

## **CHAPTER - II**

### **PREPARATION OF PHOSPHORS**

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#### 2.1 Synthesis of phosphors :

##### 2.1.1 Introduction :

There exists several methods for preparation of phosphors. Use of particular method depends upon the type of phosphor to be prepared and application desired. However, in general, every method involves the combination of a particular host matrix with specific activator and flux. The activator is introduced in the host lattice by proper heat treatment at high temperature in suitably controlled atmosphere. These days the neutron bombardment and ion implantation techniques are being used for activation.

The phosphors can be prepared as per requirements in the form of :

- i) Microcrystalline powder.
- ii) Thin film and
- iii) Single crystal.

The micro crystalline powder phosphors are prepared by heating the host material, taken in the form of fine powder along - with the activators, in a suitable atmosphere for a predetermined temp. and period.

The phosphors in thin film form are generally prepared by vacuum evaporation, sputtering, spray pyrolysis, screen printing etc. Activators are added during or after the deposition of film.

A painstaking efforts are required for preparing single crystal phosphors. The preparative parameters for preparing single crystal phosphors are very sensitive to variations. Utmost carefulness and patience is required for its preparation. The method of preparation varies from one phosphor system to other.

#### 2.1.2 General Considerations of Synthesis of phosphors :

The word phosphor is used synonymously with luminescent solid, which is an artificial (man made) inorganic material. Artificial phosphors are not only much more efficient and versatile than the naturally occurring luminescent materials, but they are also better defined, and hence more suitable for study. Basic ingredients for preparation of phosphor are :

- a) Host material,
- b) Activator,
- c) Co-activator,
- d) Flux and
- e) Charge compensation.

It is important to consider band-gap of host material before we take up phosphor preparation. For example band gap of 1.5 to 3 eV is essential to have a luminescence emission in the visible region of electromagnetic spectrum. The reason is that 1.5 eV corresponds to extreme red whereas 3 eV corresponds to extreme violet.

The incorporation of activator ions in host lattice is another aspect for luminescence to take place. The activator provides localised energy levels in the forbidden gap of host material which allow radiative transition to take place. There are various methods of doping activator in the host material. Some of the known and popular techniques are electrolytic introduction of activators into previously crystallised solid,<sup>1</sup> chemical doping, crystal growing of melts of host and activator materials etc. Of late, ion implementation<sup>2,3</sup> has been proved to be powerful technique to incorporate activator ions directly into the host material before structure undergoes a phase change.

An addition of suitable co-activator to the activated phosphor some times improvises the luminescence output of a phosphor system. The enhancement of luminescence output due to co-activator is explained in terms of energy transfer.

In some phosphors the addition of certain readily fusible salts is beneficial for increasing luminescence output. They are normally called 'flux'. Fluxes are luminescence inert materials. They do not take any part in the luminescence process, but provide liquid fluid phase to facilitate activator ions to enter in the host lattice.

Certain conditions are required to be fulfilled for doping impurity ions in the host material. The ionic radius of dopant ion should be close to ionic radius of host lattice ion. Secondly, charge balancing should not be disturbed when impurity ion substitutionally replaces host lattice ion. Many a times the ionic charge of dopant ion does not match with host lattice ion. For example when we are required to dope rare earth ions like  $Dy^{3+}$ ,  $Eu^{3+}$ ,  $Tm^{3+}$  etc. in the host  $CaSO_4$ , there is charge imbalance between dopant ion and host lattice ion  $Ca^{2+}$ . The imbalance of this kind does not allow easy entry of dopant ion into host lattice. In that case it is advisable to use some monovalent charge copensator ion like  $Na^+$  or  $K^+$  so as to achieve charge balancing. The literature on phosphor preparation reveals that such charge balancing enhances the luminescence output of a phosphor system to a large extent.<sup>4,5</sup> Kroger and Hellingmann<sup>6</sup> proposed the possible mechanism underlying the process of charge balancing.

### 2.1.3 Sensitive Parameters of Phosphor Preparation :

Luminescent properties of a phosphor usually dependents upon the number of parameters during synthesis. These are as follows.

- 1] Purity of ingredients.
- 2] Reaction vessels.
- 3] Firing temperature and its duration.
- 4] Atmosphere of firing.
- 5] Grain size of ingredients.
- 6] Rate of cooling and
- 7] Size of Charge.

#### 1] Purity of Ingredients :

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It has been proved that as little as 10 % of certain impurities can affect the luminescence of many phosphors. The purity of basic ingredients is, therefore, highly essential. The substances, materials and chemicals should at least be "luminescence Pure", (L.P.) i.e. 99.9999 % purity, if desired results are to be above suspicion. A very clean laboratory, as well as cleanliness throughout the various stages of synthesis of phosphors are essential.

