CHAPTER II - Preparation of Phosphors.
CHAPTER II

PREPARATION OF PHOSPHORS

1. General: By far the most important part of luminescence research is the preparation of the phosphor. The photoluminescent phosphors are not easy to prepare, for their composition must be rigidly controlled. Because of the desirability of having exact knowledge as to their physico-chemical properties, much research has centered upon them in the past three decades.

There are many naturally luminescent solids, typical ones being the minerals willemite (zinc orthosilicate), wurtzite (zinc sulphide) and fluorite (calcium fluoride). The phosphors synthesized under carefully controlled conditions are more efficient than those found in nature. Imperfections in the crystal have been assigned as the cause of luminescence (1, 2).

2. Ingredients of a phosphor: The phosphor has three basic ingredients,

(a) Host material — Chemical bonding is one of the determinative factors in addition to the relative ionic sizes of the cation and anion (3), in selecting the base material for phosphor preparation. In the present state of knowledge of solid state physics it is difficult to predict as to which chemical impurities will give luminescence with good efficiency in a particular host crystal and which will merely dissipate
energy into lattice vibrations. However, it is known that crystals with ionic, covalent or mixed ionic covalent binding are of utmost importance as base materials for many phosphors (4). Insulators, predominantly having ionic bonding and semiconductors, predominantly having covalent binding are widely used as base material. Alkali halides, Alkaline earth sulphides, Zinc sulphide and Cadmium sulphide are specific examples of this class.

(b) Activator — Impurities that provide localized energy levels in the energy gap of an insulator or semiconductor and which permit radiative transitions are called activators (5). With a few exceptions (6, 7) most of the inorganic materials exhibit luminescence due to the presence of specific activators (8 - 11). In some inorganic materials (7, 12, 13) which luminesce in pure state, self activation is assigned as the cause of luminescence.

Impurity ions having an excited energy level between 1.5 and 3 eV are useful for luminescence in the visible region. The activator can find its place in the crystalline base material as, either, a substitution ion or atom, or an interstitial atom or ion (if the ionic radii of activator is small compared with that of the host lattice) or an ion or atom at points of lattice defects.

Activators have been classified as follows:  

...
(i) Originator (10) - It gives rise to new emission lines or bands other than the intrinsic luminescence of the host lattice.

(ii) Intensifier (10) - It intensifies the intrinsic luminescence of the host lattice.

(iii) Killer (5) - It provides energy levels between which radiative transitions are forbidden.

(iv) Dominant and Auxiliary activator - In infra red sensitive phosphors sometimes the efficiency of a singly activated phosphor is enhanced by adding a second activator. The first and second activators are then known as dominant and auxiliary activators respectively.

(v) Coactivators (14, 15) - It provides the balance of charge in sulphide phosphors activated by monovalent atoms.

(vi) Sensitizer (16) - An activator is known as sensitizer if the energy absorbed by it is transferred to another activator without radiative emission.

(c) Flux - Preparation of phosphor often involves the presence of a readily recrystallizing medium termed flux. It consists of a readily fusible salt or mixture of salts such as \( \text{Na}_2 \text{SO}_4 \), \( \text{NaF} \), \( \text{NaCl} \), \( \text{CaCl}_2 \), Borax, Hypo etc. The ideal flux is that which melts at or below the firing temperature and the solubility of the base materials in it should be sufficient
to effect their rapid crystallization.

Although there is not complete understanding of the role of flux in luminescence processes, it is certain that it has the following roles:

(i) It increases the speed of reactions at relatively lower temperatures (17, 18).

(ii) It promotes crystal growth at lower temperatures and facilitates the incorporation of activator and its homogeneous distribution in the host lattice (17, 19).

(iii) It acts as an inhibitor of sublimation (14).

(iv) Flux promotes the formation of defects or lattice distortions and thus effects the luminescence efficiency (20).

(v) Kroger and Coworkers have shown that in many cases the flux also serves as a charge compensating agent (14, 15, 21).

