life time properties of phosphors). The chopper consists of two metallic rotating discs with alternating opaque and light transmitting sector mounted on the same axis. The two discs are set with respect to each other so that a transparent sector of the first disc permits the exciting light to impinge on the sample while an opaque sector of the second disc hides it from the other side of it. When the luminescent substance becomes visible through opening in second disc, the exciting light is intercepted by an opaque sector of the first disc. The light that is coming out through this chopper is purely due to the fluorescence of the phosphors. Both discs were blackened with black paint. This chopper is attached to a high speed motor, the speed of which was controlled with the help of dimmerstat. Most of the studies were made at 1500 r.p.m.

The above radiations (due to pure fluorescence only) were passed through the constant deviation spectrometer which acted as dispersing unit (make- Adam Hilger Ltd.). In this constant deviation spectrometer the angles of prism are calibrated in terms of wave-lengths.

These responses were detected with the help of the photomultiplier tube (make : EMIE Photomultiplier tube 6097 B) which was attached to the telescope of the constant deviation spectrometer and the photomultiplier readings were taken on a spot galvanometer.

(1) Setting and alignment of the instrument

Before starting the experiment, it is always necessary to test the instrument, which was done as follows:

One of the two discs of the chopper was first taken out and the remaining one disc was rotated at a high speed. The ultra-violet lamp was then switched on when one could adjust the alignment of the lamp with respect to the disc and the slit of the spectrometer with the help of the visible component of the lamp emission. The position of lamp was fixed when clear and strong visible spectrum was obtained. This position of the lamp was kept fixed throughout our experiments. The other metallic disc of chopper was then attached in such a way that the hole on one disc did not come in front of any hole of the second disc. The chopper was rotated again at high speed when one could not see any visible components of the exciting radiation. It clearly indicated that the direct light from the UV source was completely cut out by the chopper assembly.

For the measurements of spectral energy distribution and intensities of phosphors, the proper preparation of specimen is of great importance. Further, it is necessary to maintain the same conditions throughout the measurements. The samples were first thoroughly ground to a fine powder in a small agate mortar and pestle and the ground powders were sieved through a 325 mesh sieve. The phosphors for the measurements were taken in the form of thin layer. They were applied on one side of a micro-slide (make: Micro-Aid Belgium glass) with the help of an adhesive material. The constant layer thickness was obtained taking the fixed weight and fixed area of the phosphor. The upper position of the slides were blackened to avoid direct radiations from the ultra-violet lamp. The samples were then mounted in between the two plates of chopper at the position fixed for the maximum intensity as described above.

Before taking the measurements for the intensities, the scale of the spot galvanometer was adjusted to zero.

On making the power supply on, a small deflection was observed due to the dark current even when slit of spectrometer was kept closed. This deflection was brought to zero with the help of zero adjuster in the galvanometer.

The chopper and ultra-violet lamp were then switched on. The spectrometer was set at various wave lengths and corresponding readings were taken on the galvanometer.

Readings were corrected for the photomultiplier tube response. Furthermore, this intensity corresponds to a constant slit width and the intensities for a fixed wave lengths interval i.e. $I\ d\lambda$ were obtained by multiplying the readings with the previously determined correction factor.

The graphs were plotted for intensity $I\ d\lambda$ as functions of wave lengthsλ.

X-ray diffraction studies

The x-ray powder diffraction technique was employed to check the completion of the reaction, to determine the unit cell dimensions of the mixed halophosphate and to study where these metals are substituted in the structure. The samples were filled in this glass capillaries and Debye-Scherrer patterns were taken on a 'Radon X-ray

Diffraction Machine' using type A-2 diffraction tube with copper radiations in a 9 cm. camera. The 'd' values were obtained from the powder data in the usual way and the lattice parameters were calculated from the observed 'd' values. The patterns were indexed with the help of the standard c/a-log d chart for the hexagonal system. The cation distribution was determined by visually estimating the intensities of different diffraction lines and comparing them with those calculated for different cation distributions. The details of these calculations are given later.

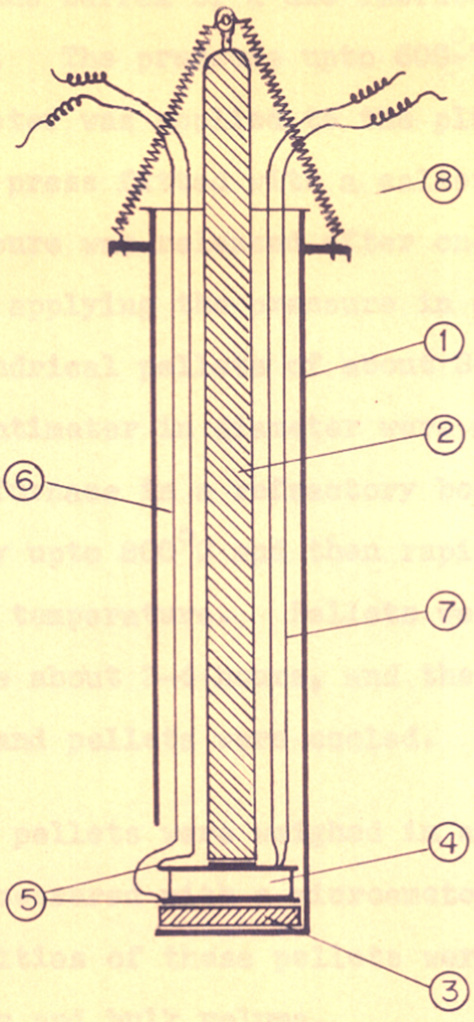
Conductivity measurements

The electrical conductivity of sintered polycrystalline samples of the various halophosphate phosphors together with that of unactivated halophosphates were measured at different temperatures to calculate the activation energies of these halophosphate phosphors.

We used the following experimental technique to study these properties.

(1) Pellet formation

About 1 g. of the finely ground powder was mixed thoroughly in an agate mortar and pestle with 1 cc. of 2% solution of polyvinyl acetate in acetone, which acted as



① SILICA TUBE, ② SILICA ROD, ③ SILICA PLATE,
④ PELLET, ⑤ PLATINUM FOILS, ⑥ PLATINUM WIRE,
⑦ THERMOCOUPLE, ⑧ SPRING.

FIG. 2. SAMPLE HOLDER ASSEMBLY FOR ELECTRICAL CONDUCTIVITY MEASUREMENTS OF PELLETS.

binder and lubricant. The powder was dried and transferred into the barrel of a die fabricated out of the die steel bar. The pressure upto 6000-7000 lbs. per square centimeter was applied to the plunger in a carver laboratory press fitted with a calibrated pressure gauge. The pressure was released after one minute and pellet removed by applying the pressure in opposite direction. Cylindrical pellets of about 3 to 4 mm. length and one centimeter in diameter were made. These were placed in a furnace in a refractory boat and were heated very slowly upto 800°C and then rapidly upto desired sintering temperature. Pellets were sintered at firing temperature about 3-4 hours, and then the furnace was switched off and pellets were cooled.

The sintered pellets were weighed in a balance and their dimensions measured with a microameter screw gauge. The apparent densities of these pellets were then calculated from their weights and bulk volume.

(2) Measuring assembly

Fig. No. 2 shows the sample holder assembly for mounting the sample pellet. It consisted of a hollow refractory tube of one centimeter diameter. At one end of this tube a groove was cut to place the pellet. On both the sides of the pellets two platinum foils nearly of the pellet size were placed. These platinum foils were soldered to two platinum wires, which in turn, were connected to two shielded wires for the measurements of conductivity. Both the platinum foils on either sides were supported by two silica discs. This refractory tube was fixed to a B19 male joint. From the other end where it was fixed with the B19 joint, a silica rod was inserted to reach the silica plate. This silica rod was flatened at the end in contact with the silica plate and had a loop on the other end. Pressure was applied with the help of a spring attached between the loop of the silica rod and a groove in the refractory tube to reduce the contact resistance. To avoid shorting of the two leads, one platinum wire was taken from inside, the other from outside the refractory tube. The platinum wires were covered with porcelain beads.

The electrical resistance measurements were carried out with the help of a Philips Conductivity bridge (P.R.9600 model) at 50 cycles. For resistance higher than 10 megΩ a R.I.E. meter (Leeds and Northrup Model No. Cat.562C) was used.

For heating the sample to high temperatures a tube furnace of nearly two inches diameter was used. Kanthal 'A' wire of 18 SWG was wound around the tube. Proper thermal insulation was provided. In this furnace another silica tube sealed at one end was placed inside where the sample was located. For the measurement of temperature a chromel-alumel thermocouple calibrated against a standard thermocouple was kept near the sample and the e.m.f. was recorded with the help of a potentiometer. For controlling and regulating the temperatures at required points, a temperature controller (Faubaugelregler medium, supplied by Hartman and Braunn, Frankfurt, W.Germany) was connected to the furnace. Another thermocouple from the furnace was attached to the temperature controller and it was possible to control the temperature at the required value.

The conductivity of the mixed halophosphate phosphors (pellets) was measured in the temperature range 25-550°C. The measurements were made in different atmospheres, namely in air and nitrogen.

Log ρ was plotted as a function of the reciprocal of absolute temperature and the activation energy was found out from the linear portions of the graph using the relationship

$$\sigma = \sigma_0 \exp \frac{-\Delta E}{kT}$$

or

$$\rho = \rho_0 \exp \frac{\Delta E}{kT}$$

$$\therefore \log \rho = \log \rho_0 \mp \frac{+\Delta E}{kT}$$

where σ = specific conductivity
ρ = specific resistance
ΔE = thermal activation energy
k = Boltzman constant
and T = absolute temperature.

Therefore, the slope of the graph of $\log_{10} \rho_0 \propto \frac{1}{T}$ would be slope = $\frac{\Delta E}{2.303 \times k}$

CHAPTER III

EXPERIMENTAL RESULTS

EXPERIMENTAL RESULTS

X-ray diffraction results

X-ray powder diffraction patterns were taken for the following compounds with the help of Cu-Kα radiation on a Debye Scherrer Camera.

Composition	Firing Temp.
$(Ca_{.5}Cd_{.5})_{10}(PO_4)_6(FCl)$	900°C
$(Ca_{.5}Mg_{.5})_{10}(PO_4)_6F_2$	1000°C
$(Ca_{.55}Be_{.45})_{10}(PO_4)_6F_2$	1000°C
$(Ca_{.90}Th_{.05}\square_{.03})_{10}(PO_4)_6F_2$	1100°C
$(Ca_{.94}Th_{.03}\square_{.03})_{10}(PO_4)_6F_2$	1100°C

Diffraction patterns showed no lines due to the free oxides, which are indications that homogeneous compounds were obtained. The patterns were indexed with the help of a standard log d chart for hexagonal system. Using the 'd' values for 'hko' reflection, a preliminary value of 'a' was calculated from the relationship:

$$a = [\tfrac{4}{3}(h^2 + k^2 + hk)]^{1/2} d$$

The preliminary value of 'c' was then calculated from the 'd' values of hkl reflections with small h, k and large ℓ . For these calculations the value of 'a' determined above was used. Now with the help of this value of 'c', the 'a' value was recalculated from the reflections with high h, k and small ℓ . This process of successive refinement was continued until the values of 'a' and 'c' became constant. The final values of 'a' and 'c' were then used to calculate the 'd' values for all the observed reflections. The observed and the calculated 'd' values together with intensities of the observed reflections and the calculated 'a' and 'c' values were recorded in Table Nos. 4 to 8. The observed values for a standard pattern are given in Table Nos. 2 and 3.

Patterns were also taken of phosphors containing activators and co-activators. The compounds chosen were the ones which gave the best fluorescence. However, no significant difference in intensity as compared to the unactivated compounds was observed. Similarly, patterns were taken of phosphors mentioned above containing Pb and Mn heated at higher temperatures. However, they also did not show any significant difference.

Table 2

X-ray diffraction data of the standard calcium fluorophosphate

No.	Intensity	d Å	hkl
1	VW	4.06	-
2	VW	3.88	-
3	W	3.45	002
4	VW	3.17	102
5	W	3.07	120
6	VS	2.79	121
7	M	2.78	112
8	S	2.70	300
9	W	2.62	202
10	VW	2.51	301
11	VW	2.29	122
12	M	2.25	130
13	VW	2.22	-
14	VW	2.13	131
15	VW	2.06	113
16	VW	1.99	203
17	M	1.93	222
18	W	1.88	132
19	VW	1.86	-
20	M	1.84	123
21	W	1.80	231
22	W	1.77	140
23	W	1.74	402
24	VW	1.72	004

VS - very strong; S - strong; MS - medium strong; M - medium; W - weak; VW - very weak.

Table 3

X-ray diffraction data of the standard calcium chloro-fluorophosphate

No.	Intensity	d Å	hkl
1	VW	408	-
2	VW	3.88	-
3	M	3.44	002
4	VW	3.17	-
5	W	3.08	120
6	VS	2.81	121
7	M	2.78	112
8	S	2.71	300
9	M	2.63	202
10	VW	2.59	301
11	VW	2.29	122
12	M	2.25	130
13	VW	2.23	-
14	VW	2.14	131
15	VW	2.10	113
16	VW	2.00	203
17	M	1.94	222
18	W	1.89	132
19	VW	1.87	-
20	M	1.84	123
21	W	1.80	231
22	W	1.78	140
23	W	1.75	402
24	VW	1.72	004

Table 4

X-ray diffraction data of (Ca,Cd)chlorofluoro phosphate

No.	INtensity	d_{obs}	d_{cal}	hkl
1	M	3.327	3.327	002
2	MS	3.069	3.069	102
3		2.802	2.792	120
4	VS	2.783	2.783	121
5	VS	2.753	2.733	112
6		2.733	2.730	300
7	VW	2.584	2.584	202
8	VW	2.485	2.505	301
9	W	2.248	2.258	122
10		2.228	2.240	130
11	VW	2.139	2.139	131
12	W	2.01	2.01	113
13	M	1.911	1.911	222
14	M	1.881	1.880	132
15	MS	1.812	1.811	123
16	M	1.753	1.755	140

Table 5

X-ray diffraction data for (Ca,Mg) fluorophosphate

No.	Intensity	d_{obs}	d_{cal}	hkl
1	W	4.05	-	-
2	W	3.772	-	-
3	MS	3.390	3.391	002
4	VW	3.126	3.126	102
5	VW	3.050	3.050	120
6	VS	2.763	2.772	121
7		2.753	2.743	112
8	M	2.634	2.624	300
9	MW	2.594	2.594	202
10	W	2.426	2.446	301
11	VW	2.268	2.268	122
12	M	2.218	2.238	130
13	W	2.040	2.040	113
14	W	1.911	1.911	222
15	M	1.862	1.862	132
16	M	1.822	1.812	123

Table 6

X-ray diffraction data for (Ca,Be) fluorophosphate

No.	Intensity	d_{obs}	d_{cal}	hkl
1	W	3.594	3.594	-
2	MS	3.43	3.43	002
3	VW	3.08	3.07	102
4	W	2.810	2.800	120
5	VS	2.763	2.763	121
6		2.753	2.753	112
7	MW	2.690	2.680	300
8	W	2.594	2.601	202
9	VW	2.456	2.486	301
10	VW	2.268	2.258	122
11	MW	2.118	2.118	130
12	VW	2.109	2.109	131
13	VW	2.00	2. 02	113
14	M	1.921	1.911	222
15		1.862	1.862	132
16	VW	1.753	1.753	140

Table 7

X-ray diffraction data for the (Ca,Th)halophosphates with $(Ca_{.94}Th_{.03})$

No.	Intensity	d_{obs}	d_{cal}	hkl
1	W	4.03	4.01	-
2	M	3.365	3.364	002
3	W	3.196	3.186	-
4	M	3.055	3.055	120
5	VS	2.798	2.798	121
6	M	2.781	2.783	112
7	MS	2.702	2.703	300
8	M	2.602	2.612	202
9	VW	2.490	2.480	301
10	VW	2.28	2.28	122
11	W	2.253	2.254	130
12	W	2.134	2.144	131
13	W	1.983	1.993	203
14	M	1.940	1.984	222
15	W	1.88	1.88	132
16	M	1.870	1.875	-
17	M	1.720	1.730	004

Table 8

X-ray diffraction data for the (Ca,Th)halophosphate with ($Ca_{.90}Th_{.05}$)

No.	Intensity	d_{obs}	d_{cal}	hkl
1	W	4.03	4.02	-
2	M	3.395	3.390	002
3	W	3.190	3.190	-
4	M	3.065	3.065	120
5	VS	2.785	2.788	121
6	M	2.76	2.765	112
7	MS	2.690	2.680	300
8	M	2.590	2.590	202
9	VW	2.534	2.524	301
10	VW	2.28	2.28	122
11	W	2.24	2.24	130
12	VW	2.20	2.20	-
13	W	2.14	2.14	131
14	W	1.97	1.97	203
15	M	1.93	1.93	222
16	W	1.87	1.86	132
17	M	1.82	1.83	123
18	M	1.72	1.73	004

	Composition	Firing Temp.
1.	$(Ca_{.5}Cd_{.5})_{10}(PO_4)_6F_2$ (5% Pb + 0.5% Mn)	900°C
2.	$(Ca_{.5}Mg_{.5})_{10}(PO_4)_6F_2$ (7% Pb + 2% Mn)	1000°C
3.	$(Ca_{.55}Be_{.45})_{10}(PO_4)\ F_2$ (3% Pb + 0.5% Mn)	1000°C
4.	$(Ca_{.90}Th_{.05}\square_{.05})_{10}(PO_4)_6F_2$ (3% Sb + 1% Mn)	1100°C
5.	$(Ca_{.94}Th_{.03}\square_{.03})_{10}(PO_4)_6F_2$	1100°C
6.	$(Ca_{.5}Cd_{.5})_{10}(PO_4)_6F_2$ (5% Pb : 0.5% Mn)	1100°C
7.	$(Ca_{.5}Mg_{.5})_{10}(PO_4)_6F_2$ (7 % Pb + 2% Mn)	1150°C

Lead-manganese and antimony-manganese activated halophosphate phosphors

During the course of preliminary work it was found that mixed halophosphate phosphors containing lead-manganese and antimony-manganese as impurities when fired in air underwent slight oxidation and gave poor luminescence. However, firing the phosphor mixtures under purified nitrogen gas atmosphere improved the intensities of these phosphors considerably. Thus, most of our work on the synthesis of Pb-Mn and Sb-Mn activated mixed halophosphate phosphors was carried out under nitrogen gas atmosphere, though the effect of the other atmosphere was also studied as one of the parameters in the investigation.

Calcium-cadmium halophosphate phosphors

1. Activated by lead-manganese

Calcium-cadmium halophosphate phosphors having the chemical formula

$$(Ca_{.5}Cd_{.5})_9(PO_4)_6(Ca_{.5}Cd_{.5})(F\ Cl)$$

were first prepared. The appropriate mixture was heated at 900°C for about one hour in air. Lead as primary activator and manganese as secondary activator were then added in the form of oxide and carbonate respectively and refired in the nitrogen gas atmosphere at 900°C for about one hour. Lead concentration was varied from 0 to 9% by wt. of the basic matrix and manganese was varied from 0-3% respectively. The effect of lead and manganese on (i) spectral energy distribution of emitted light, (ii) relative brightness, and (iii) electrical conductivity was studied. Spectral energy distribution, relative brightness, the crystal structure and the electrical conductivity of these phosphors were measured using the technique discussed in the last chapter.

