

C H A P T E R I I

P R E P A R A T I O N O F P H O S P H O R

CHAPTER IIP R E P A R A T I O N O F P H O S P H O R2.1 PREPARATION OF PHOSPHORS

Phosphors may be of (1) Single crystal form, (2) thin film form, (3) Microcrystalline powder. It is observed that the phosphors of alkaline earth sulphide type decompose before they melt and hence it is difficult to prepare such phosphors. Some phosphors in thin film form may be prepared.

One of the earliest TL phosphors known in dosimetric application is  $\text{CaSO}_4:\text{Mn}$ . Oddly enough this was used for measurement of uv radiations. Lyman employed the uv induced TL sensitivity of  $\text{CaSO}_4:\text{Mn}$  phosphors for determining the transparency of air between 1100 to 1300 $^{\circ}\text{A}$ . Tousey et al (2) used this phosphor for the determination <sup>of</sup> ~~at~~ solar extreme uv. in wavelength region 1050-1240 $^{\circ}\text{A}$  and 1230-1340 $^{\circ}\text{A}$ , Nosenko et al (3) introduced this phosphor in dosimetry of ionising radiation. The chief disadvantage of this phosphor is fast decay of the dosimetry peak, which occurs at a low temp. at about 100 $^{\circ}\text{C}$ . Yamashita et al (4) succeeded in preparing the  $\text{CaSO}_4:\text{Mn}:\text{Pb}$  phosphor which <sup>is</sup> as good <sup>in</sup> ~~as~~ sensitivity as  $\text{CaSO}_4:\text{Mn}$  with almost no fading, as the low peak temp got shifted to nearly 200 $^{\circ}\text{C}$ .

In the present case, the phosphor is taken in microcrystalline form. There are several methods of preparation of CaS phosphors. The luminescent characteristic of these phosphors depends on the atmosphere of firing, firing temperature, rate of cooling.

2.2 PHOSPHORS IN MICROCRYSTALLINE FORM :

To obtain the phosphors in microcrystalline form, the preparation method is described in detail as follows :

### 2.2.1 Basic Ingredients of Phosphors :

The method of obtaining phosphors in the powder form in general, is to start with a pure host material, mix it with suitable flux alongwith activator element<sup>is</sup> added, Preferably in the form of solution. The ingredients are thoroughly mixed and charge is finally fired at suitable temperature for <sup>a</sup> fixed time.

a) The Host material : Since the transitions of electrons responsible for luminescence are within the range of the band gap, for visible luminescence it is necessary that the band gap of matrix crystal should be between 1.5 eV to 3 eV. since there are the energies of photons corresponding to extreme red and violet region of visible spectrum.

b) Activators : The activator is one which provides localised energy levels in the forbidden energy gap of an insulator or semiconductor and that permits radiative transition. According to role performed, activators are classified in the following groups :

i) Originator : It gives rise to new emission lines or bands other than intrinsic luminescence of host lattice.

ii) Intensifier : It intensifies the intrinsic luminescence of the host lattice.

iii) Dominant and Auxillary Activator : Some times efficiency of singly activated phosphor is enhanced by adding a second activator. The first activator is called dominant activator and second is called auxillary activator.

iv) Killers : It provides energy levels between which radiative transitions are forbidden (5)

v) Co-activator : It provides a <sup>balance of</sup> charge (6,7) in phosphors activated by monovalent atoms.

Moreover it may also affect the colour of emission, its intensity, and crystalline structure of the phosphor material.

c) Flux : There are certain salts which, when added to the base material, results in good phosphors (8, 9). Such salts are known as flux material or fluxes. Flux salts play different roles in different phosphors. generally it is observed that--fluxes

- 1) Increases the rate of reaction at lower temperature. (10, 11)
- 2) Promotes the crystal growth at lower temperature.
- 3) Facilitates the incorporation of activator and its homogeneous distribution in the host lattice. (10,11)
- 4) Affects the luminescent - intensity (11)
- 5) Serves as charge compensating agent. (6,7)

Generally the effective fluxes are oxysalts and sulphates of sodium and potassium. (12)

### 2.2.2 Preparative Parameters of phosphors :

The Luminescent characteristic<sup>s</sup> of phosphors depends<sup>on a</sup> number of parameters. The important parameters are described here.

