CHAPTER II

PREPARATION OF PHOSPHORS
2.1 Introduction

Impurities and imperfections are responsible for the luminescence of certain inorganic solids. If the luminescence is caused by incorporating some desired impurity, the material is known as impurity activated phosphor. When structural defects or imperfections cause luminescence the material is called a self-activated phosphor.

Phosphors can be prepared in the following different forms, according to their practical applications and needs.

(i) Single crystal: The technique for obtaining single crystal phosphors has been developed recently and due to the reproducibility of results, these phosphors have been used extensively.(1)

(ii) Thin films: The use of thin films in luminescent studies gained impetus due to their applications in cathodoluminescent screens and electroluminescent lamps. Thin films of ZnS : Mn have been prepared by Vlasenko and Popkov(2) and films of ZnCl₂ or CdI₂ have been used by Kirk and Schulman.(3)

(iii) Microcrystalline powders: This is the most commonly used and simplest form in which the phosphors are prepared.(4,5) Powder phosphors have their commercial applications in the construction of cathode ray oscillographs and fluorescent tubes.
2.2 Composition of Phosphors

The following are the basic ingredients of an impurity activated phosphor.

(a) Host material — The pure crystalline insulating material forms the host or base and is the major constituent of the phosphor. It functions as a carrier of imperfections and as a suspension for the activator. It promotes luminescence by altering the energy levels so that storage of energy and radiative transitions are possible. The host also acts as an energy transfer medium surrounding the activator atoms. Leverenz(7) has classified the important host crystals into two groups according to the modes of decay. The O-dominated group shows exponential decay whereas the S-dominated group exhibits power law decay.

(b) Activator — The element or ion which gives rise to localised energy levels in the forbidden energy gap of the host material and permits radiative transition, is called activator. The role of activator in general is to create a domain in the host lattice where electron and hole can recombine with the emission of radiation. The site that an activator occupies within the host crystal depends upon relative ionic radii of the activator and the host crystal cation. Thus if their radii are comparable (within 15%), the activator atom occupies a substitutional site thereby forming an S-centre; otherwise it occupies an interstitial
site between regular host crystal ions leading to an i-centre. The characteristics of emission depend on the activator position. Usually transition and post transition elements and rare earths play the role of activators. Depending upon the nature of its function the activators can be classified as originator, intensifier, killer, coactivator and sensitizer etc.

(c) Flux — It has been found that the preparation of phosphors often requires the presence of a readily fusible salt, known as flux. The commonly used fluxes are the water soluble, low melting point alkali and alkaline earth halides, borates and sulphates. The precise action of the flux is not yet completely understood but the advantage of adding it in appropriate quantities during the preparation of phosphors has been realised. The various views, however regarding the important roles played by the flux in the phosphor synthesis are summarised below.

(i) It acts as an agent to promote low temperature crystallization and shortens the firing time of the base materials.

(ii) It promotes even dispersion and incorporation of activator in the host crystal lattice.

(iii) In many cases the flux also serves as a charge compensating agent, when the ionic charge of the activator differs from that of the lattice ion.

(iv) It promotes the formation of defects or lattice distortions and thus affects the luminescence efficiency.
(v) It arranges its atoms around the activator atoms and thus alters the efficiency of phosphors. (16)

Asano and Kishimoto (17) have studied the influence of flux on the visible luminescence and ultraviolet absorption of ZnS : Cu phosphors. They have shown that fluxes intensify different emission bands.

2.3 Preparation of Phosphors

The luminescent properties of phosphors are controlled by a number of preparative parameters as given below.

(a) Purity of ingredients — According to Leverenz (9) a substance used for phosphor synthesis should be 'luminescent pure' i.e. the impurity content should be less than detectable in luminescence.

(b) Particle size of ingredients — The particle size of basic ingredients is important as phosphors are usually synthesised by solid state reaction. Hence there should be large surface to volume ratio, which is possible only if the powders are extremely fine. (18) This also obviates the necessity of further grinding after final synthesis.