The result on relative brightness and colour of fluorescence of (Ca-Cd) halophosphate phosphors activated by lead-manganese and excited by the low pressure mercury vapor discharge ultra-violet lamp are recorded in the Table No.9.

Results in the Table No.9 for a typical series of calcium-cadmium halophosphate phosphors fired at 900°C for about one,hour,indicate that phosphors synthesized without addition of lead-manganese gave no fluorescence, further it was observed that lead alone produced weak blue fluorescence, and manganese alone produced no photoluminescence, but in the presence of lead it gave rise to a range colours from pale blue to orange red according to the amount present and the composition of the matrix. Good luminescence intensity was obtained from the phosphors which were prepared with lead and manganese contents 3 to 7 and 0.5 - 1% by the wt. of the matrix. It was further observed that increase in concentration of lead and manganese in phosphors shifted the colour of fluorescence from pale blue to orange and finally to deep pinkish-orange. Above 3 to 4% of manganese the fluorescence property was almost lost.

Table 9

Effect of lead-manganese concentration on intensity of (Ca,Cd)halophosphate phosphors

Phosphors mixtures were fired under nitrogen gas atmosphere at 875-900°C for about one hour.

Composition	Sensitizer	Activator		Colour of fluorescence	Relative brightness
(Ca,Cd)chloro-fluorophosphate	1% Pb	-		Blue	W
-do-	1% Pb	0.2%	Mn	Pale orange	W
-do-	1% Pb	0.5%	Mn	Orange	MS
-do-	1% Pb	1.0%	Mn	Pinkish-orange	MS
-do-	1% Pb	2.0%	Mn	Pinkish-orange	W
-do-	1% Pb	3.0%	Mn	Dull-pinkish-orange	W
(Ca,Cd)chloro-fluorophosphate	3% Pb	-		Blue	W
-do-	3% Pb	0.2%	Mn	Pale orange	W
-do-	3% Pb	0.5%	Mn	Orange	MS
-do-	3% Pb	1.0%	Mn	Pinkish-orange	S
-do-	3% Pb	2.0%	Mn	Pinkish-orange	M
-do-	3% Pb	3.0%	Mn	Dull-pinkish-orange	W
(Ca,Cd)chloro-fluorophosphate	5% Pb	-		Blue	W
-do-	5% Pb	0.2%	Mn	Pale orange	MS
-do-	5% Pb	0.5%	Mn	Orange	VS
-do-	5% Pb	1.0%	Mn	Pinkish-orange	VS
-do-	5% Pb	2.0%	Mn	Pinkish-orange	W
-do-	5% Pb	3.0%	Mn	Dull-pinkish-orange	W
(Ca,Cd)chloro-fluorophosphate	7% Pb	-		Blue	W
-do-	7% Pb	0.2%	Mn	Orange	M
-do-	7% Pb	0.5%	Mn	Pinkish-orange	S
-do-	7% Pb	1.0%	Mn	Pinkish-orange	M
-do-	7% Pb	2.0%	Mn	Dull-pinkish-orange	W
(Ca,Cd)chloro-fluorophosphate	9% Pb	-		Blue	VW
	9% Pb	0.2%	Mn	Orange	M
-do-	9% Pb	0.5%	Mn	Pinkish-orange	MS
-do-	9% Pb	1.0%	Mn	Pinkish-orange	MS
-do-	9% Pb	2.0%	Mn	Dull-pinkish-orange	W

The colour of the phosphor materials after the firing was found to be slightly dependent on the manganese content. The phosphor free of manganese or with low manganese content were white in colour. At higher concentrations of manganese the pink colour became prominent. Lead had no effect on the colour of phosphors.

Effect of different firing temperatures on intensity of phosphors

The phosphor mixtures were heated at different temperatures to find out the effect of firing temperatures on the intensity of phosphors. The brightest phosphors from (Ca-Cd) halophosphate (containing 5% lead and 0.5% Mn) was selected and was heated at different firing temperatures from 700 - 1100 °C in the nitrogen gas atmosphere.

The results are recorded in Table No.10 and it can be seen from the table that below 800°C and above 1000°C the intensity decreased. However, the colour of the fluorescence remained more or less the same.

Effect of annealing and quenching on the intensity of phosphors

The effect of slow and fast cooling after firing on the fluorescence intensities were studied. The brightest phosphor from calcium-cadmium halophosphate phosphors(containing

Table 10

Effect of firing temperature on intensity of calcium-cadmium halophosphate phosphors

with (i) Lead 5% by the wt. of the matrix, and (ii) Manganese 0.5% by the wt. of the matrix.

Phosphors fired under a nitrogen gas atmosphere at various temperatures for about one hour.

Composition	Firing Temp. °C	Phosphor colour	Colour of fluorescence	Relative brightness
(Ca,Cd)halophosphate	700	Pinkish-white	Faint orange	W
-do-	800	White	Orange	VS
-do-	900	White	Orange	VS
-do-	1000	White	Orange	M
-do-	1100	White	Dull orange	M

5% Pb and 0.5% Mn) were fired at 900°C in nitrogen gas atmosphere. In annealing experiment, phosphor was slowly cooled to the room temperature while in the quenching experiment the sample was very rapidly cooled to room temperature.

The results are recorded in the Table No.11 and it was found that there was no change of fluorescence colour, but intensity was much reduced by the quenching treatment.

Electrical conductivity measurements

The compounds under investigation were sintered in the form of pellets by the method described earlier. The apparent densities were calculated from the weight and the dimensions of the pellets.

Electrical resistivity was measured at various temperatures ranging from room temperature to about 550°C. Plots of log ρ vs 1/T are shown in Fig.3 for the compounds (i) (Ca,Cd) halophosphate with Pb + Mn in air, (ii) (Ca,Cd) halophosphate with Pb + Mn in nitrogen, and (iii) (Ca,Cd) halophosphate without Pb + Mn in air. ρ is specific resistivity and T, the temperature in °K. The electrical resistance remains practically unchanged in the temperature range 25-280°C, beyond which it starts dropping rapidly. In

Table 11

Effect of annealing and quenching after the final firing on intensity of calcium-cadmium halophosphate phosphors
with (i) Lead 5% by the wt. of matrix,
and (ii) Manganese 0.5% by the wt. of matrix.

Phosphors fired under a nitrogen gas atmosphere at 900°C in the same rate, but cooled in different ways.

Composition	Way of cooling	Colour of phosphor	Colour of fluorescence	Relative brightness
(Ca,Cd)halophosphate	Slow-cooling	White	Orange	Vs
-do-	Fast-Cooling	White	Orange	W

S - strong; MS - medium strong; M - medium;

W - weak; VW - very weak.

Table 12

Electrical resistivity data of some halophosphates

Composition	Atmosphere	Resistance at room temp.°	Activation energy	
			a	b
(Ca,Cd)halophosphate with Pb + Mn	Air	4.5×10^9	1.1	0.40
(Ca,Cd)halophosphate with Pb + Mn	Nitrogen	4.4×10^9	1.648	0.424
(Ca,Cd)halophosphate without Pb + Mn	Air	4.4×10^9	1.16	0.56

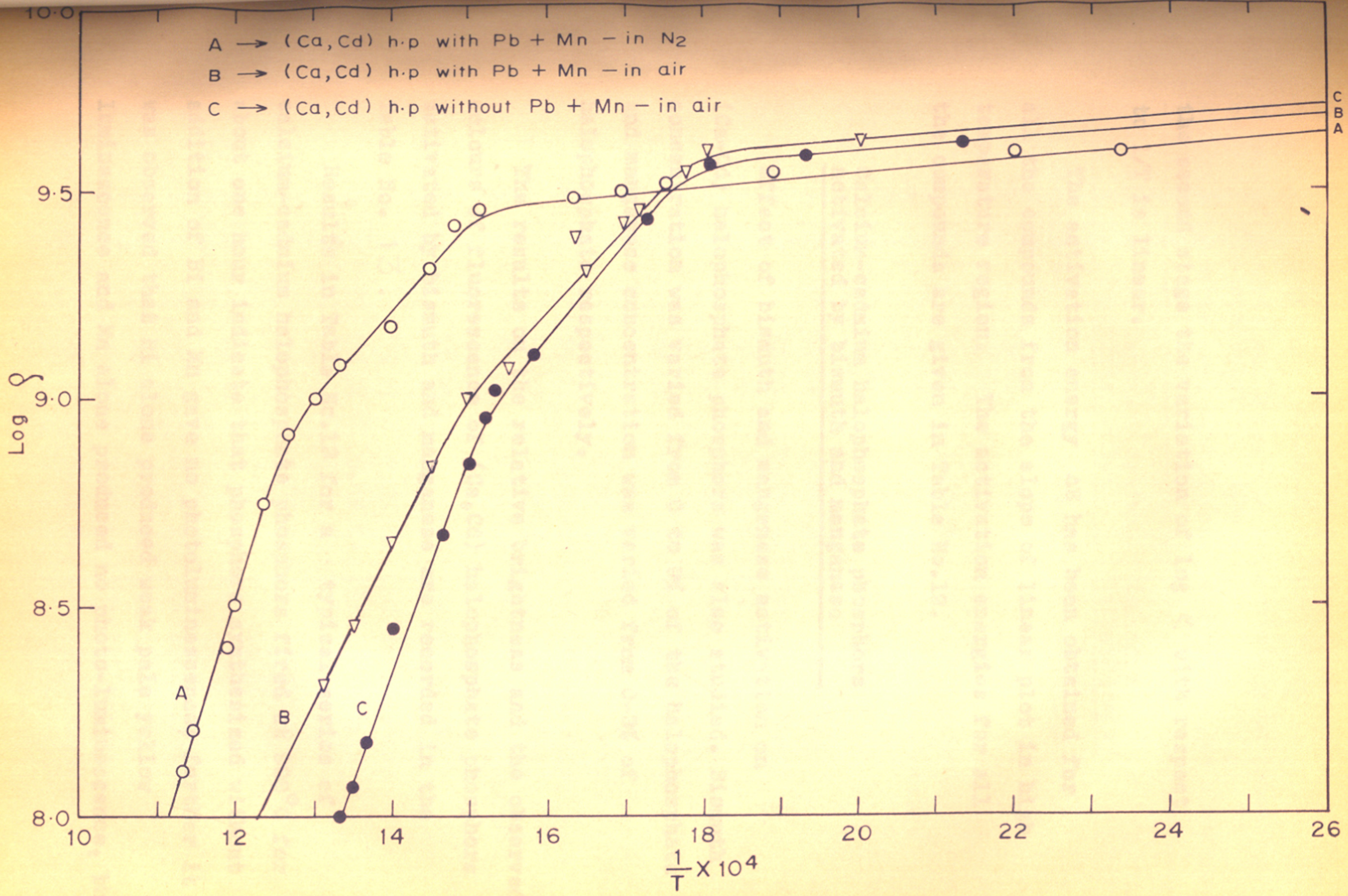

A → (Ca, Cd) h·p with Pb + Mn – in N_2
B → (Ca, Cd) h·p with Pb + Mn – in air
C → (Ca, Cd) h·p without Pb + Mn – in air
Log ρ
10.0
9.5
9.0
8.5
8.0
10
12
14
16
18
20
22
24
26
$\frac{1}{T} \times 10^4$
A
B
C
C
B
A

FIG · 3

the second stage the variation of log ρ with respect to 1/T is linear.

The activation energy ΔE has been obtained for all the compounds from the slope of linear plot in high temperature region. The activation energies for all the compounds are given in Table No.12.

Calcium-cadmium halophosphate phosphors activated by bismuth and manganese

Effect of bismuth and manganese activation on (Ca-Cd) halophosphate phosphors was also studied. Bismuth concentration was varied from 0 to 9% of the halophosphate and manganese concentration was varied from 0-3% of halophosphate respectively.

The results on the relative brightness and the observed colours of fluorescence of (Ca,Cd) halophosphate phosphors activated by bismuth and manganese are recorded in the Table No. 13 .

Results in Table No.13 for a typical series of calcium-cadmium halophosphate phosphors fired at 900°C for about one hour indicate that phosphors synthesized without addition of Bi and Mn gave no photoluminescence; further it was observed that Bi alone produced weak pale yellow luminescence and Mn alone produced no photo-luminescence, but

Table 13

Effect of bismuth and manganese concentration on intensity of (Ca,Cd) halophosphate phosphors

Phosphor mixtures were heated under a nitrogen gas atmosphere at 875-900°C for about one hour

Composition	Sensitizer	Activator	Colour of fluorescence	Relative brightness
(Ca,Cd)chloro-fluophosphate	1% Bi	~~0.2% Mn~~	Faint yellow	W
-do-	1% Bi	0.2% Mn	Orange	W
-do-	1% Bi	0.5% Mn	Pinkish-orange	M
-do-	1% Bi	1.0% Mn	Pinkish-orange	M
-do-	1% Bi	2.0% Mn	Dull-pinkish-orange	VW
(Ca,Cd)chloro-fluorophosphate	3% Bi	-	Faint yellow	VW
-do-	3% Bi	0.2% Mn	Orange	W
-do-	3% Bi	0.5% Mn	Pinkish-orange	M
-do-	3% Bi	1.0% Mn	Pinkish-orange	M
-do-	3% Bi	2.%% Mn	Dull pinkish-orange	W
(Ca,Cd)chloro-fluorophosphate	5% Bi	-	Pale yellow	W
-do-	5% Bi	0.2% Mn	Yellowish-orange	W
-do-	5% Bi	0.5% Mn	Pinkish-orange	MS
-do-	5% Bi	1.0% Mn	Pinkish-orange	MS
-do-	5% Bi	2.0% Mn	Deep pinkish-orange	W
(Ca,Cd)chloro-fluorophosphate	7% Bi	-	Pale yellow	VW
-do-	7% Bi	0.2% Mn	Yellowish-orange	M
-do-	7% Bi	0.5% Mn	Pinkish-orange	MS
-do-	7% Bi	1.0% Mn	Pinkish-orange	MS
-do-	7% Bi	2.0% Mn	Deep pinkish-orange	W
(Ca,Cd)chloro-fluorophosphate	9% Bi	-	Pale yellow	VW
-do-	9% Bi	0.2% Mn	Yellowish-orange	M
-do-	9% Bi	0.5% Mn	Pinkish-orange	MS
=do-	9% Bi	1.0% Mn	Pinkish-orange	MS
-do-	9% Bi	2.0% Mn	Deep pinkish-orange	W

in presence of Bi, it gave rise to a range of colours from weak pale yellow to orange-red according to the amount of Mn present and composition of matrix. Good luminescence intensity was obtained from the phosphors which were prepared with Bi and Mn contents 3 to 7% and 0.5 to 1% of the halophosphate respectively. It was further observed that increase in the concentration of Bi and Mn in phosphors shifted the colour of fluorescence ~~from~~ to orange and finally to deep orange. Above 3 to 4% of Mn the fluorescence property was almost lost.

Calcium-magnesium halophosphate phosphors activated by lead and manganese

Calcium-magnesium halophosphate, having the chemical formula

$$(Ca_{0.5}: Mg_{0.5})_9(PO_4)_6(Ca_{0.5} : Mg_{0.5})F_2$$

was first prepared by heating the approximate mixture in the range of 975-1000°C for about one hour. Lead and manganese were added in the form of oxide and carbonate respectively. The mixture was then refired at 1000°C in the nitrogen gas atmosphere for about one hour. Lead concentrations were varied from 0-9% and Mn from 0-5% of matrix respectively. The effect of lead and manganese on (i) spectral energy distribution of emitted light, (ii) relative brightness, and (iii) electrical conductivity, was studied.

The results on the relative brightness and observed colours of fluorescence under the ultra-violet radiation of these phosphors are recorded in the Table No.14.

Results in Table No.14 for a typical series of calcium-magnesium halophosphate phosphors fired at room temperature for about one hour indicate that phosphors synthesized without lead and manganese or with Mn but without Pb gave no photo-luminescence. However, lead alone produced a weak blue-luminescence. In the presence of both lead and manganese the emission ranged from pale blue to yellow and finally deep yellow according to the manganese concentration and the composition of the matrix. Good luminescence intensity was obtained from the phosphors which were prepared with lead content of 3 to 7 and manganese content of 0.5 to 3% by the wt. of the matrix respectively. It was further observed that increase in the concentration of lead and particularly of manganese in the phosphors shifted the colour of fluorescence from blue to yellow and finally to deep yellow. Above 5% of manganese, the fluorescence property was almost lost. As regards the appearance of phosphors after the firing, it was observed that the colours of the phosphor material varied with the manganese concentration. The phosphors

Table 14

Effect of lead and manganese concentration on the intensity of calcium-magnesium halophosphate phosphors

Phosphor mixtures were fired under nitrogen gas atmosphere at about 1000°C for about one hour

Composition	% of sensitizer	% of Mn	Colour of phosphor	Colour of fluorescence	Relative brightness
(Ca,Mg)halophosphate	1% Pb	-	White	Blue	W
-do-	1% Pb	0.5% Mn	White	Pale-yellow	MS
-do-	1% Pb	1.0% Mn	White	Yellow	
-do-	1% Pb	2.0% Mn	Faint pink	Deep yellow	MS
-do-	1% Pb	3.0% Mn	Faint pink	Dull yellow	MS
(Ca,Mg)halophosphate	3% Pb	-	White	Blue	W
-do-	3% Pb	0.5% Mn	White	Pale-yellow	S
-do-	3% Pb	1.0% Mn	White	Yellow	S
-do-	3% Pb	2.0% Mn	White	Yellow	MS
-do-	3% Pb	3.0% Mn	Faint pink	Deep yellow	MS
-do-	3% Pb	4.0% Mn	Faint pink	Deep yellow	W
(Ca,Mg)halophosphate	5% Pb	-	White	Blue	W
-do-	5% Pb	0.5% Mn	White	Pale-yellow	S
-do-	5% Pb	1.0% Mn	White	Yellow	S
-do-	5% Pb	2.0% Mn	White	Yellow	MS
-do-	5% Pb	3.0% Mn	Faint pink	Deep-yellow	MS
-do-	5% Pb	4.0% Mn	Faint pink	Dull-yellow	W

Table 14 continue ....

Composition	% of sensitizer	% of Mn	Colour of phosphor	Colour of fluorescence	Relative brightness
(Ca,Mg)halophosphate	7% Pb	-	White	Blue	W
-do-	7% Pb	0.5% Mn	White	Pale-yellow	S
-do-	7% Pb	1.0% Mn	White	Yellow	S
-do-	7% Pb	2.0% Mn	White	Yellow	MS
-do-	7% Pb	3.0% Mn	Faint pink	Deep yellow	S
-do-	7% Pb	4.0% Mn	Faint pink	Dull yellow	W
(Ca,Mg)halophosphate	9% Pb	-	White	Blue	W
-do-	9% Pb	0.5% Mn	White	Pale-yellow	S
-do-	9% Pb	0.1% Mn	White	Yellow	S
-do-	9% Pb	2.0% Mn	White	Yellow	MS
-do-	9% Pb	3.0% Mn	Faint pink	Deep yellow	MS
-do-	9% Pb	4.0% Mn	Faint pink	Dull yellow	W

free of Mn or with low manganese content were white in appearance. At the higher concentration of Mn, the phosphors were slightly pinkish in appearance; variation in the concentration of lead had no effect on the colour of these phosphors.