#### 2] Reaction Vessels :

The selection of reaction vessels is to be done on the basis of their chemical inertness, purity,

high transparency and ability to withstand thermal and mechanical shocks.

3] Firing Temperature and its Duration :

The prepared charge is to be fired at an appropriate temperature for a suitable time; which is predetermined for each phosphor system. Moreover, the temperature inside the heating chamber must be fairly uniform and constant. The existence of temperature gradient inside heating chamber or any change in temperature of furnace may change crystal structure of phosphor, consequently final product is affected as regards the structural homogeneity.

4] The Atmosphere of firing :

It has pronounced effect on characteristic emission of the phosphor; e.g. hexagonal Cds, when fired in neutral atmosphere gives emission in infrared (IR) region, while emits in green region, if fired in H<sub>2</sub>S<sub>2</sub> atmosphere.

5] Grain size of Ingradients :

The rate of solid state reaction is dependent on the grain size of basic gradients. To synthesise phosphors of good quality, solid state reaction must be continuous and of uniform rate. This can be obtained by

intimate contact of different reacting phases. Particles of very fine size with large surface to volume ratio are therefore preferred.

#### 6] Rate of Cooling :

Normally, luminescent emission, brightness, absorption and phosphorescence decay rate are strongly influenced by rate of cooling. The rapid cooling preserves the valence states prevalent at high temperature and often changes the colour of fluorescence. On the otherhand, slow cooling helps in uniform distribution of defects throughout the phosphor.

#### 7] Size of the Charge :

Phosphor synthesis in large quantities may involve different rates of cooling due to poor conductivity of prepared charge. The mixture in contact with the walls of container will attain furnace temperature earlier than central portion, giving rise to temperature gradient within it. This consequently affects homogeneity of final product. In order to avoid this a small size of the charge should be fired.

### 2.2 Preparation of BaSO<sub>4</sub> Phosphors :

Dysprosium (Dy) doped alkaline earth sulphate phosphors such as CaSO<sub>4</sub>, SrSO<sub>4</sub>, BaSO<sub>4</sub> have proved to be efficient phosphors. Recently Mulla and Desai



have shown that a trace of  $Tb^{3+}$  improves the luminescence output of  $BaSO_4:Dy$  to considerable extent.

The addition of charge compensator ion  $Na^+$  further improves the luminescent output. In view of this, an attempt is made here to investigate which other co-activators could help to enhance luminescence output of  $BaSO_4:Dy$  phosphor. The workers dealing with alkaline earth sulphate phosphors have used rare earth activators such as Dy, Sm, Eu, Tm, Tb, Pr etc. and non rare earth activators such as Mn, Cu, Y, W etc. In the present investigation an attempt is made to see the effect of trace amounts of rare earth co-activators such as Tb, Yb, Pr and non rare co-activator such as Mn, Cu in the enhancement of Dysprosium doped  $BaSO_4$  phosphor.  $Na_2SO_4$  is also used as charge compensator to see the possibility of further enhancement of doped and co-doped system mentioned above.

In the present studies the Barium sulphate phosphors doped with Dysprosium (Dy) and Co-doped with Terbium (Tb), Praseodymium (Pr), Ytterbium (Yb) Copper (Cu) and Manganese (Mn), were prepared.  $Na_2SO_4$ , has been used in preparation of some phosphors. The phosphor preparation was made in two steps.

- a) Preparation of charge and
- b) Firing.

a) Preparation of Charge :

Purified 10 grams of Barium Sulphate powder was taken in a clean corning glass beaker and then concentrated sulphuric acid was added to it till powder got completely dissolved. A batch of Twenty such beakers was arranged on a table. A predetermined quantity of  $Dy_2O_3$  on the basis of gram mole was completely dissolved in a fixed amount of double distilled water. The solution thus obtained was collected in a round bottom flask, as a stock solution with proper sealing and labelling as ML S1. Similarly a stock solution of  $Tb_2O_3$ ,  $Pr_2O_3$ ,  $Yb_2O_3$ ,  $CuSO_4$  and  $MnSO_4$ . Were also prepared on the basis of gram mole and stored in other round bottom flasks, followed by proper sealing and labelling as follows :

1)	ML S2	----->	$Tb_2O_3$
2)	ML S3	----->	$Pr_2O_3$
3)	ML S4	----->	$Yb_2O_3$
4)	ML S5	----->	$CuSO_4$
5)	ML S6	----->	$MnSO_4$

A fixed quantity of stock solution from MLS1 was added to beakers containing the dissolved barium sulphate, according to required weight percent concentration of dysprosium. To prepare mixed phosphors

of  $\text{BaSO}_4$  : Dy : Tb  $\text{BaSO}_4$  : Dy : Pr,  $\text{BaSO}_4$  : Dy : Yb,  $\text{BaSO}_4$  : Dy : Cu and  $\text{BaSO}_4$  : Dy : Mn, the predetermined quantities of stock solutions from MLS2, MLS3, MLS4, MLS5, and MLS6 were added to the beakers, as per the required weight percent concentration of Tb, Pr, Yb, Cu and Mn.

