CHAPTER II

PREPARATION OF CaS₂Zr PHOSPHOR
Preparation of Phosphors

The luminescent properties of a phosphor are to a considerable extent dependent on the condition during synthesis. Hence it will not be out of place to discuss the various parameters affecting phosphor synthesis. The essential features of phosphor synthesis are:

1. Clean washing conditions,
2. Pure ingredients, generally prepared at low temperature to preserve reactivity,
3. Accurate proportions and co-precipitation and co-communion and thorough mixing of ingredients, usually in as fine state of subdivision as possible,
4. Reaction and crystallization of ingredients at optimum temperature, for an optimum time and in an optimum atmosphere.

(a) Purity:

In principle complete purity is required. According to Leverenz (1) a substance used for phosphor synthesis should be luminescent pure i.e. 99.9999%, as even 10^{-4}% of certain impurities can affect the luminescence of certain phosphors. However, in spite of taking all care and precaution, some impurities inadvertently remain in the base material. One has therefore to distinguish between harmful impurities like Fe, Co, Ni and harmless impurities, whose presence in relatively small amounts in a phosphor does not affect the luminescence of the phosphor.
(b) **Furnace:**

As most of the phosphors are synthesized at temperatures well above thousand degrees centigrade, a furnace is necessary for reaction and crystallization of phosphors. The temperature of the furnace chamber should be as uniform as possible and should be controllable within at least $\pm 10^\circ$ because many phosphors are very sensitive to small changes of temperature (2). By using a high pressure furnace it should be possible to produce -

(i) New crystal forms (3)

(ii) To incorporate some more volatile elements as useful constituents of the phosphors.

The effect of furnace atmosphere determines the anion, cation ratio and the effective valence state. So oxidizing, reducing or neutral atmosphere is used depending on the type of furnace. The effect of furnace atmosphere has been investigated by A.L. Smith (4) in case of ZnS phosphor. Strongly reducing atmosphere such as hydrogen or hydrogen sulphide gives phosphors having ultraviolet edge emission band. In neutral or slightly reducing atmosphere such as N, SO$_2$, CO$_2$ and air blue emission band develops. Oxidation at high temperature gives green emission band having the characteristics of ZnS:Cu phosphor.

(c) **Rate of Cooling:**

For most phosphors, the rate of cooling is not critical except that slow cooling favours the attainment of equilibrium distribution of crystal imperfections. Rapid cooling tends to
(i) Preserve the valence state prevalent at high temperature,

(ii) Freeze in omission defects, imperfections which are relatively abundant at high temperature,

(iii) Afford in some cases abnormally large density of traps.

(d) **Choice of reaction vessel**:

The choice of reaction vessel is made on the basis of chemical inertness, high refractoriness and ability to withstand thermal shocks.

(e) **Particle Size**:

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

(f) **Size of Batch**:

Another important question is the absolute and relative size of batches. The small charge may reach the furnace temperature before the reaction is well underway. The synthesis then takes place at a high furnace temperature. On the other hand with large charge the outer portion will be synthesized
before the centre of charge comes up to the optimum temperature. A good portion of the batch may then be synthesized at lower temperature and heated to furnace temperature after the reaction has taken place. This will naturally result in nonuniformity. The optimum size, however, can be determined empirically, the criterion being the attainment of constant luminescent properties.

Optimum conditions for synthesis of phosphors are to be determined empirically for each phosphor. Changes in one of the parameters necessitates changes in the other parameters in order to get the required properties of the resultant phosphor. For example, increase in temperature of reaction and crystallization usually allows a decrease in time of heating and permits the use of smaller proportion of flux if any.

**Alkaline earth Sulphide Phosphors**

Alkaline earth phosphors are usually prepared from the base materials calcium carbonate or calcium oxide. Carbonate is usually converted to sulphate by addition of dilute sulphuric acid and then this is reduced to CaS by heating in a stream of hydrogen or hydrogen sulphide at a temperature of 850°C. Small amount of activating impurities and flux, usually oxysalts of sodium, are also necessary, otherwise there is much formation of calcium oxide (5). The carbonates can also be converted qualitatively to sulphides by heating at 1000°C in hydrogen sulphide gas. Lenard's method (6) consisted in heating carbonate or oxide with excess of sulphur. Tiede
and Richter (7) have prepared calcium sulphide phosphor by heating oxide or sulphates in carbondisulphide gas but the final product is contaminated with carbon. Problems of preparation of calcium sulphide phosphor have been extensively studied by Ward and his associates (8).