Effect of different firing temperatures on the intensity of phosphors

The phosphors were heated at different temperatures to find out the effect of firing temperatures on the emission intensities. The brightest phosphor from the calcium-magnesium halophosphate series having lead and manganese concentrations 7% and 2% respectively, was obtained when the firing was done in the range between 800-1150°C in a nitrogen gas atmosphere.

The results are recorded in the Table No.15 and it was observed that below 950°C and above 1050°C the intensity decreased. However, the colour of the fluorescence remained the same.

The effect of annealing and quenching on the intensity of phosphors

The effect of slow and fast cooling, after firing, on fluorescence intensity was also studied. The brightest

Table 15

Effect of firing temperature on the intensity of calcium-magnesium halophosphate phosphors with (i) lead 7% by the wt. of the matrix, and (ii) manganese 2% by the wt. of the matrix.

Phosphors fired under a nitrogen gas atmosphere at various temperatures for about one hour.

Composition	Firing temp. °C	Phosphor colour	Colour of fluorescence	Relative brightness
(Ca,Mg)halophosphate	775	White	Pale yellow	W
-do-	850	White	Yellow	M
-do-	925	White	Yellow	S
-do-	1000	White	Yellow	VS
-do-	1075	White	Yellow	S
-do-	1150	White	Dull yellow	M

phosphor containing 7% Pb and 2% Mn by the wt. of the matrix respectively were fired at 1000°C in the nitrogen gas atmosphere. In annealing experiment the phosphor was slowly cooled to the room temperature within 7-8 hours, while in the quenching experiment phosphor was cooled fast in less than 15 minutes in nitrogen gas atmosphere.

The results are recorded in the Table No.16 and it was found that there was no change in the intensity in case of quenched phosphor.

Electrical conductivity

The compounds under investigation were sintered in the form of pellets by the method described earlier. The apparent densities were calculated from the weight and the dimensions of the pellets.

Electrical resistivity was measured at various temperatures ranging from room temperature to about 500°C. Plots of log ρ vs 1/T are shown in Fig.4 for the compounds (i) (Ca,Mg) halophosphate with Pb + Mn in air, (ii) (Ca,Mg) halophosphate with Pb + Mn in nitrogen gas atmosphere, and (iii)(Ca,Mg) halophosphate without Pb + Mn in air. The electrical resistivity remained practically unchanged in temperature range 25-280°C and then showed a rapid fall. In the second

Table 16

Effect of annealing and quenching after the final firing on the intensity of calcium-magnesium halophosphate phosphors with (i) lead 7% by the wt. of matrix, and (ii) manganese 2% by the wt. of matrix.

Phosphors fired under a nitrogen gas atmosphere at 1000°C at the same rate, but cooled in different ways.

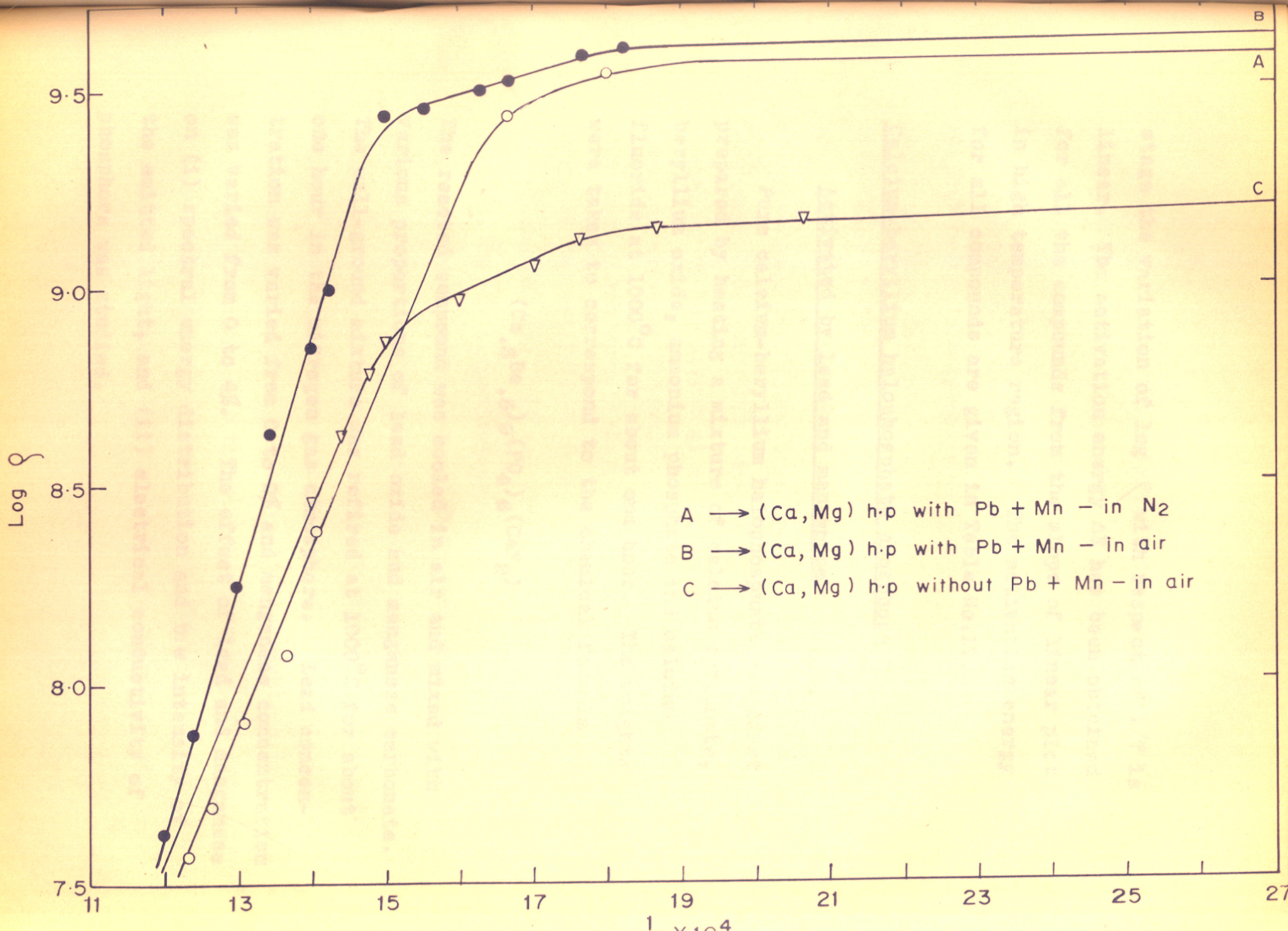
Composition	Way of cooling	Colour of phosphor	Colour of fluorescence	Relative brightness
(Ca,Mg)halo-phosphate	Slow-cooling	White	Yellow	VS
-do-	Rapid cooling	White	Pale yellow	VS

VS - very strong.

Table 17

Electrical resistivity data of some halophosphates

Composition	Atmos-phere	Resistance at room temp.	Activation energy	
			a	b
(Ca,Mg)halophosphate with Pb + Mn	Air	4×10^9	0.8	0.14
(Ca,Mg)halophosphate with Pb + Mn	Nitrogen gas	4.5×10^9	0.95	0.21
(Ca,Mg)halophosphate without Pb + Mn	Air	12×10^8	1.00	0.150



B
A
C
9·5
9·0
8·5
8·0
7·5
Log ρ
11
13
15
17
19
21
23
25
27
$\frac{1}{T} \times 10^4$
A ⟶ (Ca, Mg) h·p with Pb + Mn – in N₂
B ⟶ (Ca, Mg) h·p with Pb + Mn – in air
C ⟶ (Ca, Mg) h·p without Pb + Mn – in air

FIG·4

stage the variation of log ρ with respect of 1/T is linear. The activation energy ΔE has been obtained for all the compounds from the slope of linear plot in high temperature region. The activation energy for all compounds are given in Table No.17.

Calcium-beryllium halophosphate phosphors

Activated by lead and manganese

Pure calcium-beryllium halophosphate was first prepared by heating a mixture of calcium carbonate, beryllium oxide, ammonium phosphate and calcium fluoride at 1000°C for about one hour. The weights were taken to correspond to the chemical formula

$$(Ca_{.5}Be_{.5})_9(PO_4)_6(CaF_2)$$

The reacted compound was cooled in air and mixed with various proportions of lead oxide and manganese carbonate. The well-ground mixture was refired at 1000°C for about one hour in the nitrogen gas atmosphere. Lead concentration was varied from 0 to 9% and manganese concentration was varied from 0 to 4%. The effect of lead and manganese on (i) spectral energy distribution and the intensity of the emitted light, and (ii) electrical conductivity of phosphors was studied.

The results on the relative brightness and the observed colours of fluorescence of these phosphors are recorded in Table No.18.

Results in Table No.18 for a typical series of (Ca,Be) halophosphate phosphors fired at 1000°C for about one hour indicate that as usual the phosphors synthesized without lead (with or without Mn) gave no fluorescence. Lead alone produced a weak blue fluorescence, but in the presence of Mn it gave rise to range of colours from weak blue to deep yellow, according to the amount of manganese present in matrix. Good luminescence intensity was obtained from the phosphors which were prepared with lead and manganese contents respectively of 3 to 7 and 0.5 to 1% by the wt. of the matrix. It was further observed that increase in the concentrations of lead and manganese in phosphors shifted the colour of luminescence from blue to yellow and finally to deep yellow. Above 4% of manganese, the luminescent property was almost lost. As regards the appearance of phosphors,after firing, it was observed that colours were slightly dependent on the manganese content. At higher concentration of manganese slight pink colour was observed, otherwise all phosphors are white in colour, while lead has no effect on the colour of phosphors.

Table 18

Effect of lead and manganese concentration on the intensity of calcium-beryllium halophosphate phosphors

Phosphor mixtures were fired under nitrogen gas atmosphere at about 1000°C for about one hour

Composition	% of sensitizer	% of activator	Colour of phosphor	Colour of fluorescence	Relative brightness
(Ca,Be)halophosphate	1% Pb	-	White	Blue	VW
-do-	1% Pb	0.5 % Mn	White	Yellow	M
-do-	1% Pb	1 % Mn	White	Yellow	S
-do-	1% Pb	2% Mn	Faint pink	Yellow	S
	1% Pb	3 % Mn	Faint pink	Yellow	M
-do-	3% Pb	-	White	Blue	VW
-do-	3% Pb	0.5 % Mn	White	Yellow	VS
-do-	3% Pb	1 % Mn	White	Yellow	S
-do-	3% Pb	2 % Mn	Faint pink	Yellow	M
-do-	3% Pb	3% Mn	Faint pink	Dull yellow	M
-do-	5% Pb	-	White	Blue	W
-do-	5% Pb	0.5 % Mn	White	Yellow	MS
-do-	5% Pb	1 % Mn	White	Yellow	MS
-do-	5% Pb	2 % Mn	Faint pink	Yellow	M
-do-	5% Pb	3 % Mn	Faint pink	Dull yellow	W

Table 18 .. continue

Composition	% of sensitizer	% of activator	Colour of phosphor	Colour of fluorescence	Relative brightness
(Ca,Be)halophosphate	7% Pb	-	White	Blue	W
-do-	7% Pb	0.5 % Mn	White	Pale yellow	MS
-do-	7% Pb	1 % Mn	White	Yellow	MS
-do-	7% Pb	2 % Mn	Faint pink	Yellow	M
-do-	7% Pb	3 % Mn	Faint pink	Dull yellow	W
-do-	9% Pb	-	White	Blue	W
-do-	9% Pb	0.5 % Mn	White	Pale yellow	MS
-do-	9% Pb	1 % Mn	White	Yellow	MS
-do-	9% Pb	2 % Mn	Faint pink	Yellow	M
-do-	9% Pb	3 % Mn	Faint pink	Dull yellow	VW

The effect of different firing temperatures on the intensity of phosphors

The phosphor mixtures were heated at different temperatures to find out the effect of temperatures on the intensity of phosphors. The brightest phosphor~~s~~ from (Ca,Be) halophosphate i.e. the one containing 3% lead and 0.5% manganese was fired at different temperatures from 800-1150°C in the nitrogen gas atmosphere.

The results are recorded in the Table No.19 and it is observed that the intensity increases as the firing temperature increases, reaches a maximum when the temperature is 1050°C, beyond which it starts decreasing. However, the colour of fluorescence, more or less, remains the same.

Effect of annealing and quenching of the phosphors on the emission intensity

The effect of slow and fast cooling, after the final firing, on the fluorescence intensities was studied. The brightest phosphor containing 3% Pb and 0.5% Mn was fired at 1000°C in the nitrogen gas atmosphere and annealed or quenched as usual. The results are recorded in the

Table 19

Effect of firing temperature on intensity of calcium-beryllium halophosphate phosphors with
(i) lead - 3% by the wt. of the matrix, and
(ii) manganese - 0.5% by the wt. of the matrix

Phosphors fired under a nitrogen gas atmosphere at various temperatures for about one hour

Composition	Firing temp. °C	Colour of phosphor	Colour of fluorescence	Relative brightness
(Ca,Be)halophosphate	775	White	Pale yellow	W
-do-	850	White	Pale yellow	W
-do-	925	White	Yellow	S
-do-	1000	White	Yellow	VS
-do-	1075	White	Deep yellow	M
-do-	1150	White	Dullyellow	W

the Table No.20. Neither the fluorescence colour nor intensity of the phosphors showed any detectable change.

Electrical conductivity

The compounds under investigation were sintered in the form of circular pellets by the method described earlier. The apparent densities were calculated from the weight and the dimensions of the pellets.

Electrical resistivity was measured at various temperatures ranging from room temperature to about 550°C. Plots of log ρ vs 1/T shown in Fig.5 for compounds (i) (Ca,Be) halophosphate with Pb + Mn in air, (ii) (Ca,Be) halophosphate with Pb + Mn in nitrogen, and (iii) (Ca,Be) halophosphate without Pb + Mn in air. The electrical resistance remains practically unchanged in the temperature range 25-280°C beyond which it starts dropping rapidly. In the second stage the variation of log ρ with respect to 1/T is linear. The activation energy ΔE has been obtained for all the compounds from the slope of this linear plot in high temperature region. The activation energies for all the compounds are given in Table No.21.

The variation of intensity as a function of manganese or lead concentrations are given in Figs. 6,7 and 8 for

Table 20

Effect of annealing and quenching after the final firing on intensity of calcium-beryllium halophosphate phosphors with (i) lead - 3% by the wt. of matrix, and (ii) manganese - 0.5% by wt. of matrix.

Phosphors fired under a nitrogen gas atmosphere at 1000°C for about one hour and cooled in different ways.

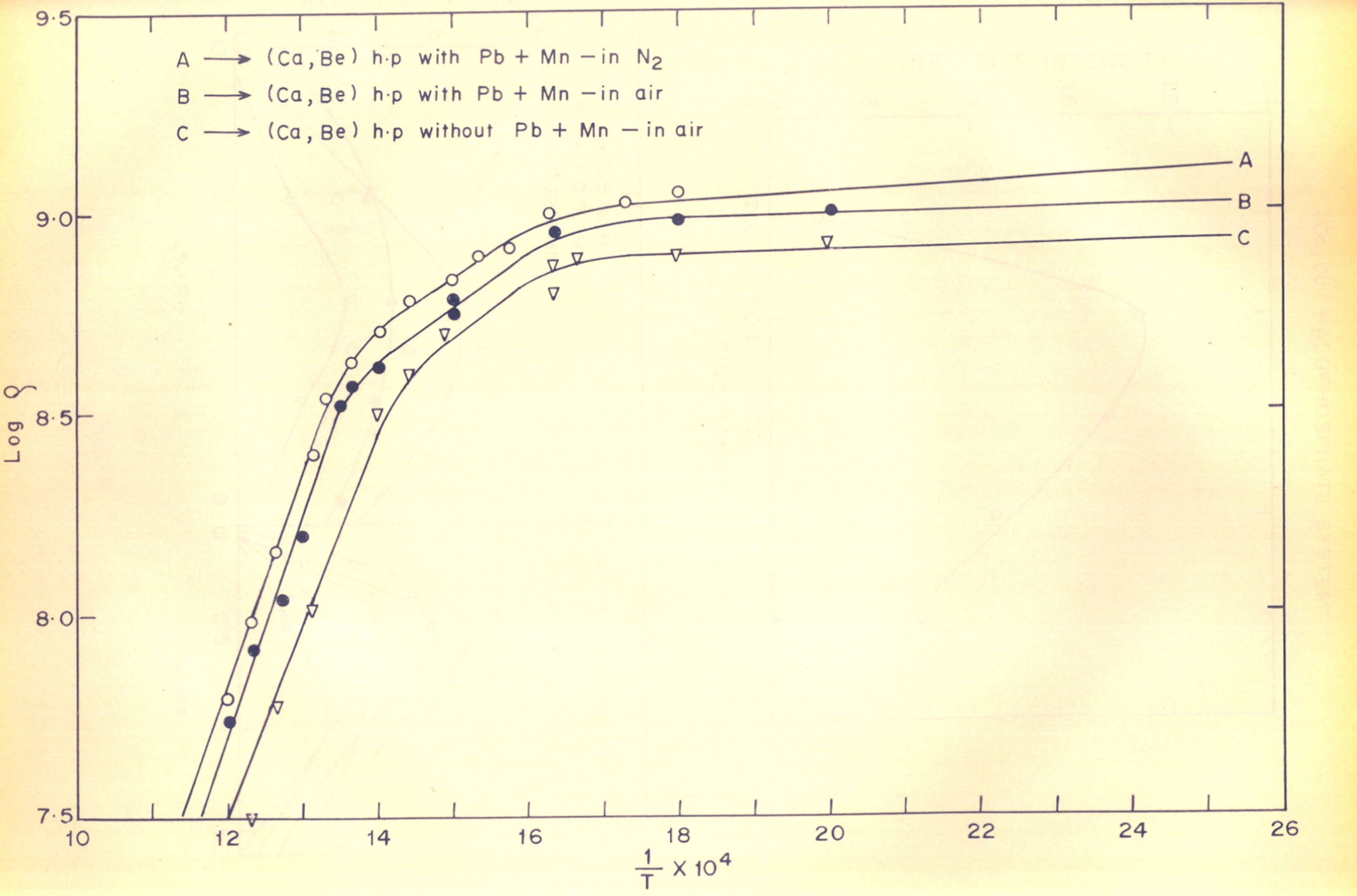
Composition	Rate of cooling	Colour of phosphor	Colour of fluorescence	Relative brightness
(Ca,Be)halophosphate	Slow	White	Yellow	VS
(Ca,Be)halophosphate	Fast	White	Yellow	VS

VS - very strong.