(c) Size of the batch — Size of the charge is another important consideration for the preparation of phosphors. The proper size of the charge should be determined empirically for uniform firing and to have constant luminescent properties.
(d) Firing time and temperature — The duration of firing may vary from a few minutes to a few hours. The temperature of firing is usually in the range of 800° to 1300°C. By using suitable flux the firing temperature is usually lowered.

(e) Atmosphere during firing — The atmosphere during firing has a profound effect on solid reactions. So an oxidising, reducing or neutral atmosphere is used depending on the type of phosphor needed and operating temperature.

(f) Rate of cooling — In general, rate of cooling affects the luminescent properties of phosphors. While slow cooling of a phosphor favours an equilibrium distribution of crystal imperfections, rapid cooling tends to preserve valence states prevalent at high temperature.

(g) Grinding and particle size of phosphor — The method of grinding and particle size of the phosphor influence the luminescent properties. The particle size affects shallow traps which are more in small particles; the deeper traps are little dependent on the particle size of the phosphor.

2.4 Preparation of alkaline earth sulphide phosphors

Alkaline earth sulphides are extremely sensitive to traces of impurities such as Fe, Ni, Si, Mn etc. even when these are present in very minute concentrations. Therefore the preparation of these phosphors requires the removal of all cationic impurities before adding the desired activator, so that reproducible phosphors may be obtained. These phosphors are
hygroscopic and the absorption of moisture affects the luminescence considerably. Hence the preparation of alkaline earth sulphide phosphors necessitates high degree of purity of the ingredients, scrupulous cleanliness and a dry and dust free atmosphere.

There are several methods reported in literature for the preparation of alkaline earth sulphide phosphors, which are generally made in the powder form. In Lenard's method(24) a mechanical mixture of alkaline earth carbonate or oxide with suitable activator and a small percentage of a flux is heated with excess of sulphur for half an hour at a temperature of about 900° - 1000°C. Heating of alkaline earth carbonate plus activator impurity in a stream of carbondisulphide produced an almost complete conversion to sulphide but the specimen was not found luminescent. Reheating with a suitable flux such as sodium oxysalts produced a good phosphor.(25)

The usual and most effective method consists in heating the sulphate of the alkaline earth metal together with a small quantity of activator and flux such as Na₂SO₄, NaCl, CaF₂ etc. in an atmosphere of sulphur vapour to a temperature of 1000°C. (26)

Lehmann precipitated alkaline earth sulphates from a purified solution of their nitrates. These sulphates were converted to the sulphides by firing in an atmosphere of H₂ and H₂S. (27)

Recently Yamashita and others(28) have prepared pure
calcium sulphide powders by the deoxidation of calcium sulphate
with hydrogen gas at 950°C. They also precipitated calcium sulphate
from calcium nitrate solution.

2.5 Present method

The present method for the preparation of calcium
sulphide phosphors is due to Bhawalkar. This method consists
in heating the sulphate with a reducing agent like carbon in the
presence of suitable activator and flux.

(a) Preparation and purification of raw materials

(1) Base material – The purest available calcium nitrate
supplied by E. Merck, Germany was dissolved in distilled water
and the solution was kept boiling for six hours in the presence
of a magnesium metal ribbon. Heavy metal impurities are
deposited on the magnesium, which afterwards were filtered out.
Calcium sulphate was then precipitated with A.R. quality of
dilute sulphuric acid (2 N). The precipitate was briefly
washed in distilled water to remove excess acid and dried in an
oven at 90°C. The final powder obtained was pure CaSO_4·2H_2O
and it was stored in a clean bottle.

(ii) Reducing agent – Since carbon is always associated with
some impurities like manganese etc. and it is not possible to
get rid of these by any method, A.R. grade glucose (C_6H_12O_6)
has been used for reduction. In place of one gram of carbon
2.5 gm of glucose can be used.
(iii) Flux used - Lehmann and Ryan\(^{(30)}\) have emphasised that addition of a halide flux in 'Calcium sulphide : rare earth' phosphor is essential, as it strongly enhances the otherwise very weak or completely absent rare earth emission. Yamashita and Asano\(^{(31)}\) have also used halide flux invariably in all of their 'alkaline earth sulphide - selenide phosphors' studied recently. Hence A. R. grade NH\(_4\)Cl has been used and found effective in the preparation of all the phosphors.

