Chapter IV

SYNTHESIS OF PHOSPHOR

Section 'A'

4.1 Preparation of phosphors

In the synthesis of phosphors, the preparation of reagents and handling of all materials have to be done carefully. This aspect cannot be over-looked if reproducible results are to be obtained. Firstly, in the purification and preparation of some reagents have been described.

General precautions

1. All the containers (beakers, flasks and reaction vessels) are made of pyrex glass.

2. All the glass and silica vessels to be employed during the course of the preparation of the phosphors are cleaned with boiling nitric acid and rinsed with distilled water. Final washing is done with de-ionised water.

3. Flasks are kept covered with inverted beakers in order to prevent contamination from dust. Similarly the dust and other contaminations were checked by covering the beaker contents with petri dishes.
4. Only deionised water is used for washing the precipitate, the samples and the alike materials.

5. Deionised water is stored in polythene containers fitted with quick-spray taps.

4.2 Purification of reagents

(i) Nitric acid

The purification is done by distilling reagent grade nitric acid in a quartz still as shown in fig. 4.1. The dust cap is made by proper cutting of a round bottom flask.

(ii) Hydrogen sulphide

Hydrogen sulphide generated, in a Kipps apparatus by the reaction of diluted hydrochloric acid and iron sulphide is bubbled through concentrated hydrochloric acid, saturated barium hydroxide solution and finally through glass wool. The apparatus has been shown in fig. 4.2.

(iii) Nitrogen gas

Pure nitrogen can be obtained by removing oxygen, carbon dioxide and moisture from commercially available nitrogen. This is accomplished by passing the gas through alkaline pyrogallol (freshly prepared), concentrated sulphuric acid and then through drying towers packed with phosphorous penta-oxide. The gas is then finally passed through activated copper turnings heated to 400°C. The arrangement has been shown in fig. 4.3.
Fig. 4.1 - Nitric acid still

Fig. 4.2 - Apparatus for the purification of hydrogen sulphide
4.3 Preparation of SrS phosphors

4.3.1 Preparation of strontium sulphate

One hundred sixty eight millilitres of reagent grade nitric acid (18 N) is added slowly to 200 gm of reagent grade strontium carbonate suspended in 455 ml of distilled water in a one litre round bottom flask. The mixture is thoroughly shaken and heated for a few minutes on a heating mantle. A small amount of strontium carbonate should remain undissolved. Approximately 1 ml (36 N) of reagent grade sulphuric acid is added to the warm solution which is then heated to boiling on a heating mantle and, after removing the flask from heating mantle, it is immediately treated with purified hydrogen sulphide for about 15 minutes. After boiling the solution on a heating mantle, it is allowed to cool and left overnight. It is thereafter, filtered.

The pH of the solution is adjusted to 7 by pH paper by the addition of freshly prepared ammonium hydroxide solution. About 9 ml of a saturated solution of reagent grade ammonium oxalate is added, the solution is then boiled and the pH is again adjusted to 7. The hot solution is saturated with purified hydrogen sulphide and allowed to stand for several hours and then filtered. By the addition of distilled nitric acid to the filtrate, the pH is lowered to 2 and 0.3 ml of reagent grade bromine is added to the solution which is then boiled to remove excess of bromine. The solution is just neutralised
with freshly prepared ammonium hydroxide and again treated
with purified hydrogen sulphide for 15 minutes. The mixture
is then boiled and the precipitate is allowed to settle. It
is then filtered after some time.

To the filtrate, 1 to 1.6 ml of distilled nitric acid is
added to lower the pH of the solution to 2. The solution is
again boiled on a heating mantle and deposit of colloidal
sulphur is obtained. The solution is allowed to stand for
several hours and then sulphur is removed by filtration. The
resulting strontium nitrate solution is then concentrated by
evaporation until bumping commences. It is cooled and fresh
nitric acid is added into the solution till the precipitation
is complete. The supernatant liquid is totally removed. The
crystalline white mass is then dissolved in the smallest possi-
ble quantity of deionised water and the solution is filtered.
The strontium nitrate is obtained by crystallization of the
saturated solution obtained by the above process. The crystal-
lization is repeated twice. The yield depends as to how much
of the strontium nitrate is recovered in the crystallization
process. Care has been taken more for the quality of the
product rather than for high yield.

The strontium nitrate obtained in this way is dissolved in
500 ml of deionised water in a round bottom flask. The solu-
tion is heated to boiling. Strontium sulphate is precipitated by
the slow addition of a solution of 50 ml of reagent grade sul-
phuric acid (36 N) in 65 ml of deionised water. The presence
of nitrate ions in precipitate can be noticed by colorimetric technique using diphenyl amine-sulphuric acid reagent. When the precipitation is complete, the supernatant liquid is removed by the inverted filtration technique and the precipitate washed with 200 ml hot dionised water. This process is repeated a number of times and, in final washing, the precipitate is transferred on to a pyrex beaker. The precipitate of strontium sulphate is dried at 200°C in an electric oven. The dried strontium sulphate is stored in a clean glass bottle.