Table 21

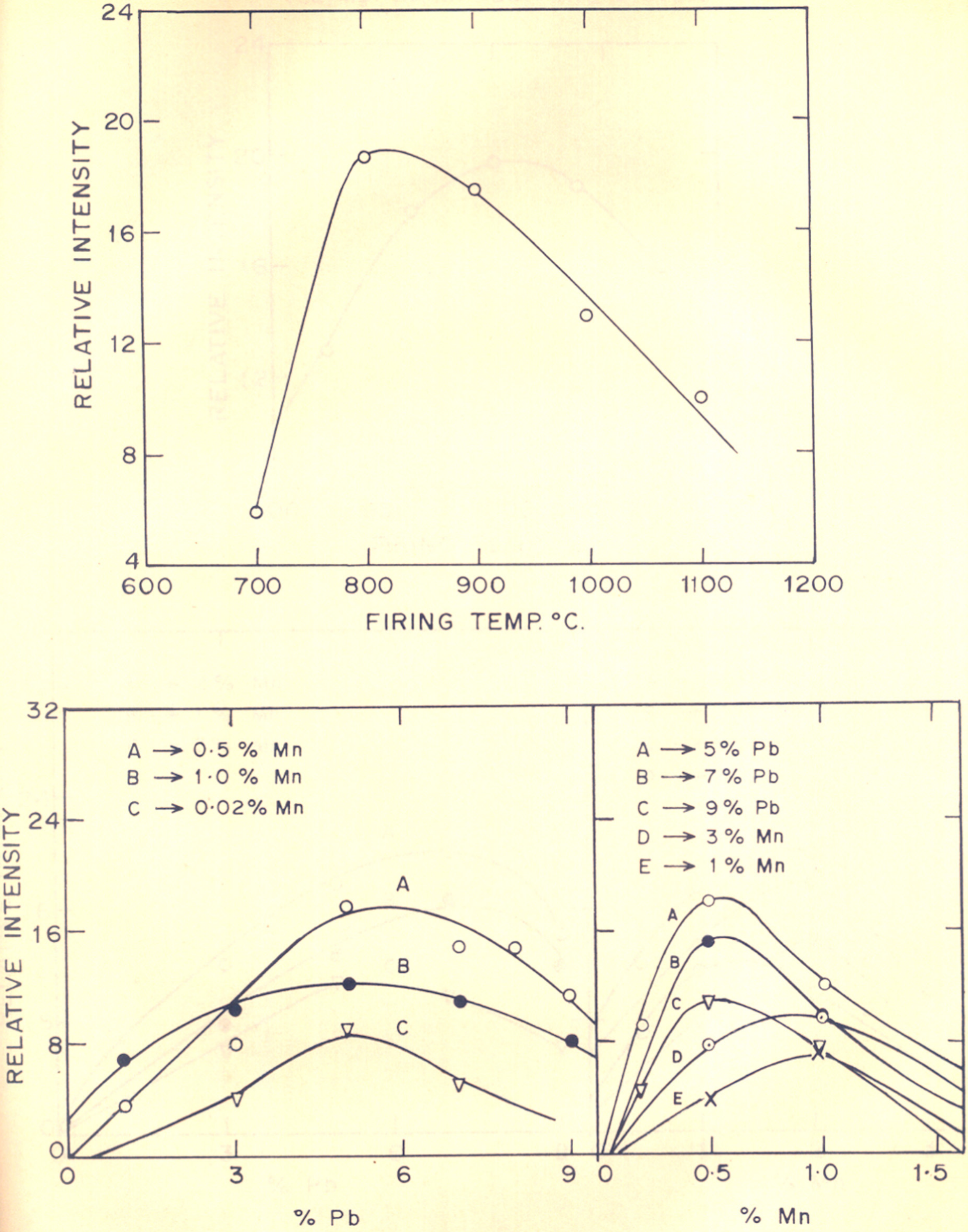
Electrical resistivity data of some halophosphates

Composition	Atmosphere	Resistance at room temperature	Activation energy	
			a	b
(Ca,Be) halophosphate with Pb + Mn	Air	10×10^8	0.910	0.174
(Ca,Be) halophosphate with Pb + Mn	Nitrogen gas	10×10^8	1.00	0.2
(Ca,Be) halophosphate without Pb + Mn	Air	8×10^8	1.2	0.12


A → (Ca, Be) h·p with Pb + Mn − in N_2
B → (Ca, Be) h·p with Pb + Mn − in air
C → (Ca, Be) h·p without Pb + Mn − in air
A
B
C
Log ρ
9·5
9·0
8·5
8·0
7·5
10
12
14
16
18
20
22
24
26
$\frac{1}{T} \times 10^4$

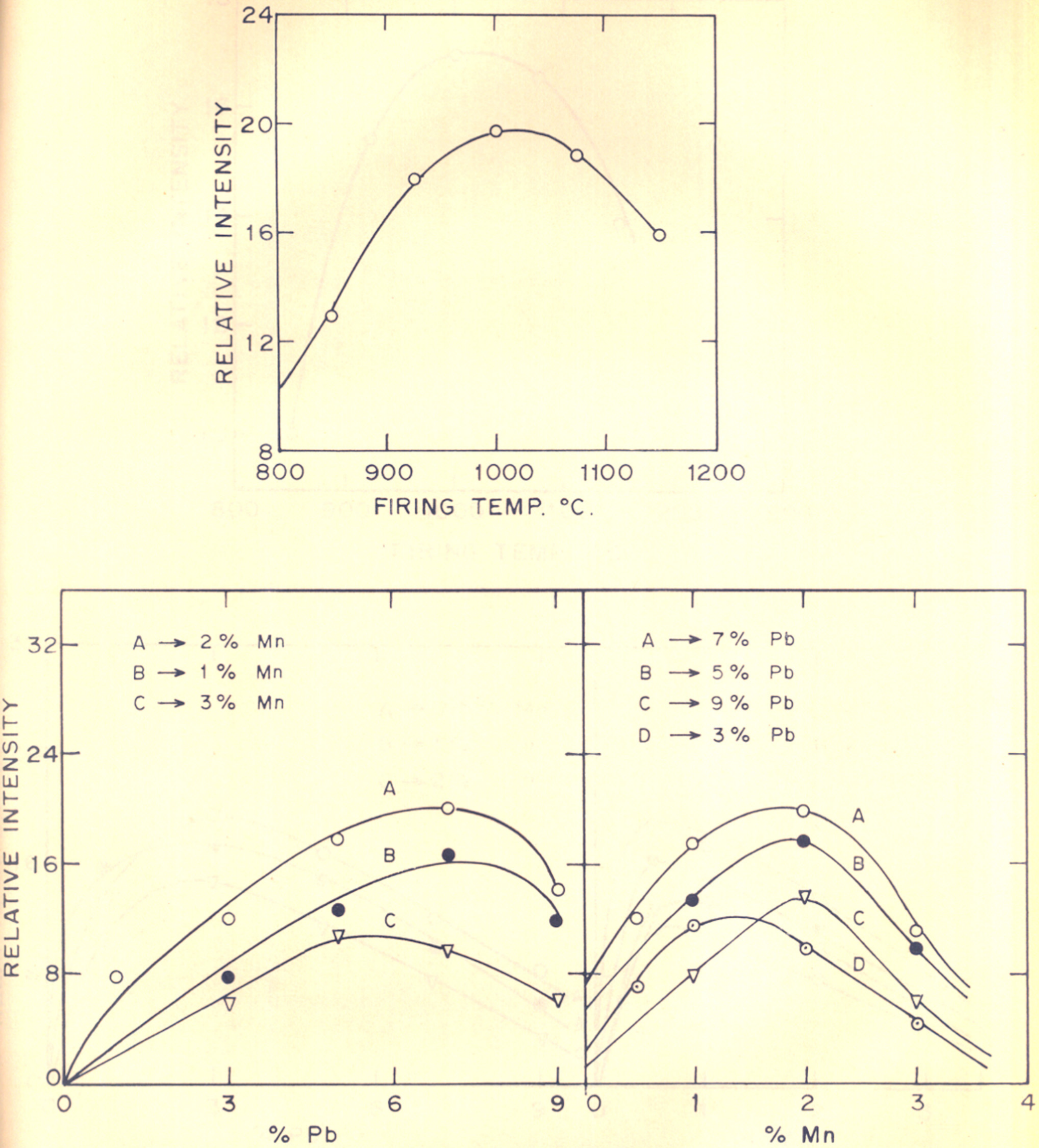
FIG·5

(Ca, Cd) HALOPHOSPHATE SYSTEM

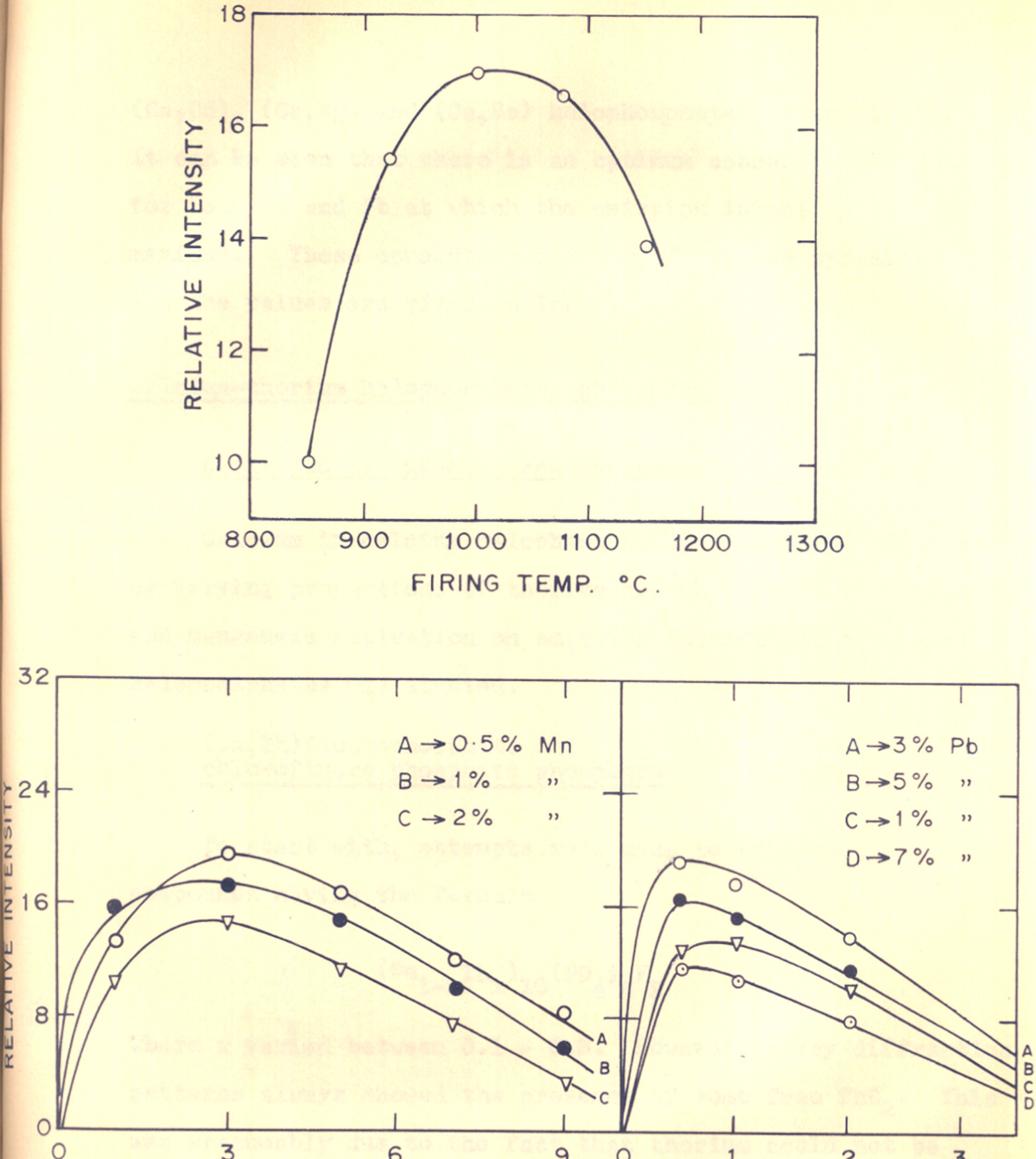


FIG·6

(Ca, Mg) HALOPHOSPHATE SYSTEM



FIG·7


(Ca,Be) HALOPHOSPHATE SYSTEM

FIG·8

(Ca,Cd), (Ca,Mg) and (Ca,Be) halophosphates respectively. It can be seen that there is an optimum concentrations for both Mn and Pb at which the emission intensity is maximum. These concentrations vary for three systems and the values are given in Table.

Calcium-thorium halophosphates phosphors

Activated by antimony and manganese

Calcium in calcium halophosphate was replaced partially by varying proportions of thorium and the effect of antimony and manganese activation on emission intensities of these halophosphates was studied.

(Ca,Th)fluorophosphate and chlorofluoro phosphate phosphors

To start with, attempts were made to synthesise compounds having the formula

$$(Ca_{1-x}Th_x)_{10}(PO_4)_6F_2$$

where x varied between 0.1 - 0.5. However, x-ray diffraction patterns always showed the presence of some free ThO_2. This was presumably due to the fact that thorium could not be incorporated as Th^{2+}. A new series of compounds where the charge compensation was taken care of by keeping the requisite metal deficiency, were therefore attempted. The appropriate mixtures corresponding to the general formula

$$(Ca^{2+}_{1-x}Th^{4+}_{x/2}\square_{x/2})_{10}(PO_4)_6F_2$$

where $\square$ represents metal vacancy, were reacted and the following compounds were successfully prepared where x-ray diffraction did not show any line due to free ThO_2 :

a) $(Ca_{.98}Th_{.01}\square_{.01})_9(PO_4)_6CaF_2$

b) $(Ca_{.96}Th_{.02}\square_{.02})_9(PO_4)_6CaF_2$

c) $(Ca_{.94}Th_{.03}\square_{.03})_9(PO_4)_6CaF_2$

d) $(Ca_{.90}Th_{.05}\square_{.05})_9(PO_4)_6CaF_2$

a') $(Ca_{.98}Th_{.01}\square_{.01})_9(PO_4)_6Ca(ClF)$

b') $(Ca_{.96}Th_{.02}\square_{.02})_9(PO_4)_6Ca(ClF)$

c') $(Ca_{.94}Th_{.03}\square_{.03})_9(PO_4)_6Ca(ClF)$

d') $(Ca_{.90}Th_{.05}\square_{.05})_9(PO_4)_6Ca(ClF)$

They were first fired at 1100°C for about one hour without adding any antimony or manganese. In second firing appropriate amounts of antimony and manganese were added and refired at 1100-1150°C in the nitrogen gas atmosphere for about one hour. Antimony concentration was varied from 3-5% and manganese concentration was varied from 0-5% respectively.

The effect of Sb^{3+} and Mn^{2+} concentration on (i) spectral energy distribution, and (ii) relative brightness was studied.

The results on relative brightness and the observed colours of fluorescence of (Ca,Th) halophosphate phosphors are recorded in the Table Nos. 22 and 23.

Results in Table Nos. 22 and 23 indicate that phosphors synthesized without addition of antimony gave no fluorescence. Antimony produced strong greenish-blue fluorescence and with Mn^{2+} it gave rise to colours from greenish-blue to dull orange-yellow, according to manganese concentration. Good fluorescence intensity was obtained from the phosphors which had manganese content from 1 to 3%.

Results in Table No.24 indicate the partial replacement of F_2 by Cl_2. Antimony gave strong greenish-blue fluorescence and with Mn^{2+} it gave rise to colours from greenish-blue to dull orange, according to Mn concentration. Good fluorescence intensity was obtained from the phosphors which had Mn content from 1-3%.

Wash treatment

After firing the phosphors surface usually gets contaminated by trace impurities of foreign materials from container etc. In addition to the Mn^{2+} or Pb^{2+} in surface, layer of phosphor may

Table 22

Effect of antimony and manganese concentration on intensity of calcium-thorium halophosphate phosphors, having calcium-thorium ratio ($Ca_{.96}:Th_{.03}$) and with fluorine only.

Phosphors mixtures were fired under nitrogen gas atmosphere at 1100°C for about one hour.

Composition	Sensitizer %	Activator %	Colour of phosphor	Colour of fluorescence	Relative brightness
(Ca.Th)halophosphate	3% Sb	-	White	Blue	MS
-do-	3% Sb	0.5% Mn	White	Bluish white	S
-do-	3% Sb	1.0% Mn	White	Greenish yellow	VS
-do-	3% Sb	2.0% Mn	White	Pale yellow	VS
-do-	3% Sb	3.0% Mn	White	Yellow	S
-do-	3% Sb	4.0% Mn	Faint pink	Deep yellow	S
(Ca,Th)halophosphate	5% Sb	-	White	Blue	MS
-do-	5% Sb	0.5% Mn	White	Bluish white	S
-do-	5% Sb	1.0% Mn	White	Greenish yellow	VS
-do-	5% Sb	2.0% Mn	White	Yellow	VS
-do-	5% Sb	3.0% Mn	White	Yellow	S
-do-	5% Sb	4.0% Mn	Faint pink	Deep yellow	W

Table 23

Effect of antimony and manganese concentration on the intensity of calcium-thorium halophosphate having calcium to thorium ratio ($Ca_{.90}:Th_{.05}$)with fluorine only.

Phosphor mixtures were fired under a nitrogen gas atmosphere at 1100°C for about one hour at different antimony and manganese concentrations.

Composition	Sensitizer %	Activator %	Colour of phosphor	Colour of fluorescence	Relative brightness
(Ca,Th)halophosphate	3% Sb	-	White	Blue	MS
-do-	3% Sb	0.5% Mn	White	Bluish white	S
-do-	3% Sb	1.0% Mn	White	Greenish yellow	VS
-do-	3% Sb	2.0% Mn	White	Yellow	VS
-do-	3% Sb	3.0% Mn	White	Yellow	S
-do-	3% Sb	4.0% Mn	Faint pink	Yellowish - orange	W
-do-	5% Sb	-	White	Blue	MS
-do-	5% Sb	0.5% Mn	White	Bluish white	S
-do-	5% Sb	1.0% Mn	White	Greenish yellow	VS
-do-	5% Sb	2.0% Mn	White	Yellow	VS
- do-	5% Sb	3.0% Mn	White	Yellow	S
-do-	5% Sb	4.0% Mn	Faint pink	Deep yellow	W

Table 24

Effect of antimony and manganese concentration on the intensity of calcium-thorium halophosphate phosphors having calcium to thorium and fluorine to chlorine ratios were ($Ca_{.94}$: $Th_{.03}$) and 1:1.

Phosphor mixtures were fired under a nitrogen gas atmosphere at 1100°C for about one hour at different manganese concentrations.