3. **Factors involved in preparation**: The properties of a phosphor are found to depend on a number of parameters some of them are given below:

(a) **Processing of the ingredients** — The particle size of the basic ingredients required for phosphor preparation has a striking effect upon the rate of solid state reactions and thereby, upon the quality of the phosphor. Reaction is smooth when different reacting phases are in intimate contact and therefore the particles of very fine size with large surface to volume ratio are required. Mechanism of the reaction depends on
the relative ease of diffusion of reaction partners, which is facilitated by the fineness of the ingredients. The method of mixing the ingredients is also important, the criterion being the attainment of a homogeneous mixture.

(b) Reaction Vessels and Furnace — The selection of reaction vessels is performed on the basis of their (i) chemical inertness, (ii) high refractoriness, (iii) ability to withstand thermal and mechanical shocks.

Uniform temperature within the heating chamber of the furnace is required. Variation in the temperature of the furnace sometimes changes the crystal structure of the phosphor from one type to the other (10).

(c) Atmosphere for firing — The observation that oxidizing, reducing or neutral atmosphere used during firing causes changes in the luminescent properties has been reported by different workers (10, 22, 23). An interesting example of the effect of atmosphere during crystallization is provided by hexagonal cadmium sulphide which emits in the infra red after heat treatment in a neutral or mildly oxidizing atmosphere but in the green after being heated in a reducing atmosphere (22). Even a neutral atmosphere such as water vapour or steam has a striking effect on the rate of reaction and final brightness of certain silicate and sulphide phosphors (24, 25).
(d) Final processing of the Phosphor — This includes cooling, grinding and mechanical handling of the phosphor after the firing process is over. In general, rate of cooling affects the luminescent properties such as absorption, brightness of the phosphor, spectral emission and often the rate of phosphorescence decay. Sudden cooling sometimes even changes the colour of fluorescence. In ZnS–Cu phosphors \((10,24)\), rapid cooling favours the long wavelength emission band, whereas the slow cooling intensifies the short wavelength emission band. Slow cooling rate helps in the uniform distribution of imperfections throughout the phosphor. On the other hand rapid cooling preserves the valence state prevalent at high temperature. The grinding affects the grain size and this has a marked influence on the luminescent properties. However, grain size has little to do with the deeper traps and it only affects shallow traps. Several phosphors such as alkaline earth sulphides are unstable in the presence of moisture and hence they must be prepared and stored under dry conditions.

4. Preparation of Alkaline earth sulphide phosphors. In the preparation of alkaline earth sulphide phosphor, freedom from metallic impurities, other than the intentionally added activators is essential. The general method of preparation by dry reactions involves, heating an intimate mixture of corresponding carbonate or oxide together with required amounts of activators and flux in an atmosphere of
sulphur vapour between 900 - 1000 °C (26). This method
does not ensure the complete conversion of the carbonate or
oxide into corresponding sulphide, but a complex mixture is
formed. Another method by Tiede and Richter, recommends
the heating of an intimate mixture of the alkaline earth
carbonate, oxide or sulphate and activating impurity in a
stream of carbon di sulphide (27). The resulting compound
is refined with suitable flux at about 900 - 1000 °C. This
method ensures complete conversion of the starting material
into the corresponding sulphide.

It is a well agreed fact that for
quantitative understanding of the luminescence mechanism,
single crystals with doped impurity are required. So far it
has not been possible to grow crystals of CaS and BaS.
However, there are reports (28) that SrS crystals can be
grown.

Present Method - The method of preparation of
alkaline earth sulphide phosphors adopted in our laboratory is
due to Bhawalkar (29). This method consists in heating an
intimate mixture of the alkaline earth sulphates and a reducing
agent like carbon together with the required amount of
activators and flux in a reducing atmosphere.

Three different series of phosphors
were prepared for the present investigations:
In general, the method of preparation of phosphors involves, the purification of raw materials and intermediates, preparation of charge, firing of the charge and then grinding and mechanical handling of the phosphor.

(i) Base material — The bases used are the ores of Gypsum and Celestite. They contain many impurities. Purification is done first by the mechanical means, such as scrapping, cutting and washing with a stream of running water. During this process the ore is cut into clear transparent pieces. These are washed with distilled water and then powdered to 120 mesh in a dust free atmosphere. In the second stage, purification is performed by chemical methods. The powder is soaked in Nitric acid (A.R.) and allowed to remain for six hours. To ensure complete conversion of metallic impurities in water soluble nitrates, the settled powder was boiled for 15 minutes, with excess quantity of fresh Nitric acid. The mixture was repeatedly washed with distilled water till the filtrate gave no test for nitrate ions. It was then dried in an oven. The dry powder was collected in clean bottles.