One gram of  $\text{Na}_2\text{SO}_4$  was added in the preparation of some phosphors. The charge so obtained was thoroughly stirred and the batch of twenty (20) beakers was kept ready for firing. Fig. 2.1 gives the flow chart showing the various stages of phosphor preparation.

b) Firing :

A muffle furnace capable of attaining the temperature of the order of  $1000^\circ\text{C}$  with automatic temperature control within  $\pm 10^\circ\text{C}$  was used for this purpose. The beakers containing charge were inserted in a specially prepared double storeyed metallic box with lid provided with nozzle at the front. Ten beakers were kept in lower half and ten in the upper half. The beakers were covered with a glass plate, taking care to leave a small gap for  $\text{H}_2\text{SO}_4$  fumes to escape. The metallic box was inserted in the muffle furnace and the front lid was closed. A long glass tube with downward bend at the rear end, was inserted in the hole of the

lid in order to give an outlet for the  $\text{H}_2\text{SO}_4$  fumes formed during the firing. The double storeyed metallic box was used in order to avoid the reaction of  $\text{H}_2\text{SO}_4$  fumes with coil of the muffle furnace. Secondly, because of long glass tube used for the outlet of  $\text{H}_2\text{SO}_4$  fumes, the problem of spreading of  $\text{H}_2\text{SO}_4$  fumes in the laboratory and creating health hazard was reduced to a certain extent.

The charge was kept for evaporation at  $300^\circ\text{C}$  for eight hours. The dried residue, thus obtained, was washed repeatedly with distilled water for two reasons :

- i] To remove the trace of undesirable soluble sulphates and
- ii] To wash off unused amount of residual  $\text{Na}_2\text{SO}_4$ .

The charge was then dried and heated to  $600^\circ\text{C}$  for two hours, followed by rapid quenching to room temperatures. Finally, the samples thus obtained were crushed, sieved out and collected in sealed bottles, with proper labelling. Table 2.1 (a) and (b) gives the list of phosphors prepared and studied in the present investigation.

Table 2.2 (a) List of BaSO<sub>4</sub> phosphors

Sr. No.	Phosphor No.	Wt% of Dy	Wt% of co-dopent	Charge compensator
1	ML1	0.075	0.001 Tb	-----
2	ML2	0.075	0.0025 Tb	-----
3	ML3	0.075	0.001 Pr	-----
4	ML4	0.075	0.0025 Pr	-----
5	ML5	0.075	0.001 Yb	-----
6	ML6	0.075	0.0025 Yb	-----
7	ML7	0.075	0.001 Mn	-----
8	ML8	0.075	0.0025 Mn	-----
9	ML9	0.075	0.001 Cu	-----
10	ML10	0.075	0.0025 Cu	-----
11	ML11	0.1	0.001 Tb	-----
12	ML12	0.1	0.0025 Tb	-----
13	ML13	0.1	0.001 Pr	-----
14	ML14	0.1	0.0025 Pr	-----
15	ML15	0.1	0.001 Yb	-----
16	ML16	0.1	0.0025 Yb	-----
17	ML17	0.1	0.001 Mn	-----
18	ML18	0.1	0.0025 Mn	-----
19	ML19	0.1	0.001 Cu	-----
20	ML20	0.1	0.0025 Cu	-----

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Table 2.2 (b) List of BaSO<sub>4</sub> phosphors

Sr. No.	Phosphor No.	Wt% of Dy	Wt% of co-dopent	Charge compensator
21	ML21	0.075	0.001 Tb	1 gm. Na <sub>2</sub> SO <sub>4</sub>
22	ML22	0.075	0.0025 Tb	---"
23	ML23	0.075	0.001 Pr	---"
24	ML24	0.075	0.0025 Pr	---"
25	ML25	0.075	0.001 Yb	---"
26	ML26	0.075	0.0025 Yb	---"
27	ML27	0.075	0.001 Mn	---"
28	ML28	0.075	0.0025 Mn	---"
29	ML29	0.075	0.001 Cu	---"
30	ML30	0.075	0.0025 Cu	---"
31	ML31	0.1	0.001 Tb	---"
32	ML32	0.1	0.0025 Tb	---"
33	ML33	0.1	0.001 Pr	---"
34	ML34	0.1	0.0025 Pr	---"
35	ML35	0.1	0.001 Yb	---"
36	ML36	0.1	0.0025 Yb	---"
37	ML37	0.1	0.001 Mn	---"
38	ML38	0.1	0.0025 Mn	---"
39	ML39	0.1	0.001 Cu	---"
40	ML40	0.1	0.0025 Cu	---"
41	ML41	0.050	0.001 Tb	
42	ML42	0.025	0.001 Tb	

**FIGURE CAPTIONS**

Fig. 2.1 Flowchart showing various stages of phosphor preparation.

