CHAPTER II

PREPARATION OF PHOSPHORS
2.1

The action of a phosphor essentially depends upon some deviation from ideal crystal structure either because of structural defects or purposeful introduction of small quantities of impurities. Preparation of a phosphor thus in principle, reduces to incorporation of an impurity or defect in a pure crystal matrix.

(i) **Powder**: Inorganic luminescent materials are generally prepared in microcrystalline powder form. This is the simplest and most widely used form in which the phosphors are prepared by one or the other method \(1,2,3\).

(ii) **Single Crystal**: The technique for obtaining single crystal phosphors have been developed in a few materials such as ZnS, CdS, alkali halides etc. \(4,5,6\). The alkaline earth sulphide phosphors are not obtained in this form due to difficulty of growth and uniform distribution of activators \(7\).

(iii) **Films**: In recent years phosphors are also made in the form of transparent films, a few microns thick. Zinc
Sulphide and Cadmium Sulphide films with As, Cu, Mn activators have been deposited on glass by chemical reaction in vapour state \( (8,9) \).

The preparation of phosphors in any of these forms involves a number of parameters, including high temperature solid state reaction. In general, it is not difficult to make a phosphor, but in practice, it is very difficult to make a good phosphor, with controlled and reproducible properties, which is highly desirable in all scientific investigations and verification of results. Generally, phosphors are prepared in any of the above forms according to the experimental need. The alkaline earth sulphide phosphors are usually prepared in the powder form. The phosphors are hypersensitive to traces of impurities and are adversely affected by certain impurities as nickel, iron, silica etc. even when these are present to an extent of \( 10^{-4} \) per cent only. Therefore, the preparation of these phosphors requires the removal of cationic impurities which may affect the luminiscence properties. These phosphors are hygroscopic and luminescent properties are considerably influenced due to absorption of moisture. Hence, the preparation of alkaline earth sulphide phosphors required a high degree of purity in all mechanical and chemical processes involved, besides dust free and dry laboratories.
2.2 PHOSPHOR COMPOSITION:

(A) **Host Crystal:**

The main constituent of a phosphor, the crystalline material itself, is known as host material or matrix. The properties of a phosphor are influenced by the crystal structure and the chemical composition of the host crystal. The ionic sizes of the anion and cation are the determinative factors of the base material. Group II elements Be, Mg, Zn, Sr, Ba predominate as the cationic constituents, whereas Group IV elements O, S, Se predominate as anionic constituents of the base material. The type of chemical bonding is equally important and the crystals with ionic covalent or mixed ionic-covalent binding are suitable base materials for many phosphors. They include insulators and semiconductors which tend to have predominantly ionic and covalent binding respectively.

(B) **Activator:**

Minor traces of impurities which play an essential part in luminescence, are termed as 'activator'. Elements playing the role of activators are usually the transition or post-transition metals, such as copper, manganese, lead, bismuth and rare earths etc. (10). In some cases two activators are
used; one acts as the dominant activator which usually determines the emission, while the other sensitizes the luminescence of the first.

The activators are supposed to require shielding for the absorbed energy which would otherwise be dissipated in the form of thermal vibrations\(^{(11)}\). Activators may be introduced into the host crystal — (i) by partial decomposition or atomic dislocation in it during high temperature crystallization, (ii) by deliberate addition of small amount of a foreign multivalent cationic element during crystallization or recrystallization.

The site that an activator occupies within the host crystal depends upon the ionic radii of the activator and crystal cation. The activator may take a substitutional or interstitial position in the crystal lattice and hence the emission characteristics may also be different\(^{(12)}\). Addition of activator above the optimum concentration in a phosphor, decreases the efficiency of the phosphor by interacting detrimentally with other activator atoms. Some transition metals like Fe, Ni, Co acts as poisons. These ions may also decrease the solubility of activator compound during formation of phosphors. The trapping action combined with a large probability of non-radiative transitions also accounts for the quenching action of these ions\(^{(13,14,15)}\). Activators may be classified into two sub-groups according to their effect
on emission spectra.(16).