Composition	Sensitizer %	Activator %	Colour of phosphor	Colour of fluorescence	Relative brightness
(Ca,Th)halophosphate	3% Sb	-	White	Blue	MS
-do-	3% Sb	0.5% Mn	White	Bluish white	S
-do-	3% Sb	1.0% Mn	White	Pale orange	VS
-do-	3% Sb	2.0% Mn	White	Orange	VS
-do-	3% Sb	3.0% Mn	White	Orange	S
-do-	3% Sb	4.0% Mn	Faint pink	Dull orange	M

get oxidised due to traces of oxygen present in nitrogen gas. These are harmful and reduce the efficiency of the phosphors. It is, therefore, the usual practice to wash the phosphors with HNO_3, HCl, EDTA and citric acid. In our phosphors, we have employed 20% citric acid, 2% acetic acid,for washing and there appears to be significant improvement in the phosphor intensity.

CHAPTER IV

DISCUSSION

DISCUSSION

X-ray results

The unit cell of the new halophosphate solid solutions is hexagonal and the general similarity between the observed intensities of these compounds and those of calcium halophosphates show that they all are isomorphous and have the apatite structure.

The unit cell dimensions of these compounds as determined by the x-ray powder diffraction data are presented in Table No.25 together with the cell parameters for some well-known compounds of the apatite structure.

The series of the three fluorophosphates show that as the size of the metal ion decreases, the 'a' value decreases, but the variation in 'c' is not systematic. On the other hand, in the three chlorophosphates neither 'a' nor 'c' shows any systematic variation. However, in all cases the variation in the volume of the unit cell is regular i.e. it decreases with decreasing radius of the metal ion, although the variation in $V^{1/3}$ is of a smaller order as compared to the ionic radius of metal ion.

Table 25

Composition	Radii of metal ions*	a_o Å	c_o Å	c/a	$V^{1/3}$
Calcium fluorophosphate $Ca_5F(PO_4)_3$: $Ca_5F(PO_4)_3$	1.06	9.37	6.88	0.734	8.05
) (Ca,Mg)fluorophosphate $Ca_5F(PO_4)_3$: $Mg_5F(PO_4)_3$	0.92*	9.32	6.78	0.728	7.99
(Ca,Be)fluorophosphate $Ca_5F(PO_4)_3$: $Be_5F(PO_4)_3$	0.68*	9.25	6.8	0.735	7.96
Pyromorphite $Pb_5Cl(PO_4)_3$: $Pb_5Cl(PO_4)_3$	1.21	9.9	7.3	0.735	8.55
Calcium chlorophosphate $Ca_5Cl(PO_4)_3$: $Ca_5Cl(PO_4)_3$	1.06	9.52	6.85	0.719	8.13
Cadmium chlorophosphate $Cd_5Cl(PO_4)_3$: $Cd_5Cl(PO_4)_3$	1.03	9.70	6.40	0.659	8.05
(Ca,Cd)chlorofluoro-phosphate $(Ca_5Cl(PO_4)_3$: $Cd_5F(PO_4)_3$	1.04*	9.38	6.66	0.710	8.22

* Average, where two metal ions are present.

It is well-known that in apatite structure, the metal ions occupy two types of sites, conventionally known as Ca(I) and Ca(II) sites. Ca(I) site is surrounded by six nearly equidistant oxygen ions and three others at a slightly longer distance. The surroundings of Ca(II) is slightly more complicated. It 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:

Ca(I) is surrounded by:

3 oxygen at $\sqrt{a^2/36 + c^2/16}$
3 oxygen at $\sqrt{7a^2/225 + c^2/16}$
and 3 oxygen at $\sqrt{13a^2/144 + c^2/16}$

and Ca(II) is surrounded by:

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

The following table gives the calculated values of the metal-oxygen distance in the various compounds studied by us.

Table 26

Composition and position	Distance Å
Position Ca(I) site	
(i) (Ca,Be) halophosphate	
3 oxygen at	2.290
3 oxygen at	2.357
3 oxygen at	2.810
(ii) (Ca,Mg) halophosphate	
3 oxygen at	2.327
3 oxygen at	2.366
3 oxygen at	2.832
(iii) (Ca,Cd) halophosphate	
3 oxygen at	2.278
3 oxygen at	2.373
3 oxygen at	2.852
Position Ca(II) site	
(i) (Ca,Be) halophosphate	
1 oxygen$_{I}$ at	2.778
1 oxygen$_{II}$ at	2.271
2 oxygen$_{III}$ at	2.257
2 oxygen$_{III}$ at	2.401
(ii) (Ca,Mg) halophosphate	
1 oxygen$_{I}$ at	2.799
1 oxygen$_{II}$ at	2.288
2 oxygen$_{III}$ at	2.301
2 oxygen$_{III}$ at	2.426
(iii) (Ca,Cd) halophosphate	
1 oxygen$_{I}$ at	2.817
1 oxygen$_{II}$ at	2.302
2 oxygen$_{III}$ at	2.215
2 oxygen$_{III}$ at	2.416

It can be seen that the nearest neighbour distances vary only slightly as we go from compound to compound. This is mainly due to the fact that the changes in 'a' and 'c' are generally mutually opposite so that their effect cancels to some extent.

This also indicates that the size of the unit cell is largely predetermined by the requirements of the bigger ions in the lattice e.g. the distance between oxygen-oxygen, which in calcium halophosphate is about 2.63 - 2.67 Å. This is just equal to sum of the ionic radii of two oxygen ions. The substitution of calcium by smaller ions would tend to decrease the size of cation-oxygen distance, but this would be hindered because it would reduce the oxygen-oxygen distance. However, the substitution of calcium by bigger ions should show an increase in unit cell, but unfortunately, in all compounds we have studied the ionic radii of substituents are smaller than that of the Ca^{2+} ions.

Furthermore, each ca(I) site is surrounded by two other Ca(I) ions linearly at a distance of c/2 (i.e. $\approx$ 3.4Å). This distance is larger than sum of the ionic radii of two Ca(I) site ions, hence this inter-atomic distance is also not expected to play a major role in determining the unit cell dimensions. On the other hand, the Ca II-F (a/4)is close to the sum of the ionic radii. The increase in size of the cation occupying Ca(II) site is, therefore, expected to increase the 'a' parameter.

X-ray intensity analysis

The distribution of the substituent metal ions over the Ca(I) and Ca(II) sites has been determined from the x-ray diffraction data. As an approximation, it was assumed that the substitution does not affect the values of the various site parameters and the same values as those known for calcium halophosphate were taken. Thus, it was assumed that the substituted metal ion distributes itself over the two available calcium sites without disturbing the position of these or the other sites. This, no doubt, is an approximation, but in view of a very limited number of diffraction intensities available, nothing better could be attempted. However, it is expected that the conclusions arrived at regarding the distribution of the cations would be qualitatively correct.

The intensities were estimated visually. The calculated intensities were obtained using the formula

$$I \propto |F|^2 . p \; \frac{1 + \mathrm{Cos}^2 2\theta}{\mathrm{Cos}\,\theta \; \mathrm{Sin}_2\theta}$$

where F is the structure factor; p is the multiplicity and the $\frac{1+ \mathrm{Cos}^2 2\theta}{\mathrm{Sin}\, 2\theta \mathrm{Cos}\,\theta}$ is Lornetz and polarization factor. No corrections for the absorption or temperature factors were applied in view of the qualitative nature of the calculation. Furthermore, it is known that they act in opposite directions so that no serious error is committed if both are neglected simultaneously.

The structure factor values were calculated from the equation

$$|F_{hkl}|^2 = A^2{}_{hkl} + B^2{}_{hkl}$$

$$A_{hkl} = \sum f_i \mathrm{Cos} 2\pi (hx_1 + ky_1 + lz_1)$$

$$B_{hkl} = \sum f_i \mathrm{Sin} 2\pi (hx_1 + ky_1 + lz_1)$$

The simplified form of this equation as given in the International Table[54] for this space group was used for the actual calculations. Appropriate equation for different reflections were obtained by substituting the values of hkl and the atomic coordinated X Y Z for the various ions of the apatite structure.

The values of the scattering power f were taken from International Table[55] for x-ray crystals. Phosphorus was assumed to present as P^{5+} and oxygen as O^{2-}. Where, more than one type of ions occupied a set of equivalent sites then the weighted average was taken to represent the scattering power for that site.

The multiplicity factors were obtained from International Table[56] for the space group. The calculated intensities were normalised so that $\sum I_{obs} = \sum I_{cal}$. The arrangement which gave the minimum value of $\frac{\sum|I_{obs} - I_{cal}|}{\sum I_{obs}}$ was taken to represent the best agreement.

The various models chosen for calculations are given at the top of each table. The calculated intensities for these models are presented along with the observed intensity of the reflections in the same table.

After examining the intensities of (Ca,Cd) chlorofluoro phosphate and comparing with the calculated intensities, it is found that the observed intensities best match in between the models B and C (as tabulated in Table No.27).

It is observed that reflection (210 + 102) is definitely stronger than reflection 002. However, the calculation shows that for the arrangement A, this pair should be stronger than 002. Furthermore, the calculated intensities for A in case of other reflections also do not agree well and therefore A is ruled out. In view of the fact that reflection 211 is nearly equal to 112 + 300,

Table 27

4f Ca(I)	6 f Ca(II)	
4 Ca	1 Ca + 5 Cd	A
3 Ca + 1 Cd	2 Ca + 4 Cd	B
2 Ca + 2 Cd	3 Ca + 3 Cd	C
1 Ca + 3 Cd	4 Ca + 2 Cd	D
4 Cd	5 Ca + 1 Cd	E

	I_{cal}					I_{obs}
hkl	A	B	C	D	E	
002	53	38.10	22.23	10.17	10.2	35
102	20.9	26.33	28.9	33.15	35.2	40
210	23.8	27.49	30.7	33.3	36.8	
211	130	115	90	64.87	59.50	100
112	31.90	46.4	58.56	75	83.2	100
300	36.3	47.8	54.8	62.2	72.0	
202	1.69	5.6	11.4	19.8	23.2	8
301	1.95	2.3	2.16	1.72	3	10
212	3.9	1.49	2.25	6.45	8	15
130	3.25	6.9	10.7	1.87	3	

the structures D and E have been excluded. Fairly good match was observed for B and C and from the general trend of the reflections it appeared that an intermediate structure would show even a better agreement.

The intensities for the structure in which Ca I site is occupied by 3.5 Ca + 1.5 Cd and Ca(II) site is 2.5 Ca + 3.5 Cd was therefore calculated and it was found that this showed the best agreement with observed intensity.

In the case of (Ca,Be) fluorophosphate the observed intensities match with calculated intensities for model E as can be seen from the Table No.28.

Table 28

4 f Ca(I)	6 f Ca(II)	
4 Ca	1.5 Ca + 4.5 Be	A
3 Ca + 1 Be	2.5 Ca + 3.5 Be	B
2 Ca + 2 Be	3.5 Ca + 2.5 Be	C
1 Ca + 3 Be	4.5 Ca + 1.5 Be	D
4 Be	5.5 Ca + 0.5 Be	E

hkl	I_{cal}					I_{obs}
	A	B	C	D	E	
002	18.9	33.50	38	68	73	70
102	0.26	0.08	0.13	0.38	0.68	2
210	25.4	18	15	17.9	14.6	12
211	49.7	45.32	52.7	79	86	100
112	140	87	65	62.8	42.6	
300	68.7	43.3	31.20	34.0	20.3	20
202	72.6	43.5	27.8	24.2	12.5	10
301	7.0	6	5.85	5.4	4.7	5
212	2.4	10.3	8.45	3.8	4.3	5
130	54.46	35.4	18.2	25.3	19.8	20

It is found that for models A, B and C the calculated values for reflections 002 and 300, 202 and 130 are not matching with observed one; for example, the calculated value for 002 is too weak as compared to the observed reflection, while 300, 202 and 130 are observed to be weak but they are calculated to be much stronger. Hence the models A, B and C are straightaway ruled out. The model D shows a fair agreement with the observed intensity but E shows the best agreement. For example, reflections 002, 202 and 130 show the best match between the observed and the calculated values for model E rather than for D. It is, therefore, concluded that the Ca(I) site is completely occupied by beryllium and the remaining beryllium, together with all the Ca, are situated in Ca(II) sites i.e. (0.5 Be + 5.5 Ca).

Intensity studies of (Ca,Mg) fluorophosphate showed that the observed intensity values of (Ca,Mg)halophosphate also match best with model E as can be seen from the Table No.29. It is found that for the models A,B, C and D, the calculated intensities for reflections 002, 300, 202 and 130, are not matching with observed ones. 002 is weak for model A and goes on increasing as we move from A to E and it matches with observed value at E only. Reflections 300, 130 and 202 also are sensitive to cation

Table 29

Ca(I)	Ca(II)	
4 Ca	5 Mg + 1 Ca	A
3 Ca + 1 Mg	4 Mg + 2 Ca	B
2 Ca + 2 Mg	3 Mg + 3 Ca	C
1 Ca + 3 Mg	2 Mg + 4 Ca	D
4 Mg	1 Mg + 5 Ca	E

hkl	I_{cal}					I_{obs}
	A	B	C	D	E	
002	28.8	30.9	41.04	51	58	55
102	6.3	5	4.40	4	4	8
210	2.3	2.1	1.25	3	2	5
211	68.2	73	80	97.5	98.5	100
112	26.1	23.8	21.6	20	14	
300	65	55.3	53.5	55	45	40
202	45.0	35.5	35.4	30	23.2	20
301	4.2	4.2	4.16	4	6	10
212	11.1	8	8	5	5	10
130	49.9	32	30	32	27	25

distribution and they decrease as one goes from A to E and a close agreement is obtained for E. It is, therefore, concluded that 4 magnesium are situated in Ca(I) site and remaining are situated in Ca(II) site.

Fluorescent emission from substituted halophosphates

The fluorescence of calcium halophosphate phosphors containing Sb^{3+} as sensitizer and Mn^{2+} as activator has been studied well. The exci~~ta~~ting radiation is first absorbed by Sb^{3+} ions and the electrons in the ground state of Sb^{3+} $(5s^2, {}^1S_o)$ are excited to state $(5sp, {}^3P_1)$. The excitation is then transmitted to Mn^{2+} ions where the electr~~i~~ons are promoted to $3d^{4d^*}$ $(4G_{5/2})$ levels. The final emission is due to a radiative transition from $4G_{5/2}$ to $6S_{5/2}$ states of the Mn^{2+} ions.

In calcium halophosphate the Mn^{2+} ion can occupy any of two types of sites i.e. Ca(I) or Ca(II) which, as already seen, have different surroundings leading to different crystal fields. The energy levels and the frequency of the emitted radiation therefore would depend on the location of the Mn^{2+} ion. It is, therefore, very important to know their location in these halophosphates. The recent work by Johnson[32] has shown that at very small concentrations, in fluorophosphate, Mn^{2+} ions occupy the Ca(I) site whereas

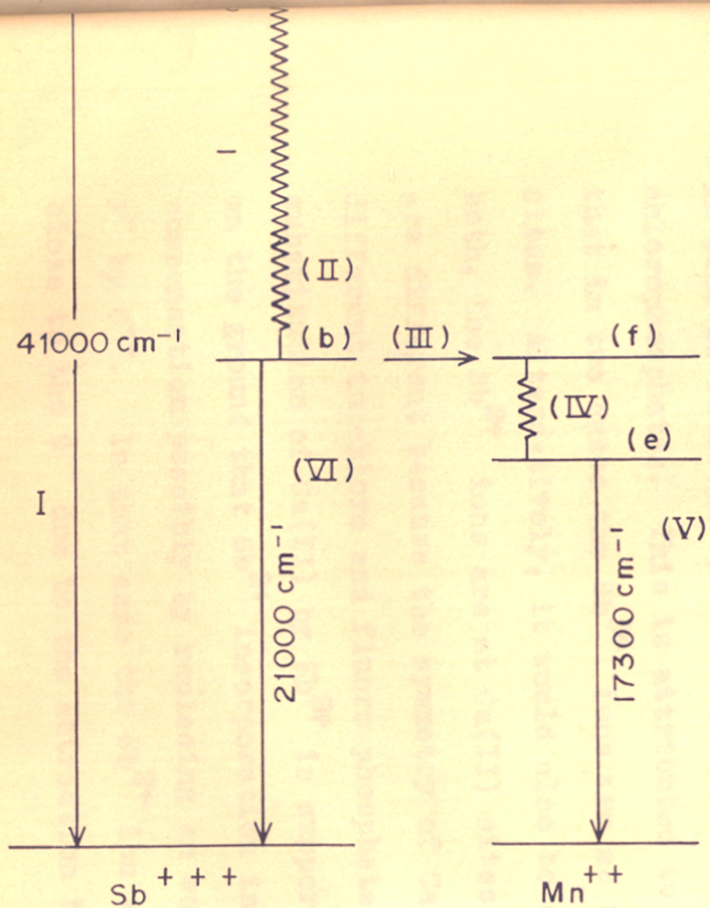


Fig. 9 a.52

Representation for mechanism of Mn^{++} in Ca-flurophosphate. (I) Excitation of Sb^{+++} ion by light wavenumber 41000 cm^{-1}. (II) Non-radiative transition. (III) Resonent transfer. (IV) Non-radiative transition. (V) Emission of Mn^{++} ion whose wavenumber is 17300 cm^{-1}. (VI) Emission by Sb^{+++} ion whose wavenumber is 21000 cm^{-1}.

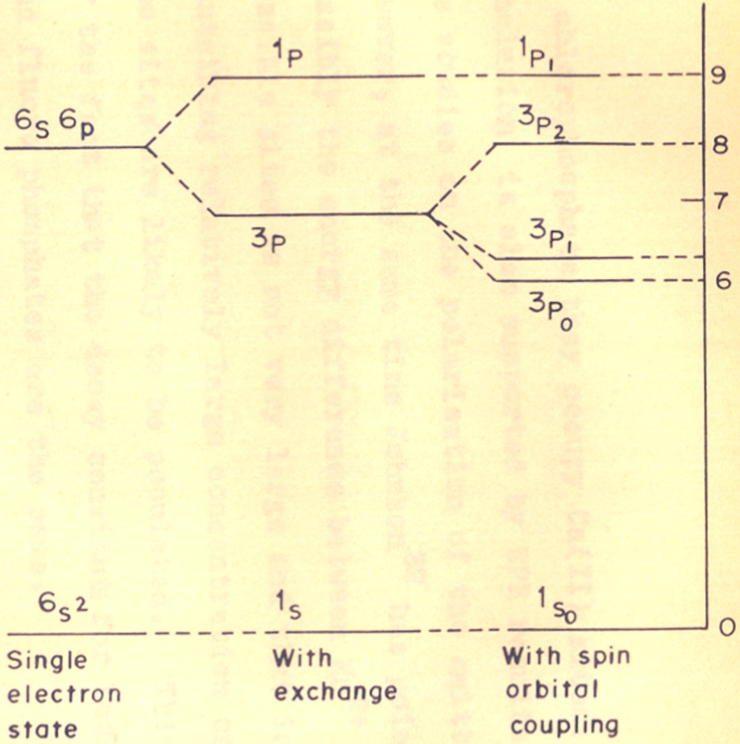


Fig. 9 b.59 Energy levels of the Tl^+ ion in chlorophosphate they occupy Ca(II) sites. This conclusion is also supported by EPR results and the studies on the polarisation of the emitted radiations. However, at the same time Johnson[32] has pointed out that possibly the energy difference between Mn^{2+} at the two possible sites is not very large and that in crystal containing relatively large concentration of Mn^{2+}, both the sites are likely to be populated. This is supported by the fact that the decay constants for both chloro- and fluoro phosphates are the same.

