CHAPTER II
CHAPTER II

PREPARATION OF PHOSPHOR SAMPLERS

AND

EXAMINATION OF PHOSPHORESCENCE INTENSITIES

1. PHOSPHOR PREPARATIONS:

Phosphors are usually prepared by incorporating traces of cationic (1,2) impurities in a pure insulating crystalline salt. They can, now a days, be obtained in three forms - (i) as single crystals (ii) in the form of thin films and (iii) in microcrystalline powder form.

1.1 Single crystals: Technique for obtaining single crystal phosphors have been developed only recently (3). In the case of ZnS, the method consists of heating the metal of the base or the salt itself in a dual zone furnace in a current of hydrogen or H2S, in presence of the activator, and depositing the crystal on a cooled quartz finger. Being free from statistical fluctuations, wherever possible single crystal phosphors are preferred these days, since precise measurement and reproducible results are more likely to obtained with them. Preparation of CsS in single crystal form seems to have not yet been achieved. No published data gives its melting point because it decomposes before it melts. With special design of a furnace withstanding very high gas pressure and in the presence of an inert or reducing gas it may be possible to produce CsS single crystals. Till then recourse has to be taken to other methods.

1.2 Thin Films: Transparent phosphor coatings have been deposited on glass by chemical reaction in the
vapour state (4). ZnS and CdS films activated with As, Cu, Mn, P and Zn can be obtained by slowly dropping zinc and the activator substance as powders into an electrically heated evaporator in an H₂S atmosphere of a few mm of Hg. The brightness of cathodoluminescence in thin samples is less than that of the usual powder form. However, they are found advantageous for certain other purposes. Recent (1966) work on CdS thin films is by Shalimova, Khirin and Korolev (27).

1.3 A new method of introducing activators - uses neutron bombardment of the host crystal (5). The nuclear reaction:

\[ ^{30}\text{Zn}^{64} + \text{neutron} \rightarrow ^{30}\text{Zn}^{65} \quad \text{250 days} \quad ^{29}\text{Cu}^{65} + \text{positron}, \]

for instance creates Cu - atoms in the place of Zn - atoms in ZnS or ZnO, which then is chemically converted into ZnS. The production of radioactive isotopes by neutron bombardment may further be used to determine the impurity centers with very high accuracy.

2. PHOSPHORS IN MICROCRYSTALLINE POWDER FORM:

Since this is the form in which phosphors are obtained in the present work, the preparation is described in details.

2.1 Phosphor composition: Method of obtaining phosphors in powder form is of quite general application. V. Klatt and P. Lenard (2) may be rightly thought of as pioneers in initiating microcrystalline phosphor preparations using fluxes. The method, in brief, is to take a pure (i) host material, mix it with .2 to 20% of a (ii) suitable
fusible salt called flux along with (iii) the activator added as its salt, preferably in the form of its solution. The ingredients are thoroughly mixed in a mortar and the mixture is finally fired at a suitable temperature for a predetermined period.

2.1-1 The host material: Leverens (6) prescribes colourless, high melting crystalline salts of monovalent elements for host material. Combinations of elements of columns 1, 2, 3B, 4A, 5, 6A of the periodic table with those of columns 6B and 7B fulfill this condition. Since the transitions of electrons responsible for luminescence are within the range of the band gap, it is necessary for obtaining visible luminescence that the band gap of the matrix crystal should be theoretically greater that 1.5 e.v., corresponding to the energy of the photon at the extreme red. For obtaining luminescence in the full visible region it should be $> 3$ e.v. - the energy of the violet extreme photon. Salts satisfying these requirements are mentioned in Chapter I, section 3.4.

2.1-2 Activators: Leverens (6) recommends multivalent elements for the activators. The metals which play the role of activators are usually of the transition or post transition metal types such as Cu, Mn, Cr, Pb, Bi, Sn, Ag, Au, Tl, Sb, Zr. Rare earth metals are also being used as activators.

2.1-3 Fluxes: These are readily fusible salts such as K$_2$SO$_4$, MgSO$_4$, NaCl, CaF etc., which are used to help the incorporation of the activator into the matrix. Prior to 1950, the role of a flux was in doubt. In some
phosphors it acts as a mineralizer i.e., it allows the use of lower firing temperatures and shorter firing times during phosphor preparation. In others it also aids the dispersion of the activator in the matrix. The main requirements (7) of a flux are:

(i) that it be a substance which will melt at or below firing temperature.

(ii) that the solubility of the base material in it will be sufficient to effect their rapid and better crystallization.

2.14 The principle of charge compensation: Since 1960, Kroger (8) and his coworkers have shown that many of the compounds lumped together under the general term of fluxes should really be called charge compensators, since this is their prime function. The mechanism of charge compensation can be illustrated using CaS:Ag. Ag⁺ enters the CaS lattice by replacing one Ca²⁺ ion. This would result in an excess of negative charge, so that the phosphor would not be electrically neutral. Electrical neutrality is restored if a charge compensator is introduced as shown by the following scheme:

(1) \( \text{Ag}^+ + \text{M}^{3+} \) replaces \( 2 \text{Ca}^2+ \) (total charge 4+).