(i) **Intensifier activator:** The activator atom upsets the crystal field symmetry and intensifies a host lattice band.

(ii) **Originative activator:** The activator may produce new emission lines or bands which have their own characteristics.

It has been observed that some activators may act primarily as an intensifier in one host crystal and as an originative emitter in another host crystal.(17,18).

(C) **Flux:**

Fluxes are essential for the preparation of good alkaline earth sulphide phosphors. On the other hand, oxygen dominated phosphors are generally prepared without fluxes. Also, when high efficiency is required under excitation by high energy particles, it is often necessary to avoid all fluxes, especially when fluxes tend to become occluded as luminescent inert material or when they react with other phosphor ingredients to form inert or vitreous phases.(19).

The precise action of the flux is as an agent that promotes low temperature crystallization of the base material. The main functions of fluxes as recognized by various workers,
by which they affect luminescence characteristics are listed below:

(1) They provide a fluid phase for solvation and transport of ingredients and thus accelerate the chemical reactions at low temperature (20, 21, 22).

(ii) They act as inhibitors of sublimation (23).

(iii) They increase surface reactivity and atomic mobility to facilitate the crystal growth (20).

(iv) Fluxes assist in homogeneous distribution of the activator in the host crystal lattice (19, 21).

(v) Formation of solid solutions of the flux and base material is suggested by Smith (24). The solid solutions promote the formation of defects or lattice distortions and thus affect the luminescence intensity and efficiency of a phosphor.

In certain cases, it is assumed that anions and cations of the flux play the role of coactivators, according to the principle of charge compensation (25, 26, 27, 28, 29). For example, in a ZnS phosphor, if a monovalent activator ion such as Cu$^+$ or Ag$^+$ is substituted for divalent zinc ion in the matrix lattice, the resulting charge difference may be compensated by the replacement of a sulphur ion (S$^{2-}$) by a chlorine ion Cl$^-$. 
2.3 GENERAL REQUIREMENTS:

(A) Purity:

The preparation of inorganic crystalline phosphors, requires in principle, first the maximum elimination of extraneous elements and then the reintroduction of some of these or others in precise amounts. Certain impurities can affect the luminescence, if present in as small an amount as $10^{-4}$ per cent\(^{(19)}\). Unfortunately, in spite of all the precautions, it is usually very difficult to avoid some of the involuntarily added impurities completely. So a distinction between relatively harmless and typically poisonous impurities is desirable. In general, purity where contaminations are either less detectable or prove to be harmless should serve the purpose\(^{(2)}\).

(B) Mixing of Ingredients:

There are different methods of mixing the ingredients for the preparation of phosphors\(^{(2)}\), viz. precipitation method, combination wet-dry method and dry synthesis method. The precipitation methods are those which yield phosphor matrices directly as insoluble precipitate, e.g. calcium tungstate phosphors. In a dry method, raw materials should be of adequate purity. Particles of different powders should
be exceedingly fine for perfect mixing of charge. On the other hand, wet dry method is useful when trace amounts of an activator have to be distributed uniformly over large amounts of coarse powder material. Both, dry and wet-dry methods depend upon heat treatment to synthesize the phosphor matrix and to incorporate activators uniformly in the base. Finally, the choice of method, rests largely with the individual characteristics of compounds involved, the types of phosphor to be prepared and with economic necessities.

(C) **Mechanics of Firing:**

(i) **Firing time and temperature:** Both these parameters have to be determined empirically for each system as these depend on the composition and size of the charge. In general, the optimum temperature is in the neighbourhood of 1000°C. If suitable flux is used, the firing temperature is usually lowered. The temperature in such cases is invariably above the melting point of the flux.

(ii) **Furnace:** Because of the marked sensitivity of many phosphors to small changes in temperature during reaction and crystallisation\(^{(30)}\), the temperature within the furnace should be uniform as possible, controllable within \(\pm 10^\circ\text{C.}\) The use of high pressure furnace makes it possible to —
(a) control selective decomposition and use high temperature for crystallising more stable phosphors with desired crystal size,
(b) incorporate some of the more volatile elements as useful constituents of the phosphors,
(c) alter favourably the composition of a phosphor by controlling the partial pressure of the gases during crystallisation, and
(d) to produce new crystal forms of the phosphor \(^{31}\).