In regard to the Sb^{3+} position, the evidences are still more conflicting. Johnson[32] has observed that polarisation of Sb^{3+} emission is perpendicular to C axis in case of fluorophosphates and parallel to C axis in chlorophosphates. This is attributed to the possibility that in two cases the Sb^{3+} ions are at two different sites. Alternatively, it would also be argued that in both, the Sb^{3+} ions are at Ca(II) sites but the emissions are different because the symmetry of Ca(II) site is different in chloro and fluoro phosphates. The substitution of Ca(II) by Sb^{3+} is supported by Ouweltjes[57] on the ground that Sb^{3+} incorporation involves a charge compensation possibly by replacing an equal amount of F^- by O^{--}. In that case the Sb^{3+} ion will tend to be close to the O^{--} due to the attraction between the oppositely charged defects i.e. it will occupy Ca(II) sites.

In case of compounds with Pb^{2+} as activator the difficulty of charge compensation does not arise, because the divalent Pb^{2+} ions replace the divalent Ca^{2+} ions. Pb^{2+} is isoelectronic with Tl^{+} and has the same set of energy levels. These are shown in Fig. 9b . The lowest state is $^1S_0$ and the next higher is $^3P_0$ with $^3P_1$ lying closely above it. The energy separation between $^1S_0$ and $^3P_0$ is about 6 e.v. The transition from $^1S_0 \rightarrow {}^3P_0$ is however forbidden and the allowed transitions are $^1S_0 \longrightarrow {}^1P_1$; $^1S_0 \longrightarrow {}^3P_2$ and $^1S_0 \rightarrow {}^3P_1$. The mercury line at 2537Å used for excitation matches in energy with the transition $^1S_0 \rightarrow {}^3P_1$. This transition being from a singlet to a triplet state, the oscillator strength is very small. The emission level of lead, however, is in blue region as can be seen from the lead-luminescence in halophosphates not doped with Mn^{2+} . It is clear, therefore, that after the absorption of radiation the electronsfall from the level C to the level b by a non-radiative transition. The separation of the level b from the ground level lead is expected to be around 22000 cm^{-1}. Some of the electrons in this excited level of Pb^{2+} transfer their energy to Mn^{2+} electrons and bring them to an excited state. The excited Mn^{2+} electrons emit radiation in the range 16000-17000 cm^{-1} when they fall to the ground state. However, it can be seen that there must be a non-radiative transition before the final emission which would account for difference between the Pb^{2+} level and the Mn^{2+} emission level (Table 30).

Table 30

Composition	Location of peak Å	Location of peak in cm^{-1}
(Ca,Cd)chlorofluoro phosphate		
i) 5% Pb	4500Å	22270 cm^{-1}
ii) 5% Pb + 0.5% Mn	5880Å	17000 cm^{-1}
iii) 5% Pb + 1% Mn	5900Å	16940 cm^{-1}
(Ca,Be)fluoro phosphate		
i) 3% Pb	4500Å	22270 cm^{-1}
ii) 3% Pb + 0.5% Mn	5600Å	18110 cm^{-1}
iii) 3% Pb + 1% Mn	5650Å	17700 cm^{-1}
(Ca,Mg)fluorophosphate		
i) 7% Pb	4500Å	22270 cm^{-1}
ii) 7% Pb + 1% Mn	5660Å	17670 cm^{-1}
iii) 7% Pb + 2% Mn	5680Å	17610 cm^{-1}

The Sb^{3+} emission in halophosphates is at 21000 cm^{-1} and that of Pb^{2+} is at 22270 cm^{-1}. The higher energy of Pb^{2+} level is likely to affect the resonance energy transfer to Mn^{2+} ions adversely as this would increase the energy difference with respect to the Mn^{2+} levels.

Physical characteristics of the mixed halophosphates with Pb:Mn activators

In absence of Mn, the Pb activated mixed halophosphates gave a weak but detectable blue emission composed of single band peaked at 4500Å. Furthermore, it was observed that the position of peak was relatively independent of the lead concentration. The addition of Mn with lead resulted in modifying the colours of the phosphors and emission peaks shifted to 5880-5900Å in case of (Ca,Cd)chloro-fluoro phosphate and 5650-5700Å in case of (Ca,Mg) halophosphate while in case of (Ca,Be) halophosphate the emission peaks shifted to 5600-5650Å.

These changes in emission peaks are due to the changes (i) in the Mn concentration, (ii) partial replacement of the fluorine by chlorine in case of (Ca,Cd) halophosphate, and (iii) by 50% replacement of calcium by cadmium, magnesium or beryllium.

The possible explanation for the shift of the emission peak towards longer wave length when fluorine is partially or totally replaced by the chlorine, is given by Fonda[21]. He explained on the basis that as the size of chlorine ion is larger than the fluorine ion its field strength i.e. the quotient of its ionic charge by its ionic radius is less. This results in lower electronic attraction between the chlorine ions and its neighbouring calcium ion, so that the spacing between such a calcium ion and its neighbouring three oxygen ions is correspondingly reduced. When a manganese is substituted for such a calcium ion, its levels are depressed and its emission shifts towards longer wave lengths.

The effect of the matrix on the wave length of emission peak

As mentioned earlier, the metal-oxygen distances are not significantly affected in the series (Ca,Me)halophosphates where Me is Be, Mg or Cd. For example, the sum of the ionic radii $(r_{me} + r_o)$ changes by 6% as one goes from Ca to $\frac{Mg + Ca}{2}$ and by 12% from $\frac{Mg + Ca}{2}$ to $\frac{Be + Ca}{2}$ but the changes in the observed inter-atomic distances are hardly 1%. In spite of this, there are two significant observations in regard to the position of emission peaks which may be mentioned here.

It would be expected that the wave length would be in the order Ca < Mg < Be. Furthermore, on the basis of the values given by Narita[51] i.e. 150 cm^{-1}(or 40Å) increase in wave length towards longer wave length for a contraction of 1% in the inter-atomic distance. We would expect the values to be as follows:

			Expected emission position in A°	Observed emission position in A°
Ca			5600	5600
	1%	contraction in inter-atomic distance		
Mg			5640	5680
Be	1%	-do-	5680	5630

Although magnesium value is in fair agreement with that expected, the beryllium value is definitely low. Even qualitative order is not observed, i.e. it would be expected that Be should give higher wave length because the Me-O is smaller but actually it gives the fluorescence at shorter wave length than magnesium.

This shows that the changes in the crystal field are not governed entirely by the Me-oxygen distances. It appears that the second nearest neighbour of metal ion may also play an important part, because as has been pointed out above, an ion at Ca(I) site (the site where Mn^{2+} goes in fluoro phosphate) is surrounded by two metal ions on the equivalent site at a distance of c/2. Furthermore, the covalent character of $Mn^{2+} - O^{--}$ bond is also dependent on the other ions surrounding the oxygen ions. This could also be responsible for the variation of emission wave length as the host matrix changes.

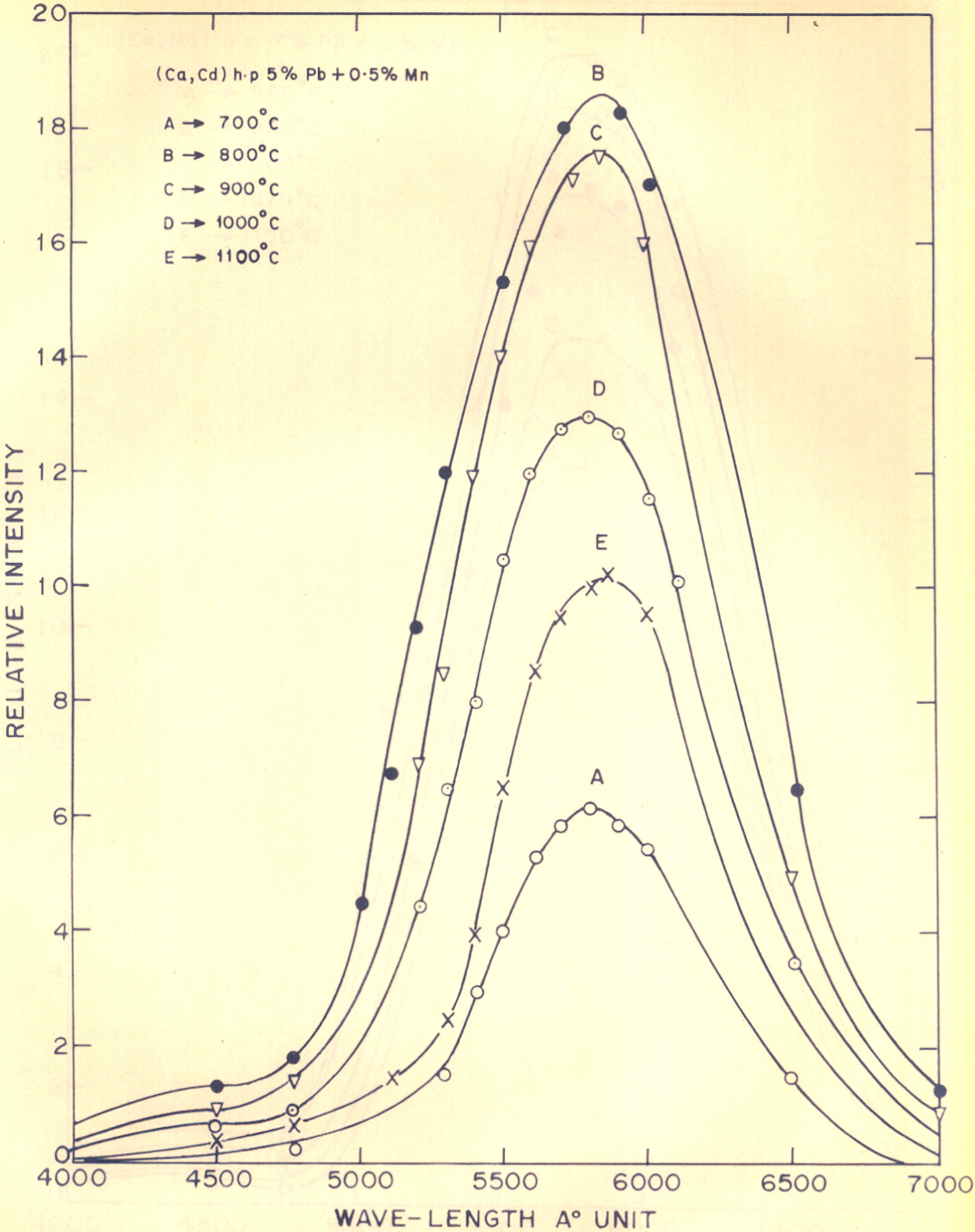
When Cd^{2+} is substituted for half of the calcium ions in the calcium chlorofluoro phosphate, the observed inter-atomic distance ~~is~~ changes by about 1%. On the basis of Narita's calculations, one would expect a shift of about 150 cm^{-1} (i.e. 40Å). However, actually a shift of 80Å towards the longer wave length side was experimentally observed.

Thus although, in general, we found the shift towards the longer wave length side when the calcium was replaced by ions of smaller atomic radii some significant exceptions were observed. Furthermore, there was no quantitative correlation between the change in the metal-oxygen distance and the exact shift in the Mn emission peak.

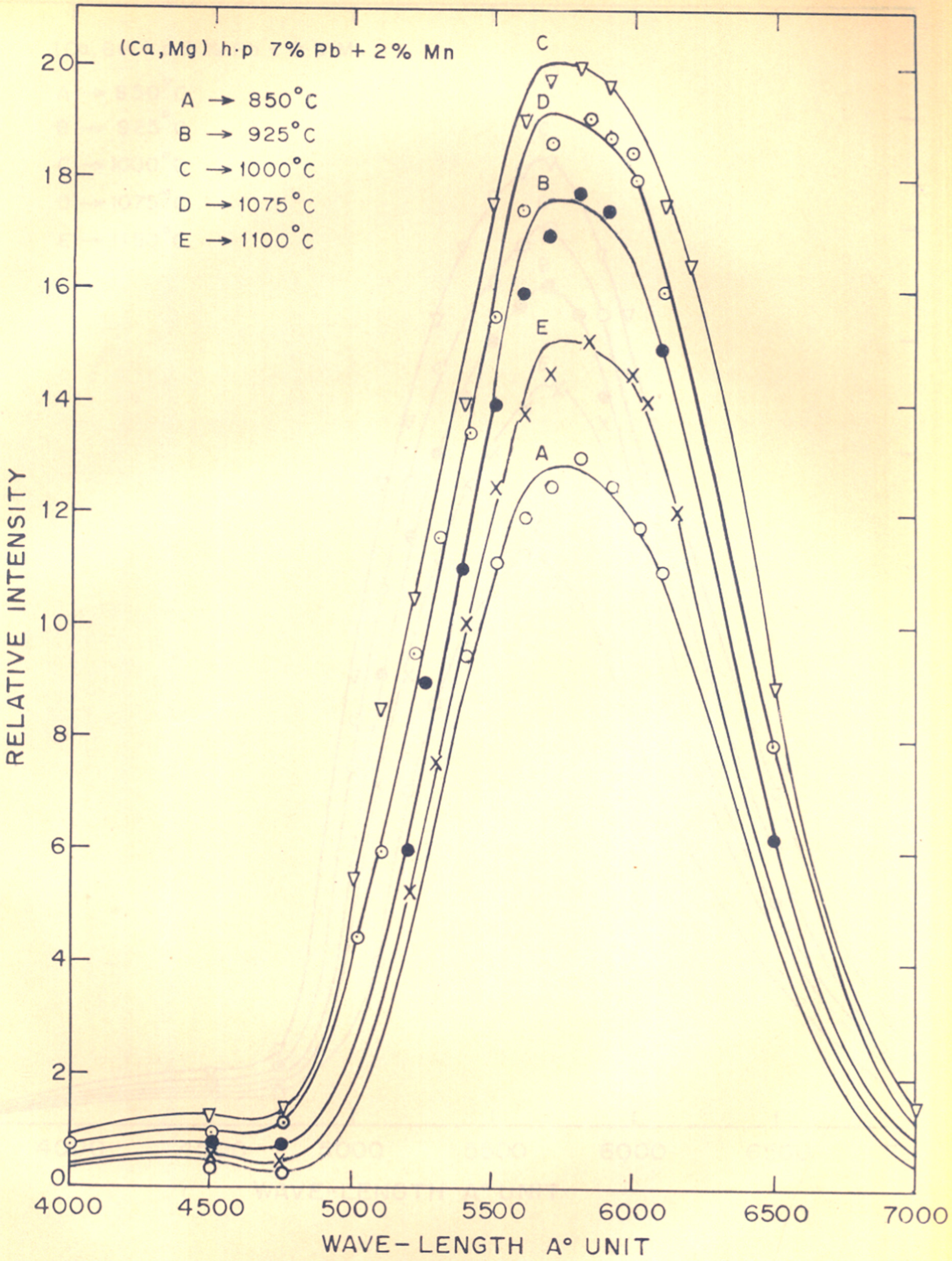
The dependence of Mn^{2+} emission peak on the Mn^{2+} ion concentration is interesting. We have found a significant dependence, higher Mn^{2+} concentration leading to a shift to longer wave length. Butler and Jerome[7] observed that manganese concentrations have no effect on the location of the emission peak in the Ca-halophosphate but intensity varies with Mn concentration. Furthermore, Fonda[8] observed that position of emission peak is independent of Mn concentration, but shift towards shorter wave length on increasing the temperature. However, Ostaszewies[26] observed the position of emission peak changes with Mn concentration and it varies from 5764Å to 5935Å. Same shift was also observed in the case of cadmium fluorophosphate when manganese concentration is varied. In our system,both the position of the Mn peak as well as intensity of the emission,changes with Mn concentration.

Effect of firing temperature on the intensity of phosphors

The firing temperature is known to play an important and dominating role on the phosphor's intensity. It is found that the final intensity of the phosphors always depends on the final heating temperature and the firing time. It can be seen from the Figs. 10, 11, 12 that the intensity rises gradually as the firing temperature increases, comes to a maximum and starts falling again. The optimum temperature is 800-900°C for (Ca,Cd) halophosphate, 1000-1025°C for (Ca,Mg) halophosphate and 975-1000°C for (Ca,Be) halophosphates. The x-ray diffraction studies, however, did not show any appreciable change on the structures of these compounds even after heating at high temperatures. The fall of intensity on heating at high temperatures could, therefore, be attributed to the changes of

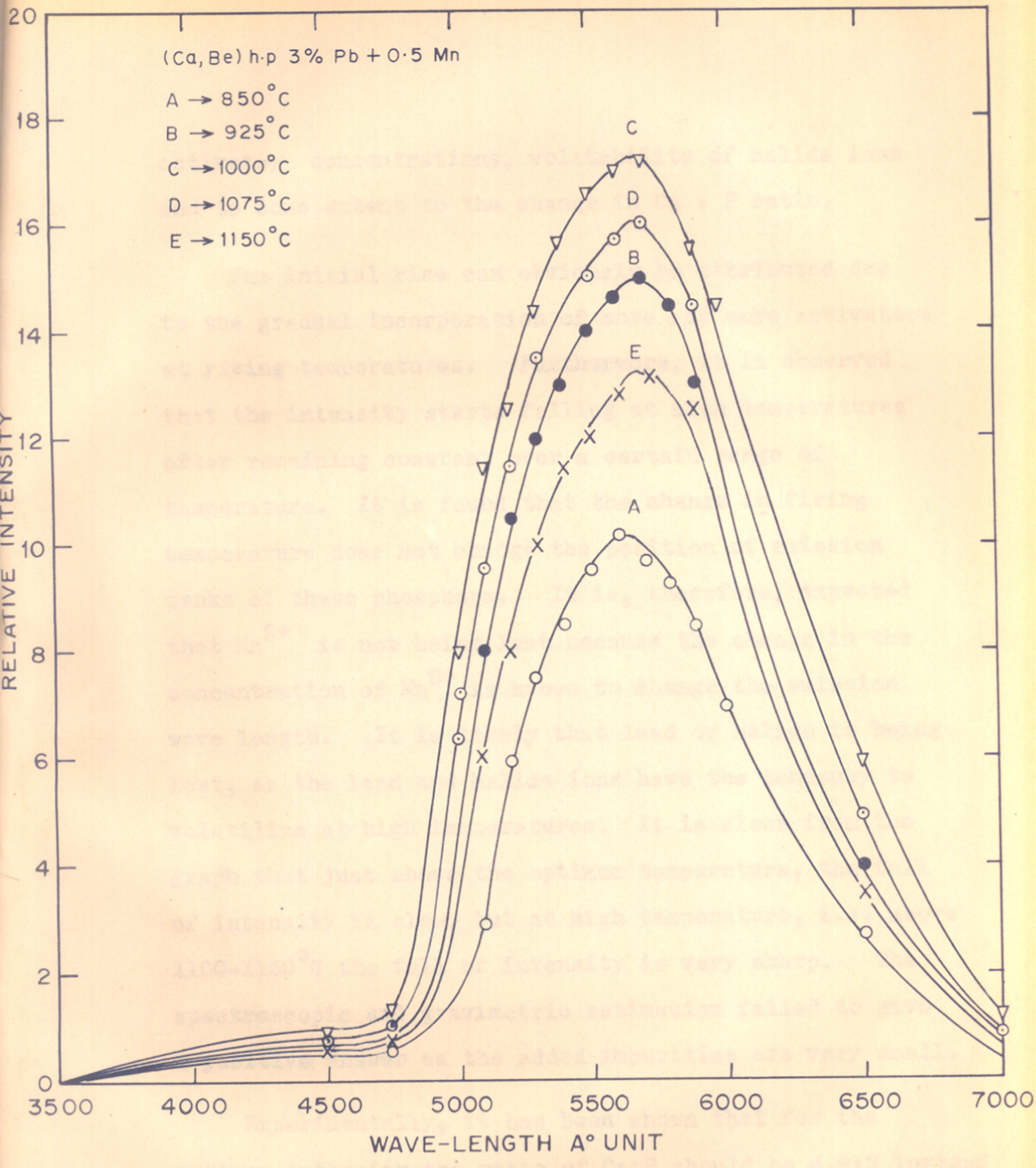

(Ca, Cd) h·p 5% Pb + 0·5% Mn
A → 700°C
B → 800°C
C → 900°C
D → 1000°C
E → 1100°C
A
B
C
D
E
RELATIVE INTENSITY
0
2
4
6
8
10
12
14
16
18
20
4000
4500
5000
5500
6000
6500
7000
WAVE-LENGTH A° UNIT

FIG· 10



(Ca, Mg) h·p 7% Pb + 2% Mn
A → 850°C
B → 925°C
C → 1000°C
D → 1075°C
E → 1100°C
C
D
B
E
A
RELATIVE INTENSITY
0
2
4
6
8
10
12
14
16
18
20
4000
4500
5000
5500
6000
6500
7000
WAVE-LENGTH A° UNIT

FIG·11



(Ca, Be) h·p 3% Pb + 0·5 Mn
A → 850°C
B → 925°C
C → 1000°C
D → 1075°C
E → 1150°C
A
B
C
D
E
RELATIVE INTENSITY
0
2
4
6
8
10
12
14
16
18
20
3500
4000
4500
5000
5500
6000
6500
7000
WAVE-LENGTH A° UNIT

FIG· 12

activator concentrations, volatability of halide ions and to some extent to the change in Ca : P ratio.