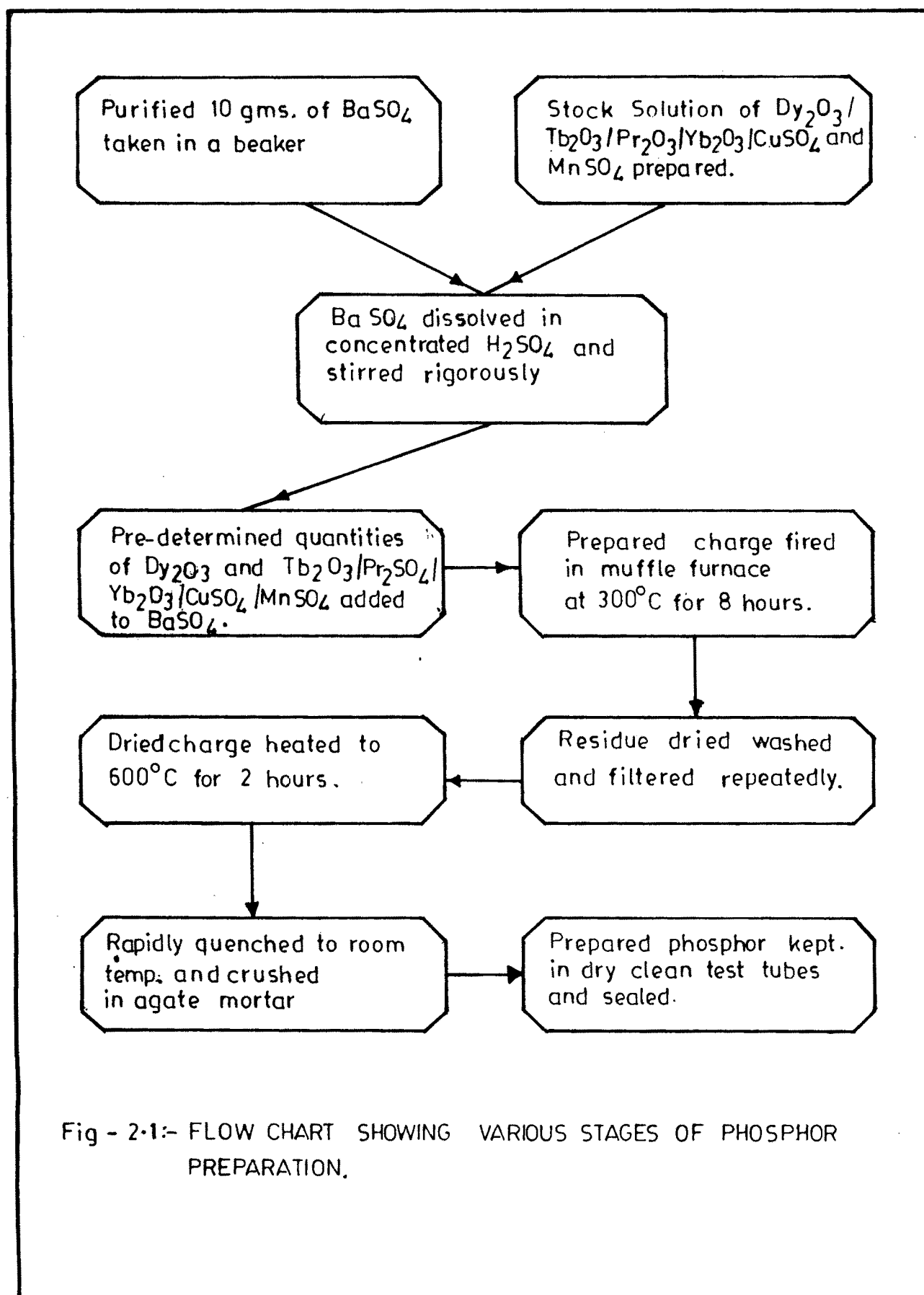


Fig - 2.1:- FLOW CHART SHOWING VARIOUS STAGES OF PHOSPHOR PREPARATION.

Fig-2.1



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