(iii) **Reaction Vessel:** The choice of reaction vessel is influenced by the purity requirements and high temperature during the synthesis. Thus it must be chemically inert, must have high refractoriness and should be able to withstand thermal shocks. There are a large number of substances that fulfil these requirements and as such the final selection depends more or less on availability, price and life. The choice varies, of course, from phosphor to phosphor, subject to its chemical composition.

(iv) **Atmosphere during firing:** The anion-cation ratio and the effective valence states in phosphors depend on the atmosphere during firing. So an oxidising, reducing or neutral atmosphere is used, depending upon the type of the phosphor.

(v) **Particle size of the ingredients:** Particle size
of the ingredients is important as phosphors are usually synthesised by solid state reactions. In such reactions, the first formation of the new compound occurs at the boundary of the component phases. So at a given temperature the quantities formed initially will depend on the surface area of the powders. Moreover, the reactants usually diffuse only one or two particle diameters away from the point of origin. So there should be a large surface to volume ratio, which is possible only if the powders are of as fine particle size as possible and are in intimate contact.

(vi) **Size of the batch:** Another important question is the absolute and relative size of the batch and furnace. A small charge may reach the furnace temperature before the reaction is well under way. The synthesis then takes place at high furnace temperature. On the other hand, with a very large charge, the outer portion will be synthesised before the centre of the charge comes up to the required temperature. A good portion of the batch may then be synthesised at lower temperature and heated to the furnace temperature after reaction has taken place. This will naturally result in considerable non-uniformity. The optimum size, however, can only be determined empirically, the criterion being the attainment of constant luminescent properties.

(vii) **Rate of cooling:** For most phosphors the rate of
cooling is not critical\((12)\). In general, slower cooling favours the attainment of an equilibrium distribution of crystal imperfections. Rapid cooling on the other hand tends to

(a) preserve the valence states prevalent at temperature.
(b) freeze in omission defects and other defects which are relatively abundant at high temperature, and
(c) affords, in some cases, an abnormally large density of traps.

Crystals with such abnormally large density of traps are often unstable and tend to return to the state which would have been obtained on slower cooling.

(viii) Phosphor particle size: The grain size of the phosphor also influences the luminescence emission\(^{(32)}\) affecting only the shallower traps, which are more in smaller grain size\(^{(33)}\). The loss in brightness due to grinding can partially be explained on the basis of an increase in scattering\(^{(34,35,36)}\). Later work has, however, revealed the existence of other effects which decrease the brightness of crystalline phosphors on mechanical crushing\(^{(37,38,39)}\).
2.4 PREPARATION OF PHOSPHORS:

The activator copper was taken in the form of its sulphate. 9.825 grams of copper sulphate (CuSO$_4$·5H$_2$O) was dissolved in 50 ml of double distilled water. Thus a solution of strength 0.05 gm copper in one ml of solution was obtained. One ml of this solution was taken in another flask and 4 ml of double distilled water was added to it. We thus obtained a solution of copper whose strength was 0.01 gm of copper in one ml of the solution. By trial the optimum concentration of copper for efficient phosphors was determined. Final samples were prepared with 0.1% of copper as activator.

The calcium sulphide and strontium sulphide were taken in different ratios and they were mixed well. A calculated quantity of flux was then added and triturated. Finally the desired quantity of activator was added and also a small quantity of absolute alcohol and the whole charge was thoroughly mixed to obtain a homogeneous mixture. The charge was then dried in a thermostat and sealed in a quartz tube which was to be heated in a furnace.

A special furnace fabricated in the laboratory for the purpose of firing the phosphors in controlled atmosphere is described below:

The furnace was made of a porcelain tube of about twenty
inches long, its diameter being one inch. Around this porcelain tube a coil of kanthal wire was wound with the help of asbestos rope. A thermocouple was placed inside the porcelain tube for recording the temperature of the furnace with the help of a pyrometer. The furnace was heated by passing suitable current controlled by a variac through the Kanthal wire thus the desired temperature was obtained. High temperature up to a maximum of 1100°C could easily be obtained in the furnace within twenty minutes.