1) Purity of Ingredient : As luminescence emission is very sensitive to the impurity atom, a slight trace of foreign element may cause either activation or poisoning. Hence the purity of ingredients to be used is an important consideration in making phosphors. A clean laboratory and special care to maintain purity and cleanliness through out the process is essential.

ii) Vessels : The selection of vessels. ( crucible etc. ) is performed on the basis of their chemical inertness, purity high refractoriness and ability to with stand thermal and mechanical shocks.

iii) Firing temperature : To achieve an optimum brightness, the phosphor is required to be fired for a suitable time at an appropriate temperature. (13) The temperature within the furnace must be uniform and constant. Variation in temperature totally changes the crystal structure of phosphors which affects the structural homogeneity of final product. (13, 14, 15)

iv) Atmosphere of firing : The atmosphere in which phosphor ingredient are fired has a pronounced effect on the character of phosphor. (16) It is observed that hexagonal CdS when fired in neutral atmosphere emits in the infrared region, while it emits in green region when fired in  $H_2S$  atmosphere (17). Also some phosphors (18) which do not show electroluminescence response when fired in  $H_2S$ , become electroluminescent if fired in presence of water vapour.

v) Grain size of ingredient : The grain size of basic ingredient required for phosphor preparation has a striking effect on the rate of solid - state reaction and there by also on the quality of the phosphor. To have phosphors of good quality, the solid state reaction must be continuous and uniform. This has been achieved by taking particles of very fine size and having large surface to volume ratio. ( 13, 19, 20 ).

vi) Rate of cooling : In general rate of cooling affects the luminescent properties such as absorption spectral emission and brightness of phosphor. It often affects phosphorescence decay also (21). Sudden cooling sometime changes the colour of fluorescence (22). Slow cooling rate helps in uniform distribution of imperfection throughout the phosphor. (23) Also rapid cooling preserves the valence state prevalent at high temperature.

vii) Size of charge : Preparation of phosphors in large quantities involves different rates of heating due to poor conductivity of the charge, and thus affects the homogeneity of the final product. (20) This effect can be minimised by taking small quantity of the ingredient each time.

### 2.3 DETAILS OF METHOD FOLLOWED TO OBTAIN (CaS : Bi : Pb PHOSPHORS) :

The method followed for preparing CaS phosphors in the present investigation was one developed by Bhawalkar (24). The method involves heating an intimate mixture of the purified calcium sulphate and carbon together with required amount of activator and fluxes (  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{NaF}$  ). The reduction is carried out at  $900^\circ\text{C}$  by heating mixture for about 3 hours. The details of procedure followed are as follow.

#### 2.3.1 PURIFICATION OF CALCIUM SULPHATE :

The host material CaS is obtained from Calcium sulphate dihydrate. of Thomas bunkar, London.  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  having molecular weight 172.17 gm. This calcium sulphate is having purity .

99% calcium sulphate is again purified by washing it with double distilled water. Residue is dried in oven at  $70^{\circ}\text{C}$  for one day. Then the powder is stored in clean and tightly sealed bottle.

### 2.3.2 Purification of Carbon :

Analytical Reagent grade charcoal was used as reducing agent. To remove water soluble impurities the charcoal is washed with double distilled water. Charcoal is mixed with distilled water, and solution is boiled on electric stove, for about  $\frac{1}{2}$  hour, then it is filtered. The residue is washed repeatedly with hot distilled water and finally it was dried on hot plate at  $90^{\circ}\text{C}$ , then powder is placed in clean bottle.

### 2.3.3 Activator :

The activator Bi was added in the form of solution. The weighed quantity of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (A.R. grade purity 99%) was taken. The molecular weight is 485.104 gm. The bismuth nitrate is dissolved in distilled water. It is taken in the form of solution. The solution of 0.1 N was prepared. The required quantity of solution is added to give various percentage at Bi.

### 2.3.4 Co-activator :

The co-activator  $\text{Pb}$ <sup>is</sup> added in the form of solution. Pb is obtained from  $\text{Pb}(\text{NO}_3)_2$  having molecular wt. 331.2 gm. Definite quantity of  $\text{Pb}(\text{NO}_3)_2$  is weighed and then it is dissolved in distilled water to give 0.1N solution. Definite amount is taken to form various concentrations of Pb

### 2.3.5 Purification of Crucible :

Clay crucibles were used as reaction vessel. These were soaked in 30% nitric acid for 8 hours to ensure complete conversion of contaminating impurities into water soluble nitrate.