The strontium sulphate so obtained is analysed spectroscopically for heavy metals and other impurities which might be associated with it. No such impurities have been detected except for barium and magnesium present in traces.

4.3.2. Preparation of pure carbon

The commercially obtained carbon, even of reagent grade, has not been found suitable for reduction of strontium sulphate into strontium sulphide as it contains some impurities. The ash analysis of this carbon powder shows the presence of metallic impurities. Furthermore, the phosphor samples prepared by using this carbon powder are black in colour and the luminescent emission is also very poor.

Therefore, pure carbon has been prepared by the author in the laboratory by charring of purified glucose at 500°C. This carbon is found to be ashless and free from impurities.
Reagent grade glucose (BDH) is heated to 500°C, in silica crucible, for half an hour. The mass so obtained is powdered by pulverisation. Oxygen and hydrogen are removed by digesting the powder first with concentrated HCl and then HF. The acids are thoroughly removed by washing with hot distilled water several times and finally with deionised water. The powder is dried in a vacuum oven at 120°C. The carbon so prepared was analysed spectroscopically and no impurity was detected.

4.3.3 Activator solution

The activators such as copper, manganese and bismuth are chosen respectively in the forms of cupric acetate, manganese acetate and bismuth trichloride/oxide. The solution of required concentration are prepared in pyrex measuring flasks. Bismuth oxide is directly added to the base materials in required quantity by weighing.

Calculation for activator strength Cu = 1 x 10⁻³ g/g.

The molecular wt. of cupric acetate \((\text{CH}_3\text{COO})_2\text{Cu}, \text{H}_2\text{O})\) = 199.65 gm.

63.54 gm of copper is present in 199.65 gm cupric acetate

1 gm. " " \(\frac{199.65}{63.54}\) gm "

1 x 10⁻³ gm. " " \(\frac{199.65}{63.54} x 1 x 10^{-3}\) gm "

If \(\frac{199.65}{63.54} x 10^{-3}\) gm of cupric acetate is dissolved in 1.0 ml, it will contain 1 x 10⁻³ gm of copper. Therefore, for 250 ml, the amount of cupric acetate required.
\[
\begin{align*}
&= \frac{192.65 \times 250}{63.54 \times 1000} \text{ gm} \\
&= 0.7855 \text{ gm}.
\end{align*}
\]

Therefore, 0.7855 gm of cupric acetate was dissolved in 250 ml of deionised water in a pyrex measuring flask. This solution will contain $1 \times 10^{-3}$ gm of copper per ml of the solution.

Similarly, in order to prepare a manganese solution having concentration $1 \times 10^{-3}$ g/ml., 0.3143 gm of manganese acetate is dissolved in 250 ml of deionised water in a pyrex measuring flask. Further dilution of the respective solution yields the amount of copper or manganese to any required concentration per millilitre.

**Coactivator (flux)**

Reagent grade sodium sulphate (\(Na_2SO_4\)) anhydrous and sodium thiosulphate (\(Na_2S_2O_3\cdot4H_2O\)), reagent grade are used as coactivators. To prepare 5% solution of each flux material, 5 gm of the flux material is dissolved in 100 millilitres of deionised water in a pyrex measuring flask.

### 4.3.4 Furnace and firing procedure

For many purposes, a furnace in the form of a tube is quite convenient. Many types are available in the market and they can also be easily constructed. We have constructed a tube furnace having uniform heating zone of about 15.0 cm at the
Fig. 4.3 - Apparatus for the purification of Nitrogen gas

Fig. 4.4 - Furnace used for the synthesis of the sulphide phosphors
middle of a translucent silica tube of length 60 cms.

having internal diameter of 2.5 cms. Kanthal tape (4.7 ohm/meter) is wound on the tube manually since tape is preferable to wire as it sticks better to the position during winding and has a greater surface area (for the same cross section) for transferring heat. A thin paper-covering is also put between the silica tube and the Kanthal tape as the tape tends to contract after it has been heated for the first time and the subsequent cooling causes considerable pressure on the tube. The paper burns on heating and permits the subsequent contraction of the tape. The ends of the winding tape are screwed to the tube with a strip of stainless steel held together with bolts. The winding is then held in position by asbestos string/tape and finally cemented with refractory material. A thick coating is made to ensure proper insulation. The furnace is calibrated with the help of a chromel-Alumel thermocouple (standardised). The power is supplied through a variable autotransformer with an ammeter connected in the circuit.