(2) \( 2 \text{Ag}^+ + \text{M}^{4+} \) replaces \( 3 \text{Ca}^2+ \) (total charge 6+)

(3) \( \text{Ag}^+ + \text{X}^- \) replaces \( \text{Ca}^2+ + 1 \frac{1}{2} \text{X}^- \) (total charge 0)

(M³⁺ may be Al, Ga, In; M⁴⁺ may be titanium or Sn; X⁻ may be Cl, Br or I)

The most popular fluxes are the water soluble, relatively low melting point alkali and alkaline earth halides,
borates and sulphates (9). It is found that fluxes producing luminescence should have marked transparency in U.V. region (10).

2.2 Purity and purification: Slightest trace of foreign element may cause activation or poisoning. Alkaline earth sulphides, in particular, are hyper sensitive to nickel, iron or silica when present in traces of $10^{-4}$ p.c. (6, 11 to 14). Hence all the material chosen for phosphor preparations has got to be extremely pure - "luminescence pure", the latter being defined by an impurity tolerance less than $10^{-4}$ p.c. A clean laboratory and special care to maintain purity and cleanliness throughout the process till the end is necessary.

All the containers and reaction vessels are kept scrupulously clean. Glass and porcelain vessels are washed with hot reagent grade nitric acid and rinsed with distilled water. Water used in the treatment of phosphor materials is distilled twice the final distillation being done in pyrex stills.

2.3 Mechanics of firing: General considerations for the selection of reaction vessels are chemical inertness, purity, high reactivity, ability to withstand thermal shocks, price and life. Fused silica, platinum, alumina, porcelain, vycor, beryllium oxide or $ZrO_2$ are the materials used. It is customary to load the cold powder mixture into the furnace held at some temperature in the range $800^\circ$ to $1300^\circ$C, usually in an atmosphere of air. It is likewise customary to withdraw the charge from the furnace while hot and let it cool in air.
2.4 The mechanism of compound formation: When a mixture of two reactive solids is heated, the first formation of the new compound will occur at the boundary or interface where the different component phases immediately touch. At a given temperature the quantity formed will be proportional to the surface area of the powders. This automatically calls for very fine particles with large surface to volume ratio and thorough mixing for intensity of contact with one another, as a prerequisite to dry reactions. Further progress depends upon the velocity of new compound formation and the velocities of inter diffusion of reaction partners. Lattice defects help the incorporation of the activator into interstitial or substitutional sites. Absolute and relative size of the batches and of the furnace is an important aspect in phosphor preparation.

2.5 The atmosphere of firing (15): The atmosphere in contact with the phosphor inside a furnace has a pronounced effect on the character of the product formed. For example hexagonal CdS emits in the infra red after heat treatment in neutral or mildly oxidizing atmosphere but in the green after being heated in a reducing atmosphere (8). Jafec (16) has recently reported an interesting case in which two unusual effects have been found according as the phosphor preparation CaO:Knx (Li) is fired in Hg or N2. Firing in Hg give orange luminescence with 2537 A., but in N2 the samples are inert to 2537 or 3650 A., but on grinding show blue luminescence with 2537 excitation.

3. GENERAL METHODS OF PREPARING SULPHIDE PHOSPHORS:

The alkaline earth sulphates are reduced to sulphi-
ides or selenides by heating in a stream of H₂, H₂S or NH₃. Sr- and Ba- sulphates are reduced at 900° to 1000°C. Lenard's (17) method consists in heating the carbonates with excess of sulphur, but the method gives mixture of sulphate, oxide and unchanged carbonate. The method of Tiede (18) and Ritcher in which the oxide or sulphate is heated in carbon disulphide vapour, is satisfactory but the product may be contaminated with carbon.

4.1 **Specific method of preparation adopted:** The method used in preparing CaS phosphors in this work is Dr. Bhavalkar's (19) "method of preparing phosphors from Indian minerals". The method, in brief, consists in calcining the purified sulphate ore (Gypsum) in the presence of chosen activator, mixed with a calculated weight of pure carbon used as reducing agent. If the activator is also added as a sulphate salt, the chemical reaction can be summed up in brief as follows:

\[ m\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + x\text{SO}_4 + (4m+1)\text{C} \]

\[ = (m\text{CaS})_x\text{S} + (4m+1)\text{CO} + 2m\text{H}_2\text{O}, \]

assuming X is a divalent activator ion and m a very large number.