The Present Method

Starting from the base material gypsum D.R.Bhawalkar (9) has developed a method for preparation of alkaline earth sulphide phosphors. The method consists in heating the sulphate with a reducing agent like carbon in the presence of suitable activator and flux.

Good quality transparent gypsum ore was broken into small bits in order to pick out good portions from it. Crystals which are mostly colourless or white are carefully picked. Surface impurities are removed by washing with distilled water. They are then dried in dust free atmosphere and powdered to 120 mesh size. The powder was subsequently heated with excess of nitric acid at 80°C for half an hour and then boiled in order to remove impurities. Powder was repeatedly washed with distilled water until the filtrate gave no test for nitrate. Powder was then dried at 80°C in an oven.

Carbon:

A.R. quality Merck carbon was used. Carbon was boiled with distilled water for half an hour and then filtered in order to remove impurities which are usually the salts of sodium and potassium and are water soluble. The residue on the filter paper
is washed with warm distilled water several times and dried in an oven.

**Activator:**

Zirconium was used as the activator in the present studies. Zirconium nitrate solution containing 0.002 gms. of Zr per c.c. of activator solution was prepared in double distilled water. The use of solution ensures better distribution of activator in the charge.

**Flux:**

In the preparation of the present series of phosphors a complex flux was used. It has been found that complex fluxes yield brighter samples (10). Flux used in the present investigation was a mixture of sodium fluoride, sodium sulphate, sodium thiosulphate or hypo. Hypo lowers temperature of phosphor preparation and phosphor with long after glow can be fired at lower temperatures. Fluorides make luminescence more lasting (11).

**Preparation of Charge:**

With the help of a porcelain pestle and mortar, gypsum powder, carbon and fluxes were finely powdered and intimately mixed. The required amount of activator solution and a few drops of rectified spirit were then added and the whole charge was mixed again.

**Method of Firing:**

Graphite crucibles were used for firing. The charge so prepared was packed in the crucibles and a layer of carbon was spread over it. The top of carbon maintains an essentially
reducing atmosphere. During firing the graphite crucible is covered with another graphite crucible.

Firing was carried out in a Heraeum muffle furnace. The heating muffle is contained in cylindrical housing filled with insulating material. Heating muffle is made of highly refractory chamber. The heating coil is made of high quality chromium nickel, and is wound around the muffle. Furnace is switched off automatically when the door of the furnace is opened to prevent the muffle from being over heated. The current is switched off by means of mercury tumbler switches. The temperature of the muffle is recorded by means of a nickel-chromium thermocouple encased in a ceramic protection tube. The furnace is provided with automatic temperature regulation of \( \pm 10^\circ C \). Firing temperature was \( 900^\circ C \). The time of firing was two hours as determined by trial and error. It has also been determined earlier by Chandy (11). After two hours the charge was taken out and pulverized while red hot and stored in clean dry test tubes and sealed with wax.

The compositions and conditions of preparation are given in Table 2.1.

**Table 2.1**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of phosphors prepared</td>
<td>--- 75</td>
</tr>
<tr>
<td>Temperature</td>
<td>--- 900(^\circ) C.</td>
</tr>
<tr>
<td>Firing Time</td>
<td>--- 2 hours</td>
</tr>
</tbody>
</table>

( contd.)
Fig. 2.1 a: Furnace (general construction)

1- Door

3 & 4- Switches

2- Temperature indicator

5- Handle
Fig. 2.1 b: Furnace (electrical connections)

1- Temperature indicator  
2- Thermocouple  
3- Voltage divider  
4- Relay  
5- Main switch  
6- Door switch  
7- Heating coil  
8- Rod regulator  
9- Connection terminals  
10- Pilot lamps
### Composition of Charge

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gypsum Powder</td>
<td>10 gms.</td>
</tr>
<tr>
<td>Carbon</td>
<td>2.5 gms.</td>
</tr>
<tr>
<td>Hypo</td>
<td>1.25 gms.</td>
</tr>
<tr>
<td>Sodium Sulphate (Anhydrous)</td>
<td>0.5 gms.</td>
</tr>
<tr>
<td>Sodium Fluoride</td>
<td>0.125 gms.</td>
</tr>
<tr>
<td>Zirconium</td>
<td>0.0008 n gms.</td>
</tr>
</tbody>
</table>

Where 'n' assumes values from 1, 2, 3, ..., 75 for different phosphor samples which are numbered accordingly. For example, RA 15 will contain 15 × 0.0008 gms. of Zirconium.
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