(ii) Reducing agent; Carbon — A.R. grade Merck carbon was used as reducing agent. The impurities present in the carbon were mostly soluble in water. To remove these impurities carbon was boiled with excess quantity of distilled water for about half an hour and then filtered. The residue was washed repeatedly with hot distilled water. The purified
carbon was then dried in an oven at about 90°C.

(iii) Preparation of Activator - For most sulphide phosphors, the value of the optimum concentration of activator is about one part by weight in ten thousand of the matrix \((10, 22)\). Hence the activator is taken in the form of a dilute solution of its salt, which provides uniform distribution as well as good control for variation in desired steps. The preparation of activator in different phosphors was as below:

(a) For \(\text{CaS (Zr)}\) system: The zirconium was taken in the form of zirconium nitrate. It was dissolved in double distilled water and a few drops of concentrated sulphuric acid were added. Many solutions of different strengths were prepared to have the desired variation of concentration in steps.

(b) For \(\text{CaS (Bi-Zr)}\) system: Bismuth was taken in the form of sub-nitrate. It was dissolved in double distilled water and a few drops of A.R. grade Nitric acid were added. The solution was made of desired strength. The zirconium was taken in the form of nitrate.

(c) For \(\text{SrS-Bi (Borax)}\) system: Here also the activator bismuth was taken in its sub-nitrate form and was made up in the way stated above.

(iv) Flux - For \(\text{CaS (Zr)}\) and \(\text{CaS (Bi-Zr)}\), compound fluxes were used. Anhydrous sodium sulphate, sodium thiosulphate and sodium fluoride of A.R. quality obtained from
B.D.H. laboratory chemical division (Bombay) were used. Hypo, provides long lasting afterglow at much lower temperature. This is due to its decomposition into low melting sulphur compounds at relatively low temperatures (14). Sodium fluoride makes the phosphor hard to grind and sometimes increases the life of the phosphor (30). For SrS:Bi, Borax was used as a flux. Its percentage was varied from sample to sample.

(v) Preparation of charge — The reaction governing the formation of CaS from CaSO₄ at high temperature is

\[
\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 4\text{C} \rightarrow \text{CaS} + 4\text{CO} + 2\text{H}_2\text{O}
\]

After systematic investigations, Bhawalkar (29) obtained the following values for the proportion of the different constituents of the charge for an efficient CaS(Bi) phosphor. Gypsum (10 gms.); Carbon (2.5 gms.); Hypo (1.25 gms.); Sodium sulphate (0.5 gm.); Sodium fluoride (0.125 gm.) and Bismuth (0.0012 gm.).

Compositions of the different series of phosphors are given (Tables 2.1, 2.2 and 2.3), shown on pages 45, 46 and 47 respectively.

The required amounts of base powder, carbon and flux were intimately mixed in a dry and clean mortar to give a uniform blend. The required amount of activator solution was added to this charge. A few drop of absolute
alcohol were added to prevent caking and uniform distribution is achieved by the activator solution itself. The whole charge was then mixed till it was dry.

(vi) Firing Process - The charge prepared this way was transferred to crucibles made of good quality graphite and a thin layer of carbon was spread on this. This crucible was covered by another fitting into it and forming nearly an air tight enclosure, and thereby preventing any air current from disturbing the reducing atmosphere formed inside. The crucibles were then loaded in an electrically heated furnace initially held at the temperature at which the phosphors were to be fired.

(vii) Grinding and Mechanical handling - After firing the charge was withdrawn from the furnace and pulverized while red hot. The phosphor was allowed to cool at room temperature since this sudden cooling was found to produce better crystals with good afterglow. The phosphors were ground in a dry atmosphere. To keep the grain size normal the powdered phosphor was passed through a 60 mesh. The phosphors were then collected in a clean and dry specimen tube and the tubes were carefully sealed with wax.
TABLE 2.1

Composition of the charge for CaS (Zr) phosphors (System - 1).