4.2 **The advantage of the method:** lies in the fact that the reduction of the sulphur to the sulphide and the act of incorporation of the activator in the freshly prepared base CaS, takes place in one step, so that in presence of the reducing agent, the CaS formed is given less chance to decompose and oxidise further to CaO. Also the presence of the activator ion while the mass of CaSO₄ is in the process of
reduction might be enhancing the incorporation of the activator into the base. For in absence of the activator ion the surface affinities of the vacant CaS molecules formed in the process might have all been used up in simply forming bigger lumps of CaS.

5. **DETAILS OF THE PREPARATION:**

5.1 **Purification of the gypsum ore:** This was done in two stages - (1) mechanical purification and (2) chemical purification.

5.1.1 **Mechanical purification:** Clean slabs of the ore were chosen and allowed to soak in water for a day. The next day the slabs were cut along cleavage planes with the help of a hammer and chisel, a knife or a razor blade according to the stage of cutting. Final separation of the flakes of crystal was done inside water in an enamelled tray. Glass-like transparent slabs having no dirt or fault in them were selected, and cut into thin flakes. The outer edges of each flake were rubbed with another clean flake while under water so as to remove any sand or dirt particles, since edges are usually the places where dirt and sand reside. Final selection of the flakes was done slowly and making use of a magnifying lens. Finally selected lot was washed in a stream of running water and finally with distilled water. The washed crystals were thoroughly dried. For rapidity and thoroughness the drying was done in a thermostat, precaution being taken not to allow the temperature to go above 60°C. Out of about 18 kilograms 3 kgms of selected stuff could thus be obtained.

5.2 **Pounding:** The dried crystals were first pounded into a fine powder with the help of a clean dry pestle and
mortar. The entire powdered lot was sieved out through a 120 mesh.

5.1-2 Chemical purification: The sieved powder was then given nitric acid treatment in small instalments. A hemispherical porcelain bowl was half filled with 30% A.R. nitric acid and the sieved powder was put into it until it occupied about \( \frac{1}{4} \)th of the acid by volume. The acid and the powder were allowed to stand overnight. The next day the powder was digested into the acid by boiling it over an electric heater. The charge was continuously stirred with a long glass rod while the digestion was continued. The powder first swelled and then settled down. All the impurities present were supposed to dissolve in the nitric acid. The overlying acid was decanted off from the bowl and the residual treated powder was boiled with distilled water twice and then amply with cold distilled water, until the wash was found to be free of nitrates as tested by the well known ring test. The entire powder was thus acid treated, washed free of impurity nitrates, well dried and stockerd in big bottle. The final substance was pure \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \) in the form of clean white crystallites.

5.2 Purification of carbon: A.R. quality Merc carbon was used. About \( \frac{1}{4} \) kgm of it was boiled with distilled water for half an hour to dissolve any trace of impurity and then filtered. The residue on the filter paper was washed with fresh boiling distilled water and dried in an oven.

5.3 Choice of the activator salt and preparation of its solution: Cerium salts in general do not directly dissolve in water to give stable solutions. Ceric ammonium sulphate was chosen as the activator salt since it gave a ready
solution capable of standing long when dissolved in pure distilled water to which appropriate (20) percentage of A.R. quality concentrated sulphuric acid was added. The ammonia contained could help in keeping atmosphere reducing during firing. A stock solution of about H/40 strength of accurately known concentration was prepared. This could be diluted subsequently to suit the various concentrations of the activator to be added.

5.4 Variables to be decided for setting optimum phosphors: It was at this stage that the investigation of the optimum conditions for obtaining successful phosphor may be said to have started. For preparing phosphors successfully by such method it is necessary to determine by trials, the appropriate temperature (6,21) of firing and its duration (22,23) as well as a suitable flux or fluxes and their proportion (6,24,25,26). An account of first trials with fluxes as well with those for temperature and duration and their effects is given later.

5.5 Preparing the charge for firing:

5.5-1 Mixing: Purified gypsum and carbon were taken in the proportion of 4:1 by weight, a weighed quantity of chosen flux was added to it and the ingredients were ground and mixed thoroughly with the help of a clean pestle and mortar. Measured drops of activator solution were added to the powdered mixture together with a few drops of absolute alcohol. Thorough mixing was continued until the mixture was dry. The activator taken in the form of solution, together with a few drops of alcohol added to it, were very helpful in diffusing and dispersing the activator uniformly
throughout the mixture. (Figs. II.1 & II.2 are the photographs of the appliances used for preparation. The raw material and finished products are also seen in photograph II.2).

5.5-2 Packing and placing for firing: Special reaction vessels consisting of a pair of Morgan Crucibles lined with graphite all through were used. Graphite lining was used particularly to keep the atmosphere reducing. Morgan Crucible pair 03,04 was cleaned a day ahead and then fired for half an hour at the temperature of the furnace so as to remove any contaminating gases. The mixed and dried charge was then packed in one of the crucibles to about 2/3 depth, a thin layer of pure carbon (fixed quantity) was spread over the filled charge to keep the atmosphere reducing, and the second crucible was fitted over it to act as lid. Finally a little quantity of carbon was also put in the lid. The charged vessel was then inserted into the furnace maintained at a desired temperature for a desired duration.