The initial rise can obviously be attributed due to the gradual incorporation of more and more activators at rising temperatures. Furthermore, it is observed that the intensity starts falling at high temperatures after remaining constant over a certain range of temperature. It is found that the change in firing temperature does not change the position of emission peaks of these phosphors. It is, therefore, expected that Mn^{2+} is not being lost because the change in the concentration of Mn^{2+} is known to change the emission wave length. It is likely that lead or halide is being lost, as the lead and halide ions have the tendency to volatilize at high temperatures. It is clear from the graph that just above the optimum temperature, the fall of intensity is slow, but at high temperature, i.e. above 1100-1150°C the fall of intensity is very sharp. The spectroscopic and gravimetric estimation failed to give a positive answer as the added impurities are very small.

Experimentally, it has been shown that for the optimum intensity the ratio of Ca:P should be 4.9:3 instead of 5:3. That clearly indicates that the excess of phosphates ions are necessary for the good intensity and this possibly helps the incorporation of Mn^{2+} by charge compensation. In our system, we have also kept the Me:P ratio as 4.9 : 3. If at high temperature, the phosphorus is volatilising then the ratio of Me:P must be getting beyond the optimum and hence the fall in intensity.

The effect of quenching and annealing on intensity of phosphors

The results of experiments on quenching and annealing are quite significant because in case of these Pb activated (Ca,Cd) chlorofluoro phosphate phosphors, quenching gives poorer emission than annealing,while reverse is true for (Ca,Mg) and (Ca,Be) fluoro phosphates,studied in this series. In fact, later is true for Sb-activated phosphors which have been studied by several other workers. When the phosphors are annealed, the impurity ions migrate to the low energy sites whereas on quenching they remain randomly distributed over the various available sites. This may indicate that the low energy site for the activator is not always the favourable site for its efficient action as an activator. Thus, annealing might be bringing the Pb ions to the wrong sites, whereas quenching would, at least, be leaving a part of the Pb ions at the proper activator site. Sb^{3+} being trivalent may be stabilized at Ca(II) sites because it will then be close to the O^{--} which replaces F^-/Cl^- for the charge compensation. However, as sensitizer Sb may be required at Ca(I) site which can be achieved only by quenching the sample from high temperature. As lead is divalent, the difficulty due to charge compensation does not arises and it can replace Ca(I) site with ease.

GENERAL CONCLUSION

The mixed halophosphate phosphors

The x-ray diffraction studies have shown that cadmium, magnesium and beryllium can replace calcium in calcium halophosphates. The solid solution retains the apatite structure. By the x-ray intensity analysis it has been found that the beryllium and magnesium occupy the Ca(I) sites while most of the cadmium occupies the Ca(II) sites. From these results it appears that lighter elements are substituted in I sites and heavier ones are substituted in the II sites.

Johnson with the help of polarisation of luminescence and electron spin resonance of synthetic single crystal have shown that the Mn^{2+} is in Ca I site in fluorophosphate while it is in Ca(II) site in chlorofluoro and chloro phosphate. This clearly indicates that the (Ca,Mg) and (Ca,Be) fluoro phosphate phosphors, Mn^{2+} which is going to I site must be substituting for Mg^{2+} and Be^{2+} and it is substituting the Cd^{2+} in chlorofluoro phosphates. Furthermore, it is observed that relatively less intensity was observed in case of (Ca,Be) halophosphate phosphors. The probable reason appears to be the large difference between the ionic radii of Mn^{2+} and Be^{2+}. This is in agreement with the observation of Henderson, Mash and Ranby[58] on barium pyrophosphate, where the poor intensity was observed and this was attributed to the large difference in the ionic radii of Mn^{2+} and Ba^{2+}.

The location of Pb^{2+} is not conclusively established. From our x-ray intensity analysis it appears that the Pb^{2+} ions may be substituting Ca(II) sites because we have found that the heavier elements are going in Ca(II) sites. Furthermore, Ranby has shown that the Ag^{+} is replacing the Ca^{2+} in Ca(II) sites. This also supports the above fact. We, therefore, tentatively decide that the Pb^{2+} is substituting in Ca(II) sites in the fluorophosphates studied.

In case of (Ca,Cd) and (Ca,Be) halophosphates relatively smaller amounts of Mn^{2+} ~~is~~ are required for the optimum intensity whereas in case of (Ca,Mg) halophosphates relatively large amount of Mn^{2+} is required. In this respect the former two are similar to cadmium halophosphates, while the last one is similar to calcium halophosphate phosphors. However, in all these cases a sensitizer is required (Pb^{2+}) whereas in case of Cd halophosphate it is not required at all.

These mixed halophosphates are prepared at relatively lower temperatures. This is a great advantage as it has often been found that the phosphors requiring higher temperatures for firing lead to an excessive sintering and oxidation of the Mn^{2+} ions.

The electrical conductivity

The electrical conductivity plots show two distinct regions; one at lower temperatures when the slope is small and other in the high temperature region where the slope is high.

The first region can clearly be attributed to some low lying states which are ionized even at room temperatures. Such states can be due to a thin conductions layer on the surface of individual grains in the polycrystalline phosphor. This type of behaviour is often observed in sintered samples because during the sintering process the oxide tends to gain or loose the oxygen so that one gets a non-stoichiometric surface layer on the grains which is more conducting than the bulk. At higher temperatures, however, the bulk conductivity rises and dominates over the conductivity due to the non-stoichiometric surface layer. The slope of $\log \rho$ vs 1/T at high temperature is therefore representative of the bulk.

An examination of the values of activation energies shows that there is no pronounced effect of adding activator and co-activator on the value of this activation although there is a small decrease to which, it is not clear, whether any significance could be attached. However, the value of activation energy is too small to be due to band to band transition of electron and is to be attributable to excitation of electron or hole from impurity level in the forbidden band. Furthermore, the fact that the conductivity decreases and activation energy increases in nitrogen atmosphere as compared to air suggest that these are oxygen excess of metal difficient compounds and the conductivity is expected to be p-type. This would contradict the formation of Cd in the cadmium halophosphate which would have been possible in metal excessphosphor. On the other hand, this would suggest that the oxygen excess has arisen due to the loss of halide ion due to volatization and its replacement by 0 due to oxidation. The replacement of (Cl,F) by oxygen give rise to 0^- species. This can be treated as a hole bound to 0^{--} ions. These holes can ionise at higher temperature and give rise to p-type electronic conductivity.

(Ca,Th) halophosphate phosphor system

(i) The x-ray diffraction studies on the formation of solid solution shows that thorium forms a solid solution with calcium halophosphate and gives the structure similar to apatite, when the composition is taken according to the following formula

$$(Ca_{1-x} : Th_{x/2} \square_{x/2})_{10}(PO_4)_6F_2$$

instead of the formula

$$(Ca_{1-x}Th_x)_{10}(PO_4)_6F_2.$$

The latter formula showed some unreacted ThO_2 lines and this was presumably due to the fact that Th could not be incorporated as Th^{2+}.

The unit cell is hexagonal and the general similarity between the observed intensities of these compounds with those of calcium halophosphates shows that they are isomorphous and have the apatite structure.

The 'a' and 'c' values are calculated by usual formula given in the last chapter and the 'd' values were obtained which are given in Table No.7&8 for x = .05 and .03 respectively.

	a	c	Ionic radii
(Ca,Th) halophosphate	9.33	6.80	1.0
Ca-halophosphate	9.37	6.88	1.06

From the above values it is clear that there is not much change in dimension of the unit cell of the new phosphate.

X-ray intensities for thorium have been calculated but our patterns are taken for the small quantities of the thorium and it is not possible to do any quantitative cation distribution calculations accurately. However, there are general indications that the thorium may be substituting in the Ca(II) sites.

(ii) Physical characteristics of (Ca,Th) halophosphates

The antimony activated (Ca,Th) halophosphate produced a strong greenish-blue fluorescence, which has peak at 4800Å. Furthermore, it was observed that the position of antimony emission peak is relatively independent of the antimony concentration, even small traces of antimony are giving good luminescence. In presence of manganese, the emission colours of the phosphors changed from blue to deep yellow according to manganese concentration in the fluorophosphate, while it is changed from blue to pinkish orange in the chlorofluorophosphate. Maximum peaks in these two cases were obtained at 5600Å and 5850Å respectively. The shift of the emission peak is due to the change in Mn concentration and partial replacement of fluorine by chlorine and not so much due to the incorporation of thorium, which can be seen from the above x-ray results to have only a small effect on the unit cell dimensions in view of its small concentration.

There is a definite increase in emission intensity as compared to calcium fluoro phosphate phosphor when a small amount (1-10% Th) is incorporated. However, at higher concentration the intensity decreases progressively. This clearly shows that thorium plays an active role in host as an activator. In fact, the behaviour of the thorium appears to be very parallel to that of Sb^{3+} and Pb^{2+} where they act as efficient activators at low concentration. However, when the concentration becomes high, the different atoms of the activator come in close proximity and the energy transfer takes place from one to another. This results in a decreased transfer of excitation to the Mn^{2+} ions and thereby decreasing the intensity. It appears that the same reasoning would hold for decrease in intensity with increase in thorium concentration.

SUMMARY

SUMMARY

A number of mixed halophosphates with the general formula $(Ca_{1-m}Me_m)_{10}(PO_4)_6X_2$ (where Me = Be, Cd, Mg and Th and X = Cl, F or both) have been synthesized and their structural, optical and electrical properties have been studied.

It has been found that cadmium, magnesium, beryllium and thorium can replace calcium in calcium halophosphates and in all the cases the solid solutions (m = 0.5) have the apatite structure. In case of thorium, it has been observed that it is not incorporated as Th^{2+}, but as Th^{4+}. With the help of x-ray intensity analysis, the location of the substituting ions has been determined. It is found that, generally, the lighter ions go to the Ca(I) sites and the heavier ions to the Ca(II) sites. On this basis, it appears probable that Pb^{2+} ions occupy Ca(II) sites in fluoro phosphates.

The above halophosphates have been doped with suitable concentrations of Pb^{2+} and Mn^{2+} activators and the spectral energy distribution has also been studied.

Wave length of maximum emission is found to change with the substituents. This change is attributed to alterations in metal-oxygen distance, metal-metal distance and the covalent character of Mn^{2+} - O^{--} bond.

The optimum conditions for the preparation of good fluorescent phosphors have been determined in respect to the concentration of activators, co-activators, firing temperatures, gas atmosphere and wash-treatment.

Role of Pb^{2+} and Sb^{3+} as sensitizers

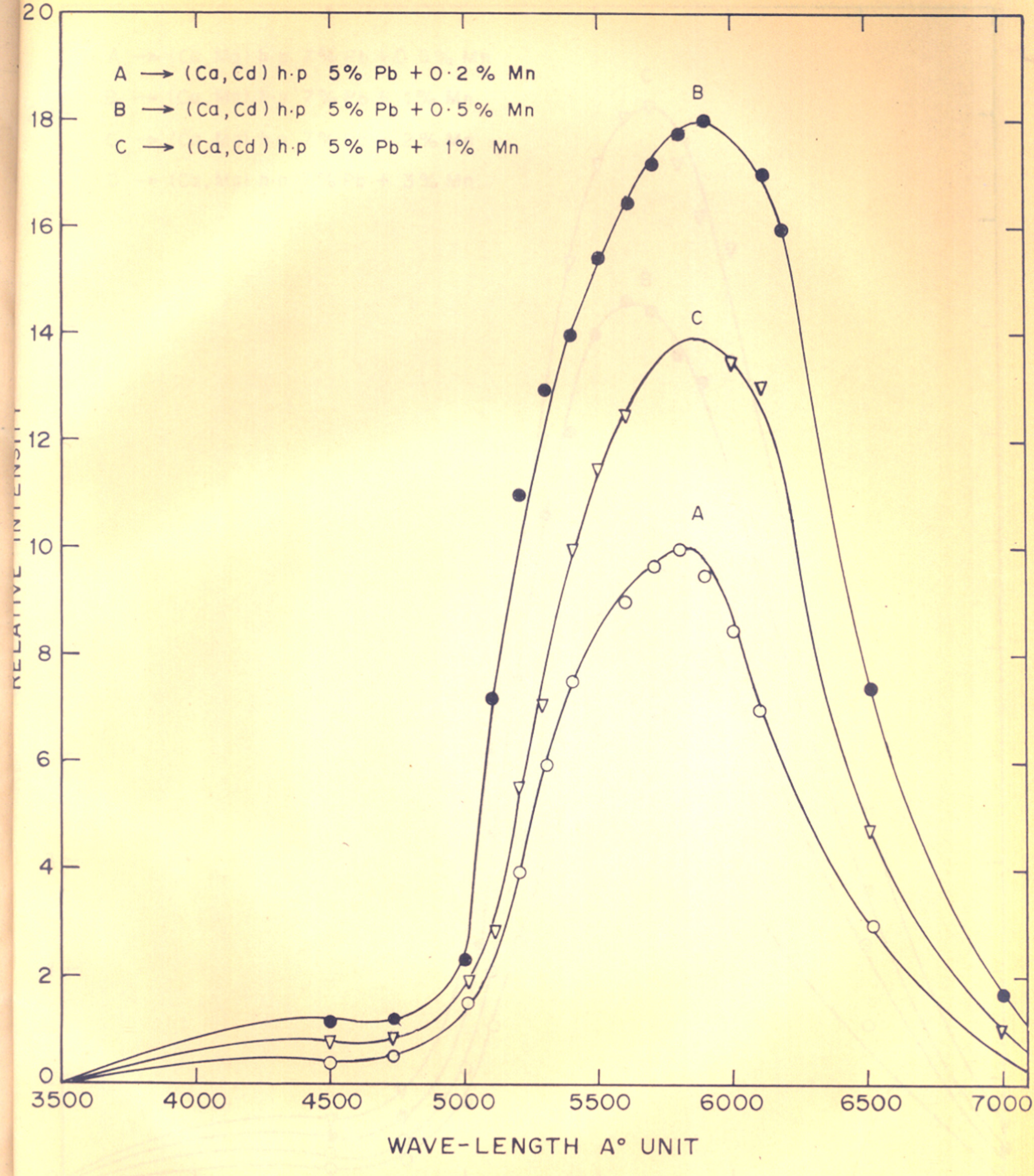
It has been found that the presence of lead and antimony is very essential to induce the fluorescence in mixed halophosphates. Furthermore, it has been observed that lead and antimony produce blue fluorescence, having emission peaks at 4500Å and 4800Å respectively and these peak positions are found to be independent of Pb^{2+} and Sb^{3+} concentrations. The concentrations of lead and antimony have been varied from 0-9% of the halophosphates. At very high concentrations of these sensitizers, phosphors lose their fluorescent properties.