Duration of firing 2 hours. Temperature of firing $900 \pm 10^\circ C$.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Zirconium concentration in gms.</th>
<th>Additional remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>C - 1</td>
<td>0.0008</td>
<td></td>
</tr>
<tr>
<td>C - 5</td>
<td>0.0040</td>
<td></td>
</tr>
<tr>
<td>C - 10</td>
<td>0.0090</td>
<td></td>
</tr>
<tr>
<td>C - 15</td>
<td>0.0120</td>
<td></td>
</tr>
<tr>
<td>C - 20</td>
<td>0.0160</td>
<td></td>
</tr>
<tr>
<td>C - 25</td>
<td>0.0200</td>
<td></td>
</tr>
<tr>
<td>C - 30</td>
<td>0.0240</td>
<td></td>
</tr>
<tr>
<td>C - 35</td>
<td>0.0280</td>
<td></td>
</tr>
<tr>
<td>C - 40</td>
<td>0.0320</td>
<td></td>
</tr>
<tr>
<td>C - 45</td>
<td>0.0360</td>
<td></td>
</tr>
<tr>
<td>C - 50</td>
<td>0.0400</td>
<td></td>
</tr>
<tr>
<td>C - 55</td>
<td>0.0440</td>
<td></td>
</tr>
<tr>
<td>C - 60</td>
<td>0.0490</td>
<td></td>
</tr>
<tr>
<td>C - 65</td>
<td>0.0520</td>
<td></td>
</tr>
<tr>
<td>C - 70</td>
<td>0.0560</td>
<td></td>
</tr>
<tr>
<td>C - 75</td>
<td>0.0600</td>
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</table>

In addition to the concentration of activator (Zr), each sample contains:
- Gypsum (10 gms), Carbon (2.5 gms)
- Hypo (1.25 gms), Sodium
- Sulphate Anhy. (0.5 gm) and Sodium Fluoride (0.125 gm).
### TABLE 2.2

**Composition of the charge for CaS (Bi-Zr) phosphors (System - 2).**

- **Duration of firing:** 2 hours.
- **Temperature of firing:** $900 \pm 10^\circ C$.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Zirconium concentration in gms.</th>
<th>Additional remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2 - 1$</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>$C_2 - 7$</td>
<td>0.0004</td>
<td></td>
</tr>
<tr>
<td>$C_2 - 15$</td>
<td>0.0016</td>
<td></td>
</tr>
<tr>
<td>$C_2 - 20$</td>
<td>0.0056</td>
<td></td>
</tr>
<tr>
<td>$C_2 - 25$</td>
<td>0.0076</td>
<td></td>
</tr>
<tr>
<td>$C_2 - 30$</td>
<td>0.0092</td>
<td></td>
</tr>
<tr>
<td>$C_2 - 35$</td>
<td>0.0300</td>
<td></td>
</tr>
<tr>
<td>$C_2 - 40$</td>
<td>0.0550</td>
<td></td>
</tr>
<tr>
<td>$C_2 - 45$</td>
<td>1.0000</td>
<td></td>
</tr>
</tbody>
</table>

In addition to the concentration of activator (Zr), each sample contains:
- Gypsum (10 gms),
- Carbon (2.5 gms), Hypo (1.25 gms),
- Sodium Sulphate Anhydrous (0.5 gms),
- Sodium Fluoride (0.125 gms) and Bismuth (0.0024 gms).
TABLE 2.3

Composition of the charge for SrS-Bi (Borax) phosphors (System - 3).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Borax concentration in gms.</th>
<th>% of Borax w.r.t. SrS.</th>
<th>Additional remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₁ - 1</td>
<td>0.0000</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>S₁ - 5</td>
<td>0.7942</td>
<td>12</td>
<td>In addition to the concentration of Borax, each sample contains:</td>
</tr>
<tr>
<td>S₁ - 10</td>
<td>1.7646</td>
<td>27</td>
<td>Celestite (10 gms), Carbon (2.6 gms) and Bismuth (0.0008 gm).</td>
</tr>
<tr>
<td>S₁ - 15</td>
<td>2.7450</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>S₁ - 20</td>
<td>3.7254</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>S₁ - 23</td>
<td>4.3136</td>
<td>66</td>
<td></td>
</tr>
</tbody>
</table>
REFERENCES

(1) Vernaille, A. - Compt. rend. 103, 600 (1886).


(7) Seitz, F. - J. Phys. Chem. 6, 454 (1933).