5.5-3 Taking off the fired products: The furnace was attended during the firing time so as to see (and adjust if necessary) that the indicator showed the same temperature throughout. In the meanwhile the pestle and mortar was washed dried and kept ready to receive the fired charge. After the firing time was over the crucible was taken off with help of a pair of tongs, lid removed (using another small pair of tongs) and the fired mass was transferred to the mortar and quickly pulverized. The pulverized powder was filled in a glass sample tube, corked, sealed in molten wax and stocked. Symbols indicating the particular sample (series, act. concentration etc.) were written down with ink
on the cork before sealing. Sealing with wax was necessary as CaS products are affected by moisture.

6. **Trial Series with Mixed Fluxes:**

To start with tentatively the data used was that given in Dr. Bhavalkar's paper assuming it to be applicable in general to all CaS phosphors. Hypo, Sodium sulphate and Sodium fluoride all were used in the ratio 12.5:5.0:1.25. Firing time was kept 2 hours and the temperature of firing 940°C. 18 samples with varying activator concentrations from .025 to .51 molar percent were prepared.

6.1 **Examine the Products:** The prepared samples had dark green appearance as seen by day light the degree of darkness depending upon the activator concentration. Even after exciting the samples for sufficiently long time by U.V. (3650 A.U.), its phosphorescence could be detected visually in the dark, only with great efforts. A special previous training in adapting the eye for darkness was necessary. However, it was possible to estimate roughly activator concentrations that produced the maximum effect. The sample between .1 to .15 Molar pc. activator concentration, showed more or less similar phosphorescence, that with .125 Molar pc. showing the maximum.

However, when excited by iron arc light (a quasi continuous U.V. source) through a quartz window showed much better phosphorescence and nearly the same maximum brightness was seen for all samples from .125 to .3 molar pc. concentration. This indicated that the excitation of the product was in the region less than 3650 A.U.
6.2 Search for excitation region visual: Phosphor sample of .25 molar p.c. composition was spread as a thin film between the folds of a thin transparent polythene film (this was found to be semitransparent to all U.V. upto 2000 Å.U.). This fold was then placed in position in the plate-holder of a quartz (Medium Hilger) spectrograph and the slit was illuminated with light from an iron arc. On examining the phosphor film from the other side from under a dark cover, the phosphor exhibited a weak greenish fluorescence which extended between 2400 Å.U. to 3000 Å.U. with a maximum between 2800-2900 Å.U. This indicated that 2800-2900 Å.U. was, perhaps, the excitation band for the phosphor formed.

6.3 Conclusion from observations: However, the overall performance of phosphors of this series was not encouraging. Hence improvement was sought by altering the parameters. Modification in the flux was undertaken first.

7. TRIALS WITH CHANGES IN FLUXES:

7.1-1 The three fluxes used in 6 were eliminated one by one as well as tried singly. It was found that out of the three, it was Na₂SO₄ used singly, that could better the results. The other two were actually found to have a negative effect. Hence now a series of nine samples by changing the flux (Na₂SO₄) quantities from 5% to 40% by wt. of flux in gypsum were prepared, keeping activator concentration constant and equal to that which gave relatively good results in the first series.

7.1-2 Results: Observations on these samples showed that there was no systematic increase or decrease of brightness of phosphorescence with gradually increasing flux. 7½,
17½% and 40% flux percentages were found discretely brighter than the remaining ones. Also, although the excitation of phosphorescence by 3650 Å showed improvement over the previous trials, the result was not still encouraging. Hence it was thought to try entirely a new material for flux.

7.2 Considerations for choosing new flux: In the light of the function of a flux stated in 2.1-3, it is evident, that since the activator ions are not directly assimilable inside the crystal lattice of the base, a flux is essential to act as a catalyst, whose action it is first to assimilate the activator ions in itself and then to transfer them to the base during the process of solution of the base into the molten flux and recrystallization from out of it. Entry of an activator ion in the flux material will ease if the ionic radius of the activator ion is less than the metallic ion of the flux salt. With this consideration it was resolved to try \( K_2SO_4 \) as a flux in place of \( Na_2SO_4 \) (tried earlier) for incorporating the Ce ions. The radii of the ions \( Ce^{+3}, Na^+ \) and \( K^+ \) are 1.07, 0.97 and 1.33 Å, in order. Thus \( Ce^{+3} \) ion radius is larger than \( Na^+ \) but is much smaller than that of \( K^+ \) ion.

Once \( K_2SO_4 \) is chosen as a new flux to be tried, as per requirement (1) stated in 2.1-3, it is necessary to have a firing temperature greater than or equal to the melting point of \( K_2SO_4 \) which is 1076°C. A new furnace capable of being maintained up to 1200°C was employed and the trial was pushed up further.