Role of manganese as an activator

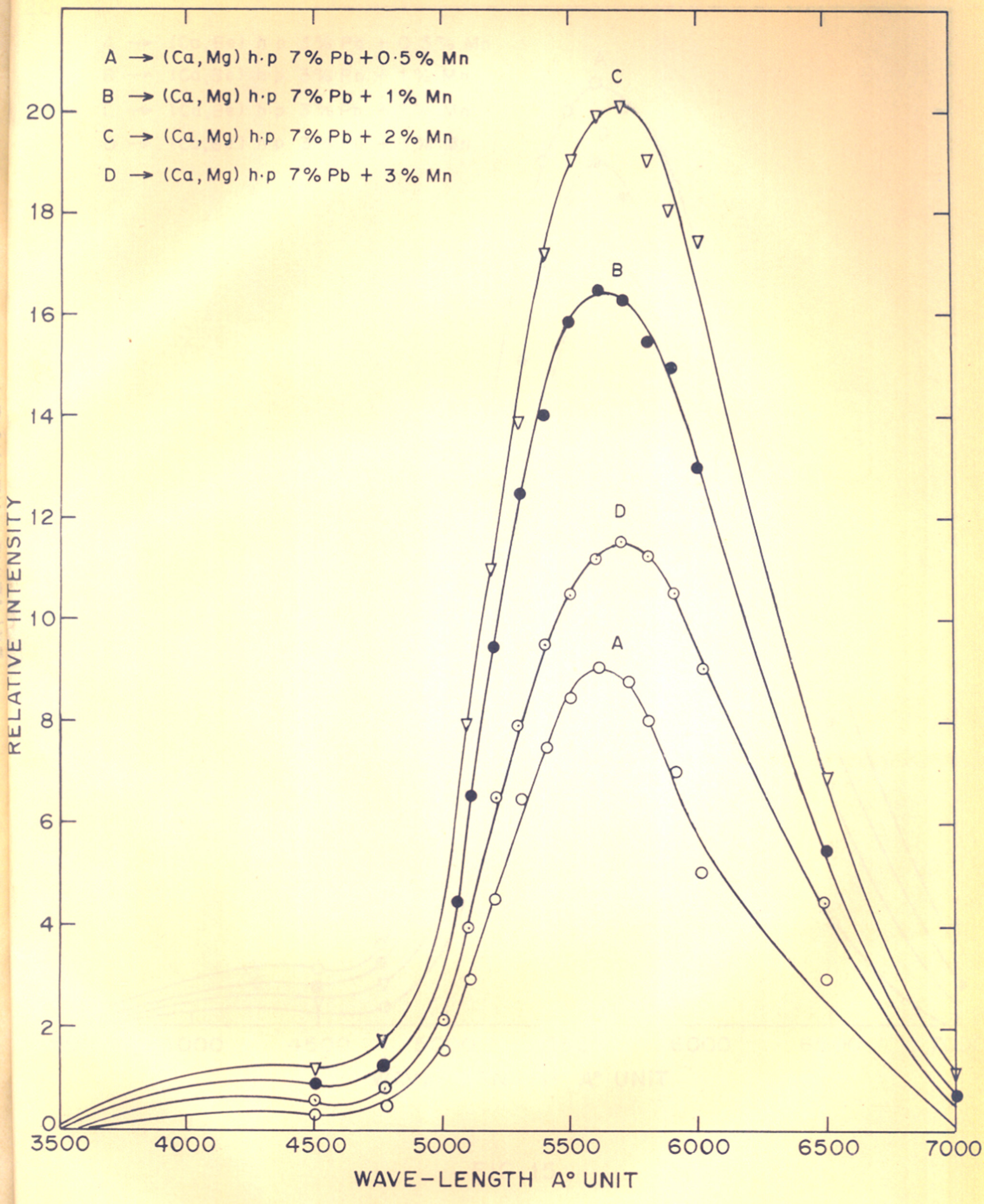
Manganese acts as a colour modifying agent. Manganese alone does not produce any fluorescence, but in presence of lead it gives rise to colours from blue to yellow in fluorophosphate and blue to orange in the chlorophosphates. The manganese concentration has been varied from 0.5 to 2%. Furthermore, it has been observed that relative intensity and spectral energy distribution depend upon the Mn^{2+} concentration, as we can see from the figures 13 to 17. It has been found that the phosphors lose their fluorescent properties at high concentrations. The optimum conditions for the preparation of these phosphors from each series are tabulated in the Table No. 32 & 33

Role of firing temperature

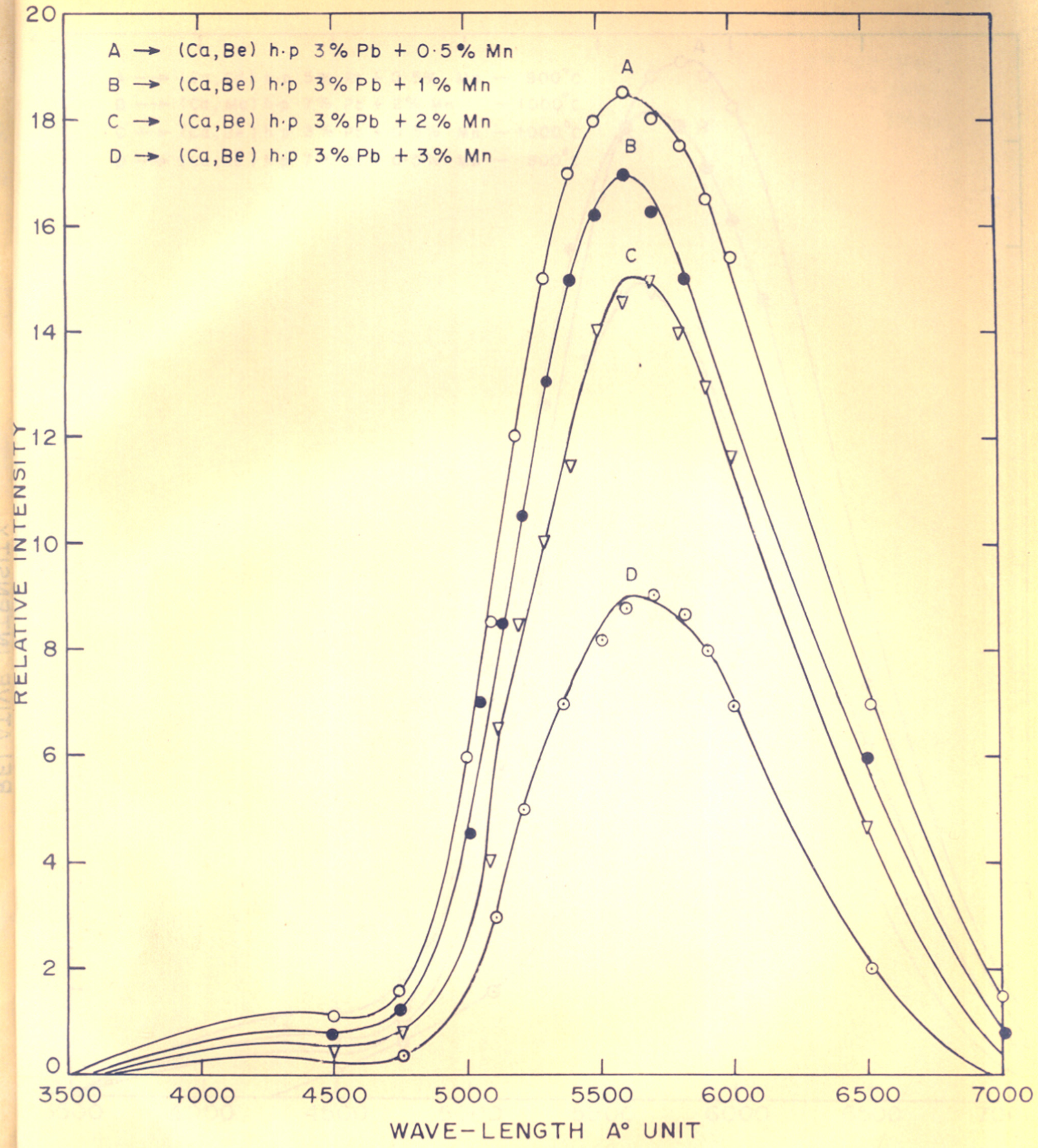
The emission intensity is maximum for a certain optimum firing temperature in each system and decreases on increasing or decreasing the temperature from their optimum value. The lower intensity at lower temperature has been attributed to incomplete incorporation of the activators in the matrix and that at higher temperature due to the loss of lead and halide constituents. Furthermore, it has been observed that the Me:P ratio also gets disturbed at higher temperatures.


A → (Ca, Cd) h·p 5% Pb + 0·2% Mn
B → (Ca, Cd) h·p 5% Pb + 0·5% Mn
C → (Ca, Cd) h·p 5% Pb + 1% Mn
B
C
A
20
18
16
14
12
10
8
6
4
2
0
3500
4000
4500
5000
5500
6000
6500
7000
WAVE-LENGTH A° UNIT

FIG·13


A → (Ca, Mg) h·p 7% Pb + 0·5% Mn
B → (Ca, Mg) h·p 7% Pb + 1% Mn
C → (Ca, Mg) h·p 7% Pb + 2% Mn
D → (Ca, Mg) h·p 7% Pb + 3% Mn
C
B
D
A
RELATIVE INTENSITY
0
2
4
6
8
10
12
14
16
18
20
3500
4000
4500
5000
5500
6000
6500
7000
WAVE-LENGTH A° UNIT

FIG· 14


A → (Ca, Be) h·p 3% Pb + 0·5% Mn
B → (Ca, Be) h·p 3% Pb + 1% Mn
C → (Ca, Be) h·p 3% Pb + 2% Mn
D → (Ca, Be) h·p 3% Pb + 3% Mn
A
B
C
D
RELATIVE INTENSITY
0
2
4
6
8
10
12
14
16
18
20
3500
4000
4500
5000
5500
6000
6500
7000
WAVE-LENGTH A° UNIT

FIG· 15

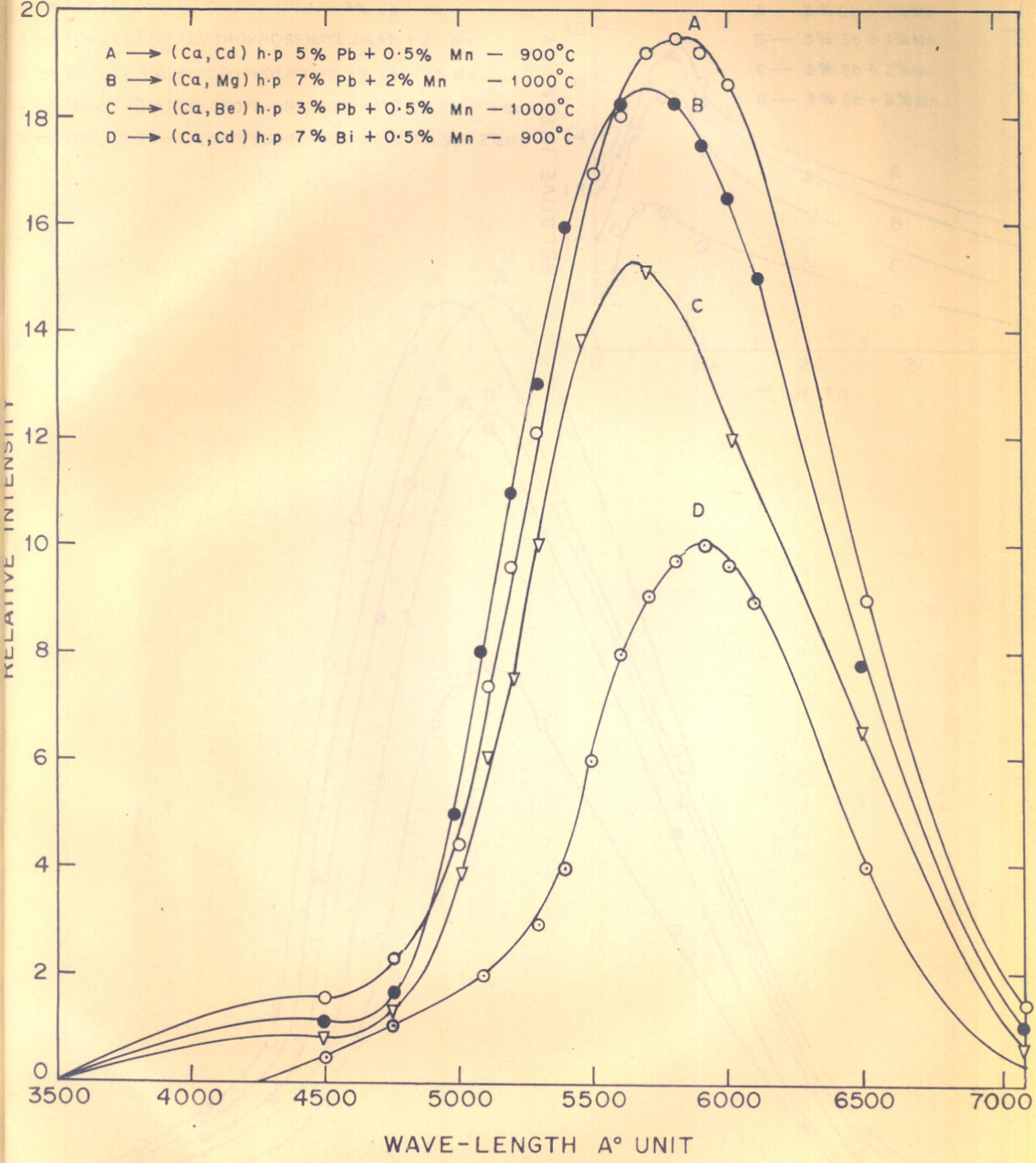
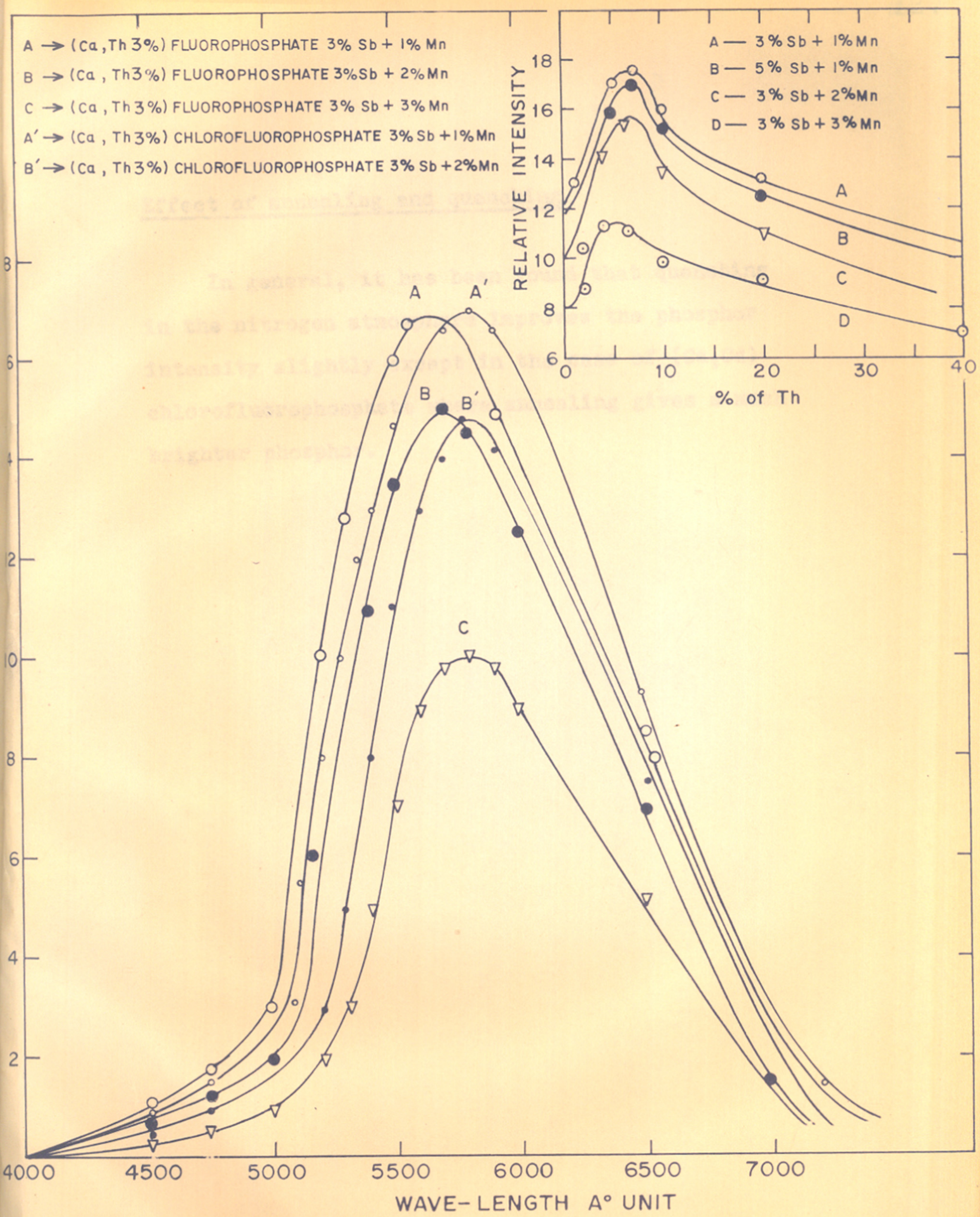

A → (Ca, Cd) h·p 5% Pb + 0·5% Mn — 900°C
B → (Ca, Mg) h·p 7% Pb + 2% Mn — 1000°C
C → (Ca, Be) h·p 3% Pb + 0·5% Mn — 1000°C
D → (Ca, Cd) h·p 7% Bi + 0·5% Mn — 900°C
A
B
C
D
RELATIVE INTENSITY
0
2
4
6
8
10
12
14
16
18
20
3500
4000
4500
5000
5500
6000
6500
7000
WAVE-LENGTH A° UNIT

FIG. 16


A → (Ca, Th 3%) FLUOROPHOSPHATE 3% Sb + 1% Mn
B → (Ca, Th 3%) FLUOROPHOSPHATE 3% Sb + 2% Mn
C → (Ca, Th 3%) FLUOROPHOSPHATE 3% Sb + 3% Mn
A′ → (Ca, Th 3%) CHLOROFLUOROPHOSPHATE 3% Sb + 1% Mn
B′ → (Ca, Th 3%) CHLOROFLUOROPHOSPHATE 3% Sb + 2% Mn
A
A′
B
B′
C
8
6
4
2
10
8
6
4
2
4000
4500
5000
5500
6000
6500
7000
WAVE-LENGTH A° UNIT
A — 3% Sb + 1% Mn
B — 5% Sb + 1% Mn
C — 3% Sb + 2% Mn
D — 3% Sb + 3% Mn
RELATIVE INTENSITY
18
16
14
12
10
8
6
0
10
20
30
40
% of Th
A
B
C
D

FIG· 17

Effect of annealing and quenching

In general, it has been found that quenching in the nitrogen atmosphere improves the phosphor intensity slightly except in the case of (Ca,Cd) chlorofluorophosphate where annealing gives a much brighter phosphor.

Table 32

Optimum conditions giving the best results with lead and manganese in N_2 atmosphere

Composition	Sensitizer	Activator	Firing Temp. °C	Quenching or Annealing	Fluorescence colour
$(Ca_{.5}Cd_{.5})_9(PO_4)_6\cdot(Cd_{.5}Ca_{.5})Cl\ F$	5% Pb	0.5% Mn	900	A	Orange
$(Ca_{.5}Cd_{.5})_9(PO_4)_6\cdot(Ca_{.5}Cd_{.5})Cl\ F$	7% Bi	0.5% Mn	900	A	Orange
$(Ca_{.5}Mg_{.5})_9(PO_4)_6\cdot(Ca_{.5}Mg_{.5})F_2$	7% Pb	2% Mn	1000°C	Q	Yellow
$(Ca_{.5}Be_{.5})_9(PO_4)_6\cdot CaF_2$	3% Pb	0.5% Mn	1000°C	Q	Yellow

Table 33

Optimum conditions giving best result with antimony and manganese in N_2 atmosphere

Composition	Sensitizer	Activator	Firing temp. °C	Fluorescence colour
$(Ca_{.94}Th_{.03}\square_{.03})_9(PO_4)_6CaF_2$	3% Sb	1% Mn	1100°C	Yellow
$(Ca_{.94}Th_{.03}\square_{.03})_9(PO_4)_6Ca(ClF)$	3% Sb	1% Mn	1100°C	Orange
$(Ca_{.96}Th_{.02}\square_{.02})_9(PO_4)_6CaF_2$	3% Sb	1% Mn	1100°C	Yellow
$(Ca_{.96}Th_{.02}\square_{.02})_9(PO_4)_6Ca(F\ Cl)$	3% Sb	1% Mn	1100°C	Orange

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