A quartz tube about 25 cms long and one cm in diameter, after being washed with nitric acid, distilled water and then by absolute alcohol and finally dried well, was connected with the help of a pressure rubber tube, to the outlet of a three-way tab. One inlet of the three-way tab was connected to the vacuum pump and the other inlet of the three-way tab was connected to a Kipp's Apparatus which was required for producing H₂S. The whole apparatus was sealed with sealing wax for achieving a good vacuum (Fig. 2.1).

To begin with, the sample to be fired was kept inside the quartz tube whose open end was plugged with glass wool. It was then connected to the outlet of the three-way tab and sealed with sealing wax. All the sealed joints were kept cool by wet cloth wound round them. The vacuum pump was switched on and was connected to the quartz tube by turning the knob of the three-way tab. The air inside the quartz tube
was pumped out for ten minutes and then $H_2S$ gas was passed into the tube by turning the knob of the three-way tap in the reverse direction. The hydrogen sulphide gas was also passed into the tube for ten minutes. After this the vacuum pump was again connected to the quartz tube and the remaining air and $H_2S$ were pumped out, for ten minutes. $H_2S$ was then again passed in for another ten minutes. The above process was repeated several times to ensure that oxygen from the quartz tube was completely removed. This is essential to avoid the oxidation of the samples during the firing.

Now the furnace was switched on and after it attained a temperature of 900$^\circ$C, the quartz tube was inserted gently into the furnace. During the whole firing process the vacuum pump was operated connected to the quartz tube. After two hours the furnace was switched off and the quartz tube was cooled down after taking it out of the furnace. It was then detached from the vacuum pump and the sample was taken out from it and mixed well in a mortar. The phosphors were stored in clean and sealed test tubes.

In addition to CaS:Cu and SrS:Cu phosphors, nine other samples were prepared containing varying proportions of CaS and SrS. Table I gives the percentage by weight and also the molar percentage of the constituents in different samples.
Table I

Composition of Samples

Firing Temperature: 900 ± 20°C
Flux (Na₂SO₄): 5%
Duration of firing: 2 hrs
Concentration of Activator (copper): 0.1%

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample</th>
<th>Percenta of CaS by weight</th>
<th>Mol. Percentage of CaS</th>
<th>Mol. Percentage of SrS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CaS</td>
<td>100</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2.</td>
<td>CaS:SrS : 9:1</td>
<td>90</td>
<td>89.3</td>
<td>10.7</td>
</tr>
<tr>
<td>3.</td>
<td>CaS:SrS : 8:2</td>
<td>80</td>
<td>79.3</td>
<td>21.2</td>
</tr>
<tr>
<td>4.</td>
<td>CaS:SrS : 7:3</td>
<td>70</td>
<td>68.3</td>
<td>31.53</td>
</tr>
<tr>
<td>5.</td>
<td>CaS:SrS : 6:4</td>
<td>60</td>
<td>58.5</td>
<td>41.7</td>
</tr>
<tr>
<td>6.</td>
<td>CaS:SrS : 5:5</td>
<td>50</td>
<td>47.9</td>
<td>51.8</td>
</tr>
<tr>
<td>7.</td>
<td>CaS:SrS : 4:6</td>
<td>40</td>
<td>38.6</td>
<td>61.7</td>
</tr>
<tr>
<td>8.</td>
<td>CaS:SrS : 3:7</td>
<td>30</td>
<td>28.8</td>
<td>71.5</td>
</tr>
<tr>
<td>9.</td>
<td>CaS:SrS : 2:8</td>
<td>20</td>
<td>18.9</td>
<td>81.1</td>
</tr>
<tr>
<td>10.</td>
<td>CaS:SrS : 1:9</td>
<td>10</td>
<td>9.5</td>
<td>90.6</td>
</tr>
<tr>
<td>11.</td>
<td>SrS</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>
REFERENCES