\( \text{Photograph of the furnace is shown in Fig. II.3 and the} \) 
\( \text{description is given in section 9.2.1 of this chapter.} \)
7.2-1 First trial with $K_2SO_4$ flux. First two test samples fired had the following composition:

- Purified gypsum ($\frac{M}{50}$) 2.861 gms.
- $K_2SO_4$ ... 0.143 & 0.286 gm respectively for the two samples.
- Carbon ... 0.725 gm.

Activator solution added: 1 c.c. of $0.0005 \text{ Mole/cc.}$ concentration.

After firing for two hours they were taken out, pulverized and sealed in sample tubes. On examining their phosphorescence the first remark made on the observation diary (25-1-1967) runs thus: "The phosphor prepared showed lemon yellow appearance. These were examined for phosphorescence from Woods lamp (3650 Å V. band) and with only 1 to 1½ minutes exposure gave good greenish white glow in the dark - never given before by any of the previous samples either with mixed flux or with $K_2SO_4$.

7.2-2 Further trials: Trials were made for further improvement by varying the parameters, the percentage of flux, the temperature and duration of firing. It is interesting to note that decision for changing the duration was quickly taken over because of an accident in which fused went off and the furnace stopped functioning only after about 35 minutes of firing. The sample was immediately taken out pulverized and examined. It was found to give a much better glow.

Final charge composition and optimum conditions for good products were found as follows:

- Purified gypsum 5.732 gms $\sim \frac{M}{50}$
- $CaSO_4 \cdot 2H_2O$  
- Carbon 1.450 gms.
Flux $\text{K}_2\text{SO}_4$ 0.573 gms (10% by wt of gypsum)

Temperature of firing: $1150^\circ\text{C}$.

Duration of firing: 45 minutes.

Keeping these conditions fixed and varying the activator concentration added from $3\times10^{-2}$ to $150 \text{ SO}_4^2$ Molar percent, a complete series of 13 phosphors was prepared for detailed study of their luminescent properties.

### 7.3 A series with $\text{Na}_2\text{SO}_4$ flux at higher temperature:

The higher temperature $1150^\circ\text{C}$ does not debar $\text{Na}_2\text{SO}_4$ flux. Hence for comparison purposes a series of 11 phosphors with varying activator concentration was prepared with $\text{Na}_2\text{SO}_4$ flux also.

Composition of the ingredients was kept the same percentage of flux being purposely kept the same viz. 10% as that of $\text{K}_2\text{SO}_4$. The variables obtained for best performance of the products in this case were:

- Temperature of firing: $1150^\circ\text{C}$.
- Duration of firing: 1 Hr. 40 Mts.

### 7.4 Unfluxed series:

To help draw theoretical conclusions independent of flux inclusion in the base lattice, a series of 14 samples with unfluxed base and varying activator concentrations was also prepared. Composition of gypsum and carbon was kept unchanged. Variables for the best products obtained were:

- Temperature of firing: $1150^\circ\text{C}$.
- Duration of firing: 1 Hr. 30 Mts.

### 8. Some Observations of the Products Formed:

#### 8.1 Appearance:

(a) $\text{K}_2\text{SO}_4$ fluxed series - These
**FIGURE II.4**

**ACTIVATOR CONCENTRATION VS PHOSPHORESCENCE INTENSITY**

*JUDGED VISUALLY*

A → K₂SO₄ FLUXED SERIES
B → Na₂SO₄ " " 
C → UNFLUXED " "

**FIGURE II.5**

**ACTIVATOR CONCENTRATION VS PHOSPHORESCENCE INTENSITY**

*JUDGED BY PHOTOTUBE*
powder samples are soft voluminous tending towards amorphousness. The colour as seen by day light is violet for unactivated sample (Zero), with gradual increase in activator concentration the violet colour fades and light yellowish green colour takes its place, the green colour becoming darker and darker. With still higher concentration the green changes into yellow and finally for highest concentration used it assumes deep yellow colour.

(b) \( \text{Na}_2\text{SO}_4 \text{ fluxed series:} \) For lowest activator concentration the colour is light violet which become yellowish green, deepening with increasing activator concentration. The phosphor product is compact and granular.

(c) \( \text{Unfluxed series:} \) All the samples have the same bluish grey colour.

8.3-1 Excitation of phosphorescence by 2650 A.U.: The phosphorescence intensity after three minutes excitation was examined visually in the dark as well as by phototube. The comparative phosphorescence intensity of all the samples judged visually as well as by phototube is summed up in graphs shown in Fig. II.4 and II.5 respectively.

8.3-2 Explanation of the graphs: In both the figures 1 and 2, activator concentration is plotted along the X-axis and phosphorescence intensity along Y-axis in arbitrary units. Graphs for \( \text{Na}_2\text{SO}_4 \text{ fluxed series} \) are displaced on the left by 20 units to avoid confusion. The scale, however, is the same. It is seen that

(1) in general, in each series, as the activator concentration is increased the phosphorescence intensity increases till a maximum is reached and from there onwards it drops with further increase in activator. This is in accord with the
phenomena of concentration quenching - well known in the field of luminescence.