These were washed repeatedly with distilled water. The crucibles were then fired at  $900^{\circ}\text{C}$  for one hour to remove any contamination of other gases. This also tests their ability to withstand thermal and mechanical shocks.

#### 2.3.6 Fluxes used :

The trial samples were prepared both with Flux and without fluxes. It was observed that the addition of fluxes enhances luminescence phenomenon. The fluxes used were (a) Sodium Sulphate anhydrous, Hovard make

- b) Sodium thiosulphate E-Merck
- c) Sodium Fluoride BDH variety.

#### 2.3.7 Preparation of charge :

The charge was prepared by taking the following quantities :

- 1) Calcium sulphate .. 5 gm.
- 2) Carbon .. 1.25 gm.
- 3) Sodium Sulphate .. 0.25 gm.
- 4) Sodium thiosulphate .. 0.625 gm.
- 5) Sodium Fluoride .. 0.75 gm.
- 6) Activator of required quantity.
- 7) Co-activator - definite amount depending on concentration to be added.

All these quantities are thoroughly mixed to form a uniform mixture. Few drops of alcohol are added which facilitate dispersion and diffusion of activator throughout the charge. Then the paste of this mixture is dried in oven at  $70^{\circ}\text{C}$ .

#### 2.3.8 Firing of charge :

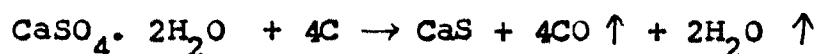
The dried charge was thoroughly <sup>GROUND</sup> ~~grinded~~ to a fine particle size and then packed in crucible, which were prefired. Above this charge a thin uniform layer of purified carbon was spread to keep



the reducing atmosphere above this crucible. A second crucible was placed above this to form a lid. In second crucible little quantity of purified carbon was added. Then whole thing is placed in furnace which was maintained at 900°C. The charge is fired for 3 hours. The temp 900°C was kept constant throughout the time.

After firing charge was removed and immediately pulverised when it was red hot. Pulvarisation was carried out <sup>with</sup> in quartz <sup>pestle</sup> and mortar.

The reduction of calcium sulphate into Calcium sulphide occurs accordingly :



since alkaline earth sulphides are hygroscopic the prepared samples were immediately stored in sealed and numbered bottles and then bottles were placed in dessicator.

### 2.3.9 Prepared Phosphors :

The details of samples prepared are shown in table, 2.1 where concentration of Bi is varied from 0.05, 0.1, 0.2, 0.3, 0.5, 0.7, 1, 2, 3, 5 wt. % of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and Pb is at 1 wt. % of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

In table no.2.2 concentration at Bi was fixed 1 wt. % and concentration of Pb is varied from 0.05, 0.1, 0.2, .3, 0.5, 0.7 2, 3, 5 wt % at  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Samples contain<sup>ing</sup>  $\text{CaS}:\text{Bi}$  1 wt % and  $\text{CaS}:\text{Pb}$  1 wt% and only  $\text{CaS}$  were also prepared.

Table No. 2.1

Phosphors with individual concentration of Bismuth and lead  
activators in percentage by wt. of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  prepared for study.

Sample number	Concentration of Bi wt%	Concentration of Pb wt.%
S <sub>1</sub>	0.05	1
S <sub>2</sub>	0.1	1
S <sub>3</sub>	0.2	1
S <sub>4</sub>	0.3	1
S <sub>5</sub>	0.5	1
S <sub>6</sub>	0.7	1
S <sub>7</sub>	1	1
S <sub>8</sub>	2	1
S <sub>9</sub>	3	1
S <sub>10</sub>	5	1

Table No. 2.2

Phosphors with individual concentration of Bismuth and lead  
 $2\text{H}_2\text{O}$   
 activators in percentage by Wt. of  $\text{CaSO}_4$  prepared for study.

Sample number	Concentration of Bi Wt %	Concentration of Pb wt. %
S <sub>11</sub>	1	0.05
S <sub>12</sub>	1	0.1
S <sub>13</sub>	1	0.2
S <sub>14</sub>	1	0.3
S <sub>15</sub>	1	0.5
S <sub>16</sub>	1	0.7
S <sub>17</sub>	1	2
S <sub>18</sub>	1	3
S <sub>19</sub>	1	5
S <sub>20</sub>	1	00
S <sub>21</sub>	00	1
S <sub>22</sub>	00	00

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