(b) Preparation of activator solution :

To obtain uniform distribution in the host crystal, the activators have been taken in the form of a dilute solution of their salts. The solution also provides an easy and controlled variation of activator concentration in desired steps.

In the present investigation europium oxide and terbium nitrate of the highest available purity have been used as activator salts.

Europium oxide (supplied by Koch - Light Laboratories, England) was used for the first activator. As per calculation 0.062 gms of the salt per four gms of the host was required for one molar percentage. Hence this quantity of the salt was dissolved in 10 cc of conductivity water and a few drops of concentrated nitric acid (A.R.) were added to dissolve the salt completely. The solution was further diluted to obtain desired concentrations.

The second activator terbium was taken in the form of
terbium nitrate (K. and K. Laboratories Inc., N.Y.). For one molar percentage per four gm of the host 0.104 gm of the salt was required. The salt was found sparingly soluble in water. Hence this quantity of the salt was dissolved in 10 cc of conductivity water, and one cc was taken for 0.1 mole percent. The solution was further diluted to obtain desired concentrations.

(c) Preparation of charge:

(1) Reduction of sulphate — The following chemical reaction takes place in the reduction of calcium sulphate to calcium sulphide in the presence of carbon,

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

The quantity of carbon and hence that of glucose required for the reduction of host material was calculated from the above equation. In order to ascertain complete reduction, glucose was taken in excess.

(ii) Formula for samples — The ingredients used in the synthesis of various samples were taken in the following proportions.

\[ \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \quad 4 \text{ gm} \]
\[ \text{Glucose} \quad 5 \text{ gm} \]
\[ \text{Ammonium chloride} \quad 0.2 \text{ gm} \]
\[ \text{Activator Eu or Tb} \quad X \text{ gm} \]

(iii) The required amounts of the base powder and flux were mixed intimately in a clean and dry porcelain mortar with a pestle.
The required amount of activator solution was added and mixed thoroughly. A few drops of absolute alcohol were added to avoid caking. The mixture was dried and to it was added the requisite amount of glucose and the entire charge was mixed intimately.

(d) Firing procedure and Furnace:

Silica crucibles were used for firing the charge. The crucibles were previously cleaned and baked at the temperature of firing. The prepared charge was packed in a crucible and a thin layer of glucose was spread over the surface of the charge. The crucible was then covered with a lid, so that the high temperature of firing, the system formed an air tight chamber. The charge was thus fired in a reducing atmosphere of carbon monoxide and oxidation was thus prevented to a large extent.

The firing was carried in a muffle furnace provided with an automatic temperature control. The temperature was thus maintained fairly constant within limits of ± 25°C. The duration of firing was 2 hours at 1000°C. These parameters were determined by a series of trials.

After one hour of firing, the charge was taken out and mid-way grinding was done and the firing was again continued for one more hour. Finally the charge was withdrawn and pulverized while red hot. The phosphor was allowed to cool at room temperature. It was then collected in a clean and dry tube which was corked and sealed properly with paraffin wax to avoid any contact with moisture.
Four series of samples have been prepared. In the first series the concentration of Eu is varied from 0.001 – 1 mole %. In the second, the concentration of Tb is varied from 0.001 – 0.3 mole % of host material. From these two series the optimum concentrations of Eu and Tb were determined as 0.05 mole % and 0.1 mole % respectively.

The third series was prepared by keeping Eu content constant at 0.1 mole % and varying the concentration of Tb from 0.00001 – 0.9 mole %. The fourth series was prepared by keeping Tb constant (0.1 mole %) and varying Eu from 0.00001 – 0.2 mole %. The composition of various samples is listed in Tables 2.1 – 2.4.