(ii) In visual estimation (as per graphs) the maxima for K$_2$SO$_4$ fluxed, Na$_2$SO$_4$ fluxed and unfluxed series in order were 7.1:6.3:4.3, indicating K$_2$SO$_4$ flux is giving best results. However, the ratio of the maxima as measured by the phototube was 6.1:7.7:1.4 in the same order showing Na$_2$SO$_4$ sample superior to K$_2$SO$_4$ sample but unfluxed samples were the weakest in both estimates. However, in both figures it can be seen that the curve for K$_2$SO$_4$ samples is wider and has larger area under it than that for Na$_2$SO$_4$ samples. The activator got incorporated at lower concentration for K$_2$SO$_4$ series and continued to be incorporated over a wider range. This means that K$_2$SO$_4$ flux gives a wider tolerance range for activator incorporation.

(iii) The activator concentration corresponding to the maximum phosphorescence intensity is the same viz. 7.5 units (on the same scale) for both the Na$_2$SO$_4$ as well as K$_2$SO$_4$ fluxes, while that for no flux case it is 22 units.

8.3 Measurement of phosphorescence by phototube: Complete apparatus for this purpose was the same that was used later for decay study. It is described in details in Chapter III. Here only the special adaptation that was done for comparative estimates is described.

Ferrand electrophotomultiplier using IP 21 phototube in conjunction with a Rubicon Galvanometer was used to measure photo currents corresponding to the phosphorescence intensities. The sensitiveness of the galvanometer could be changed according to the intensity of phosphorescence so as
<table>
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<tr>
<th>Sample No.</th>
<th>Concentration</th>
<th>Molar %</th>
<th>Universal Shunt Multiplier</th>
<th>Deflection</th>
<th>Reduced to Unity in cms.</th>
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<td>0.540</td>
<td>1</td>
<td>5.00</td>
</tr>
<tr>
<td>17</td>
<td>Ce 8</td>
<td>22.0</td>
<td>0.660</td>
<td>1</td>
<td>2.22</td>
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<tr>
<td>18</td>
<td>Ce 9</td>
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<td>0.900</td>
<td>1</td>
<td>1.50</td>
</tr>
<tr>
<td>19</td>
<td>Ce 10</td>
<td>50.0</td>
<td>1.500</td>
<td>1</td>
<td>0.30</td>
</tr>
</tbody>
</table>
### Table II.2

**Observations for Phosphorescence Intensity**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration</th>
<th>Molar %</th>
<th>Universal Galvanometer</th>
<th>Shunt</th>
<th>Galvanometer</th>
<th>Reflection</th>
<th>Reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>of Activator in multiplier</td>
<td>of Activator in the base</td>
<td>to the charge</td>
<td>to the charge</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Mole</td>
<td>%</td>
<td>Shunt</td>
<td></td>
<td></td>
<td>Reading</td>
<td></td>
</tr>
<tr>
<td></td>
<td>of Activator</td>
<td></td>
<td>Multiplier</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Added (in</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>moles)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Zero</td>
<td>0.0</td>
<td>0.000</td>
<td>1</td>
<td>5.32</td>
<td>5.32</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Q I</td>
<td>1.0</td>
<td>0.030</td>
<td>1</td>
<td>2.00</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Q II-A</td>
<td>1.5</td>
<td>0.045</td>
<td>1</td>
<td>1.30</td>
<td>1.30</td>
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<tr>
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<td>Q II</td>
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<td>0.060</td>
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<tr>
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<td>0.090</td>
<td>1</td>
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<tr>
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<td>Q III</td>
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<td>0.105</td>
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<td>0.180</td>
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<td>7.00</td>
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</tr>
<tr>
<td>8</td>
<td>Q V-A</td>
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<td>0.195</td>
<td>10</td>
<td>1.50</td>
<td>15.00</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Q V</td>
<td>7.5</td>
<td>0.225</td>
<td>10</td>
<td>0.50</td>
<td>8.00</td>
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<tr>
<td>10</td>
<td>Q VI</td>
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<td>0.300</td>
<td>10</td>
<td>1.10</td>
<td>11.00</td>
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</tr>
<tr>
<td>11</td>
<td>Q VII</td>
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<td>0.375</td>
<td>1</td>
<td>2.30</td>
<td>2.30</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Q VIII</td>
<td>15.0</td>
<td>0.450</td>
<td>1</td>
<td>0.50</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Q IX</td>
<td>20.0</td>
<td>0.600</td>
<td>1</td>
<td>0.50</td>
<td>0.50</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE II.2