Silica tube furnaces can be safely used up to a temperature of 1100°C. Above this temperature softening or appreciable devitrification of silica takes place. The silica tube furnace is shown in fig. 4.4.

The photograph of the experimental setup for the preparation of sulphide phosphors has been shown in fig. 4.5. The
Fig. 4.5 - Photographs of the experimental arrangement for the synthesis of sulphide phosphors
required quantity of activator and coactivator is added to
the weighed amount of strontium sulphate, mixed thoroughly
and then dried. Next, a suitable quantity of carbon is
further mixed and the powder is transferred into a silica
tube. The tube ends are closed with graphite caps and the
powder is heated to nearly 1000°C for 2 hour in an inert gas
atmosphere. The phosphor samples thus prepared are sieved
and properly preserved.
4.4 Preparation of ZnS phosphors

4.4.1 Preparation of luminescent grade zinc sulphide

Following procedure has been found suitable in the preparation of luminescent grade zinc sulphide. Its important features are:

(a) displacement method using spectroscopically pure zinc column to remove metals with lower electrode potential at 90°C from solution (hot solution).

(b) partial precipitation of ZnS in ammonical solution to carry down Co, Ni and Mn which might otherwise remain in colloidal state.

(c) reprecipitation of zinc sulphide after dissolving the precipitate in acid.

Commercial grade ZnO (added in excess) is dissolved in hydrochloric acid (AR), well stirred and filtered. The filtered solution of zinc chloride is heated to 90°C and spectroscopically pure zinc granules are then added to the hot solution. The solution is left for overnight. If the zinc metal tarnishes, fresh zinc granules are added. The above process is repeated three or four times and the metal is separated by filtration.
Bromine solution is then added to this solution drop by drop till the solution becomes brownish in colour and then it is heated to boiling. After cooling the solution to room temperature, Ammonia solution (AR) is added slowly till a white precipitate is obtained, more ammonia is added to redissolve the white precipitate. The solution is left overnight again so that impurities of iron and chromium etc. would settle down. It is then filtered through the fine fritted glass filter.

Purified hydrogen sulphide gas is now passed through the above filtrate to coprecipitate the impurities together with some ZnS, and the precipitate is filtered out and discarded. Hydrogen sulphide gas is passed again through the filtrate to bring out complete precipitation of ZnS (bulky white precipitate). The precipitate is allowed to settle and the supernatant liquid is decanted off. Hydrogen sulphide gas is passed through it and a white precipitate is again obtained. The above process is repeated a number of times till whole of the zinc sulphide is precipitated. ZnS so obtained is washed several times with hot distilled water and finally with hot deionised water until it is freed from chloride ion. The precipitate is oven dried at 110°C.

Spectrographic analysis of the zinc sulphide powder reveals that the product is spectrally pure. X-ray powder pattern analysis shows three broad diffused lines corresponding to cubic zinc sulphide.
4.4.2 Activator and coactivator solution

The activators used are chosen in the form mentioned below and they are of AR variety. In some cases, further purification is also carried out either by recrystallisation or by other chemical methods.

Copper - copper sulphate
Silver - silver acetate
Manganese - manganese sulphate/chloride

Since these are readily soluble in water, the solution facilitates uniform distribution of the activators. All the activator solutions are prepared in deionised water in pyrex measuring flasks.

Calculation for activator strength

Suppose we have taken 10 gm of ZnS in which we want to add 0.1% Cu

Copper is added in the form of CuSO₄·5H₂O

which has molecular wt. 249.69 gm.

100 gm ZnS requires = 0.1 gm Cu

\[ \frac{0.1 \times 10}{100} \text{ gm Cu} = 0.01 \text{ gm} \]

63.54 gm copper is present in 249.69 gm CuSO₄·5H₂O

\[ \frac{249.69 \times 0.01}{63.54} \]

= 0.03928 gm CuSO₄·5H₂O
Thus, if we prepare 1000 cc with 0.03928 gm CuSO₄·5H₂O and add whole of the solution in 10 gm of ZnS, we will be having 0.1% Cu. If we add 1 cc of this solution in 10 gm of ZnS, the activator will be 0.0001%. Therefore, for different strengths of the activator, different volumes of the activator solution are to be added.

Coactivator

NaCl/NH₄Cl (AR) are used as coactivators.

4.4.3 Firing procedure

A silica tube furnace, which has already been described in sec.4.3.4, is used for the heat-treatment purpose. The calculated quantity of activator and coactivator is added to a weighed amount of zinc sulphide. The mixture is then dried and the powder is transferred into the silica tube and heated to 1150°C for about an hour in an inert gas atmosphere. The preparation of individual ZnS phosphor would be mentioned in detail, along with their experimental results, in Chapter VI.