2.6 Visual observation and Result

Pure CaS reduced from calcium sulphate with or without flux was a white powder, non luminescent under UV (3650 Å) and X-ray excitation.

The fluxed samples activated with Eu having characteristic pink body colour were found to be luminescent under UV and X-ray excitation. The emission colour was red. The unfluxed CaS : Eu was nearly non luminescent under both UV and X-rays.

The fluxed CaS : Tb, having light pale body colour was weakly excited by UV (3650 Å) but well excited by X-rays. The emission colour was bluish green. The unfluxed CaS : Tb was non luminescent under UV and X-rays.
### Table 2.1

**Composition of CaS : Eu phosphors before firing**

Temperature of firing $1000 \pm 25^\circ C$; Duration of firing 2 hours

In addition to the activator (Eu) each sample contains:
- Calcium sulphate 4 gm; Ammonium chloride 0.2 gm; Glucose 5 gm

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<th>Sample No.</th>
<th>Europium concentration in mole %</th>
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### Table 2.2

**Composition of CaS : Tb phosphors before firing**

Temperature of firing $1000 \pm 25^\circ C$; Duration of firing 2 hours

In addition to the activator (Tb) each sample contains:
- Calcium sulphate 4 gm; Ammonium chloride 0.2 gm; Glucose 5 gm

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<th>Sample No.</th>
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<td>T₅</td>
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<tr>
<td>T₆</td>
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Table 2.3

Composition of CaS : (Eu 0.1, Tb x) phosphors before firing
Temperature of firing 1000 ± 25°C; Duration of firing 2 hours
In addition to the activators (Eu & Tb) each sample contains:
Calcium sulphate 4 gm; Ammonium chloride 0.2 gm; Glucose 5 gm

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<tr>
<th>Sample No.</th>
<th>Eu concentration in mole %</th>
<th>Tb concentration in mole %</th>
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<td>R₂</td>
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<td>0.001</td>
</tr>
<tr>
<td>R₃</td>
<td>0.1</td>
<td>0.01</td>
</tr>
<tr>
<td>R₄</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>R₅</td>
<td>0.1</td>
<td>0.2</td>
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<tr>
<td>R₆</td>
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<tr>
<td>R₇</td>
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Table 2.4

Composition of CaS : (Tb 0.1, Eu x) phosphors before firing
Temperature of firing 1000 ± 25°C; Duration of firing 2 hours
In addition to the activators (Tb & Eu) each sample contains:
Calcium sulphate 4 gm; Ammonium chloride 0.2 gm; Glucose 5 gm

<table>
<thead>
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<th>Sample No.</th>
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<th>Eu concentration in mole %</th>
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</tr>
<tr>
<td>(2)</td>
<td>N.A. Vlasenko &amp; Y.A. Popkov</td>
<td>Opt. and Spectros. (USSR) 8, 39 (1960)</td>
</tr>
<tr>
<td>(5)</td>
<td>H.C. Froelich</td>
<td>Cornell Symposium, John Wiley N.Y. p. 44 (1948)</td>
</tr>
<tr>
<td>(13)</td>
<td>R.H. Bube</td>
<td>J. Chem. Phys. 20, 708 (1952)</td>
</tr>
<tr>
<td>(14)</td>
<td>H.A. Klasens</td>
<td>J. Electrochem. Soc. 100, 72 (1953)</td>
</tr>
<tr>
<td>(15)</td>
<td>A.L. Smith</td>
<td>J. Electrochem. Soc. 96, 75 (1949)</td>
</tr>
</tbody>
</table>
(17) S. Asano & T. Kishimoto - Science of Light 6, 101 (1957)
(21) G.F.J. Garlick - Cornell Symposium, John Wiley, N.Y. p. 87 (1948)
(23) W. Lehmann - J. of Lumi. 5, 87 (1972)
(29) D.R. Bhawalkar - The Sagar University Journal, Sagar, India, 1, 203 (1952)

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