**Observations for Phosphorescence Intensity**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Molar % of Activator</th>
<th>Universal Multiplier</th>
<th>Galvanometer Deflection</th>
<th>Reduced to Unity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>0.000</td>
<td>1</td>
<td>0.30</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>0.030</td>
<td>1</td>
<td>1.03</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>0.045</td>
<td>1</td>
<td>0.60</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>0.060</td>
<td>1</td>
<td>0.58</td>
</tr>
<tr>
<td>5</td>
<td>3.0</td>
<td>0.090</td>
<td>1</td>
<td>1.02</td>
</tr>
<tr>
<td>6</td>
<td>4.5</td>
<td>0.125</td>
<td>1</td>
<td>1.02</td>
</tr>
<tr>
<td>7</td>
<td>7.0</td>
<td>0.210</td>
<td>1</td>
<td>0.70</td>
</tr>
<tr>
<td>8</td>
<td>10.0</td>
<td>0.300</td>
<td>1</td>
<td>0.90</td>
</tr>
<tr>
<td>9</td>
<td>15.0</td>
<td>0.450</td>
<td>1</td>
<td>1.52</td>
</tr>
<tr>
<td>10</td>
<td>20.0</td>
<td>0.600</td>
<td>1</td>
<td>2.40</td>
</tr>
<tr>
<td>12</td>
<td>25.0</td>
<td>0.750</td>
<td>1</td>
<td>2.38</td>
</tr>
<tr>
<td>13</td>
<td>30.0</td>
<td>0.900</td>
<td>1</td>
<td>1.30</td>
</tr>
<tr>
<td>14</td>
<td>40.0</td>
<td>1.200</td>
<td>1</td>
<td>0.95</td>
</tr>
</tbody>
</table>
to keep deflections within the range of the scale. However, the multiplying factors of the sensitiveness dial were unknown and required calibration. To avoid this and to ease computations, the arrangement was put in full sensitiveness and a universal shunt was used in conjunction. By this arrangement the sensitiveness could be changed by exact factors of 10 and the deflections observed could be reduced to the sensitiveness corresponding to unity, thus enabling absolute comparison of the samples of the three series.

8.4 An experiment to find out excitation regions photographically: Kroger (28,29) has indicated a possibility of photographic recording of the excitation spectrum using only one spectrograph. This requires a plate carrying the luminophor, made of a material transparent to luminescence and a filter to absorb the exciting radiation but to transmit the luminescence. Taking this hint following arrangement was tried to record exciting radiation.

A uniform thin layer of the phosphor powder was sandwiched between a piece of cellophane tape on one side and a clean transparent piece of mica film on the other. The arrangement was kept in contact with a photographic film with the mica side touching the film; and the film was loaded in the cassette of a Quartz spectrograph. The cassette was fitted in position so as to receive a spectrum of a hydrogen source and that of iron arc. The spectral radiation had to pass through cellophane tape, the phosphor film and mica in order, and finally it fell on the photographic film. Cellophane was found to be transparent to all U.V. radiation upto 2000 A.U. while mica was found to be transparent to visible
but opaque to U.V. Hence the exciting U.V. radiation on striking the phosphor produced visible luminescence (green) which after passing through mice was recorded on the photographic film. The blacking of the photographic film in the U.V. region even after passing through mice, then indicated the exciting wavelengths. A photograph taken with the arrangement is shown in Fig. II.11.

9. FURNACES USED FOR FIRING:

9.1 Heralnus Muffle Furnace (German make) NR 170 - was used for early work with mixed flux series. It had a cylindrical outer housing with heat resistant aluminium bronze spread on outer surface. It was filled with heat insulating material and heating muffle was enclosed in it. The control was operated through a mercury vapour valve. Within two hours after putting the power on, the desired temperature 940° could be reached. Variation of temperature inside the furnace space from front to back was \( \sim 20^\circ \text{C} \).

9.2 Muffle Furnace type 302 G manufactured by Hugo Tillquist of Stockholm:

9.2.1 Description: This furnace whose temperature could be raised upto 1400°C was employed for preparing final samples which were fired at 1150°C. The construction and circuitry of the furnace are shown in figs. II.6 to II.10. The firing space was enclosed in a heat resistant material of about 7" thickness all around; enclosed in a aluminum casing provided with a door for opening. Crucible filled with the phosphor charge could be kept on a firing bench. The heating of the space (6"x4") was achieved by passing an electric
SECTIONAL VIEW FROM ONE SIDE (REDUCED SCALE)
MUFFLE FURNACE TYPE 302 G

BLOCK DIAGRAM OF CONNECTION FOR MUFFLE FURNACE TYPE 302 G
COUPLING SCHEME FOR MUFFLE FURNACE.
current through 2 silicon carbide rods set parallel to each other. The rods were arranged in two rows connected in parallel, each row having four rods connected in series. One of the two rows of four rods was fitted above and the other below the heating space, the electric current being fed through thick nickel connecting strips, screwed round the thickened portions of the heating rods. Sectional view of the furnace from the front and side is shown in Fig. II.6 and II.7 and the block diagram of connections in Fig. II.8.

The temperature of the furnace could be recorded by a chromel alumel couple, the junction being kept in the heating space inside a porcelain tube. The indicating instrument, essentially a galvanometer calibrated directly to read the temperature of the furnace, was included in a separate unit, Instrument 901 (Fig. II.9), used for regulating the temperature of the furnace. The control of the steady temperature to be attained was done through the operation of a bimetal strip. Once the steady condition was attained, the temperature remained constant to within 5°C. Also the temperature at all parts of the firing space was found to be the same within this limit as observed by a mercury thermometer reading up to 500°C, the observations being done by a special pilot experiment in which the furnace was maintained at temperatures lower than 500°C.

The current from the mains was first fed to the effect regulator (Instrument 901) and from thence through the bimetal contact to a separate transformer. From the output of the transformer the current was finally fed to the pair of silicon carbide heating elements of the furnace. The voltage
of the transformer could be increased in steps of 10 volts from 130 volts up to 250 volts.

9.2-2 Special procedure and precautions - were necessary to bring the temperature of the furnace to the steady value 1150°C. These were:

(i) The transformer output voltage was kept to the lowest step in the early heating stage up to 300°C. The simmerstat of the regulator was also kept to the lower side.

(ii) After an hour and a half when the temperature came to 300°C, the transformer steps, as well as the simmerstat stages were gradually increased keeping both of them at one particular stage for about an hour.

(iii) This procedure was repeated and adjustment of the transformer and the simmerstat made, until the desired high temperature was attained.

(iv) The transformer - out put voltage was finally brought down until a balance of the rate of supply of heat to the furnace and rate of loss of heat from the furnace to the surrounding was achieved, as indicated by the constancy of the temperature shown by the indicator. It took several hours (from 8 to 12) for the furnace to bring it to a steady temperature of 1150°C from the room temperature.

The supply of electrical energy to the furnace was done intermittently through an automatic relay operated by the bimetal. The periods of the supply of energy and that of relaxation were controlled by the simmerstat position. At the lowest setting, the periods were 15 seconds supply followed by 3 minutes relaxation. This could be changed to about 40 seconds of supply followed by about 20 seconds relaxation. During the relaxation period (period of no supply of energy) the
heat absorbed is allowed to diffuse uniformly throughout the material.

10. CONCLUSIONS:

(1) For every base activator pair, the flux its quantity, firing temperature and duration of firing has to be determined separately. Data like ionic radii of ions and melting points of fluxes may help in making choice for expecting success.

(2) Fluxed samples show much better phosphorescence intensity and duration than unfluxed samples.

(3) Considering the case of Na₂SO₄ flux where there is a possibility of alternate choice between two temperatures of firing (e.g. 950°C and 1150°C), the appropriate duration of firing is lesser for the higher temperature than that for the lower temperature. Also the products at higher temperature are better than those at lower temperature.

(4) For the K₂SO₄ fluxed CaS:Ce phosphors the appropriate conditions for good products are:
   (a) K₂SO₄, 10% by wt. of Gyphium taken
   (b) Firing temperature 1150°C
   (c) Duration of firing - 45 minutes.

The complete conventional formula for this phosphor can be written as:

\[ \text{CaS:Ce (K₂SO₄,10%) } 1150°C = 45 \text{ minutes duration.} \]

(5) Comparing K₂SO₄ and Na₂SO₄ fluxed phosphors it is seen that all other conditions being constant the duration of firing in the case of K₂SO₄ is nearly half that in the case of Na₂SO₄.
(6) From trial experiments, the best percentages, on the lower side, for Na₂SO₄ and K₂SO₄ used as fluxes are 7.5% and 10%. The ratio 7.5:10 is very roughly near to the ratio 142:176 of their molecular weights. It appears very likely, that the same molar percentage of the two fluxes produce the best results. This matter is worth investigating further and finer details by preparing independent flux samples with very small variations in the flux percentage.

(7) Activator concentrations in mole percent producing best phosphorescence intensity, i.e., concentrations corresponding to the peaks (in graphs Fig. II.4 & II.5) in the case of the three series prepared are:

<table>
<thead>
<tr>
<th>Activator Concentration</th>
<th>Intensity arb units</th>
<th>Visual</th>
<th>Phototube</th>
</tr>
</thead>
<tbody>
<tr>
<td>-------------------------</td>
<td>--------------------</td>
<td>-------</td>
<td>-----------</td>
</tr>
<tr>
<td>(a) For K₂SO₄ fluxed series:</td>
<td>2.1x10⁻²</td>
<td>7.1</td>
<td>6.1</td>
</tr>
<tr>
<td>(b) For Na₂SO₄ fluxed series:</td>
<td>1.95x10⁻²</td>
<td>6.3</td>
<td>7.7</td>
</tr>
<tr>
<td>(c) For unfluxed series:</td>
<td>6.0x10⁻²</td>
<td>4.2</td>
<td>1.4</td>
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REFERENCES

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