CHAPTER II

SYNTHESIS OF S$_r$ SO$_4$ PHOSPHORS

2.1   Phosphors :

It is well known that the materials exhibiting luminescence are termed as 'Luminophors' and the artificially produced luminescent materials are called as 'Phosphors'. They may be either organic or inorganic, but most of interesting and commercially important ones are inorganic[1] phosphors. The phosphors are broadly classfied as phosphors in pure form, impurity activated phosphors and mixed Phosphors. The Phosphors in pure form are highly purified and they are self activated. Only the heat treatment is sufficient to make them luminescent. Zinc oxide, tungstates, molybdates and diamond are some of the examples of the phosphors in pure form [2,3]. In the impurity activated phosphors, there is a addition of small amount of one or two foreign ions into the host lattice. Such a phosphors exhibit better luminescence than those phosphors in pure form. Some times, phosphors are prepared from solid solutions of two compounds and they are named as mixed phosphors. The notable examples of mixed phosphors are (Cd, Zn) S, (Zn, Cd) Te, (Ca, Cd) S, (CaS, BaS) etc. They can be activated with various impurities to make them luminescent.

Oxygen dominated phosphors are generally wide band gap semi-conductors or insulators and they were known to exhibit luminescence for many years in naturally

occuring phosphates; silicates, carbonates and other
minerals. These phosphors have gained importance due to
their utility in the lamp industry and significant amount
of technical efforts were expanded in studying and
developing these phosphors. They have immense use in
fluorescent lamps to give special colours or colour
radiation, in high pressure mercury lamps for colour
correction, and in cathode ray tube screens. The
tremendous commercial importance of these phosphors has
motivated many workers to prepare new compositions with
the hope of finding new and useful phosphors for
fluorescent lamps. These phosphors were known to exhibit
electroluminescence, cathodoluminescence, photolumines-
cence and thermoluminescence.

2.2 General Considerations of Phosphor Synthesis :

Various methods have been followed for
synthesis of luminescent materials depending upon the
phosphor system. Out of these methods, ion implanta-
tion[4,5] has proved to be powerful technique to
incorporate activator ions directly into the host
material before structure undergoes a phase change. This
method has many advantages,

1. The implantation is not limited to any
particular type of ion.

2. The crystal may be kept at any chosen
temperature during or after the implant.

3. The depth distribution is controlled by suitable choice of energy.

4. The experiment may be made under high vaccum (i.e. clean) conditions. And if necessary only one isotope is used. And

5. The inherent radiation damage produced during the implantation can be annealed at low temperature, so that spatial control of the implant is not lost. The electrolytic introduction of activators into previously crystallised is also prevalent.[6] However, generally for the preparation of phosphors chemical doping method is used. Irrespective of these methods used for preparation of the phosphor, certain aspects of phosphor preparation are common to all these methods.

The basic ingradients in phosphor preparation are -

I. Host Material.

II. Activator.

III. Flux.

I. **The Host Material** :

Since the transistions of electrons responsible for luminescence are within the range of the band gap, for visible luminscence, it is necessary that the band gap of the host material should be greater than 1.5 ev,

the energy of the photon corresponding to the extreme red. To obtain luminescence in the full visible region, it should be smaller than three electron volt, the energy corresponding to the extreme violet. In order to satisfy above condition Leverenz[7] made combination of elements of cololumns I, II, IIIB, IVA, V & VIA of periodic table with those of columns of VIB & VIIB.

II. Activators :

Activator provides localised energy levels in the forbidden energy gap of an insulator or semiconductor[8]. The activators depending upon the way of functioning, are classified as follows -

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

b. Intensifier - It intensifies the intrinsic luminescence of the host lattice.

c. Dominant and auxillary activators - Some times the efficiency of single activated phosphor is enhanced by adding a second activator. The first and second activators are known as dominant and auxillary activators respectively.

d. Killer - It provides energy levels between which radiative transitions are forbidden[8].

e.   <u>Co-activator</u> - It provides the balance of charge[9,10] in phosphors activated by monovalent atoms. More over it may also affect the colour of emission, its intensity and crystalline structure of the phosphor material.

III. <u>Flux</u> :

There are certain salts which when added to the base material, results in good phosphors[11,12] such a salts are known as the flux materials or fluxes. Fluxes plays different roles in different phosphors and it is well known that inclusion of fluxes is benificial in certain phosphors for promotion of luminescence efficiency. The role of fluxes varies from one system of phosphor to another[13]. They usually lower the temperature of crystallisation and accelerates the chemical reaction. They also acts as a charge compensators for more or trivalent ions. They are also used to remove killers like iron and nickel as volatile hallides.

NaF, KF, Na_2SO_4 and K_2SO_4 are popular flux materials used in sulphide phosphors. Chakravarti et al.[14] have reported that Na_2SO_4 shows best performance in luminescence of CaS:Zr. Na_2SO_4 is reported to function as a charge compensator in $CaSO_4$:Dy Phosphors[15]. The fluxes have been reported to remove killers like iron and nickel as volatile hallides. In many cases only the

requisite amount of flux takes· part in phosphor preparation and residual flux is removed by washing of the phosphor with distilled water. However, if the host material is water soluble then certain organic solvents such as alcohol, methyl alcohol or glycerine are used to dissolve the alkali hallide fluxes. Recently NH_4Cl has been reported to act as a flux in $CaS:Dy:Tb$[16].

Thus the fluxes in the preparation of phosphor achieve the following.

a. Increase the speed of the reactions at lower temperature[17,18].

b. Promotes the crystal growth at lower temperature.

c. Facilates the incorporation of activator and its homogeneous distribution in the host lattice[17,18].

d. Affects the luminescence intensity[19].

e. Serves as charge compensation agent[9,10].

2.3   **Preparative parameters of Phosphors** :

The luminescent properties of a phosphor are usually dependant upon the number of parameters involved during synthesis. These are -

            a.   Purity of ingradients
            b.   Reaction vessel
            c.   Firing temperature and its duration
            d.   atmosphere of firing
            e.   Grain size of ingradients
            f.   Rate of cooling and

g.   Size of charge.

a.   <u>Purity of ingradients</u> - As already discussed lumin-
escence emission is very sensitive to the impurity
atoms i.e. a slight trace of foreign element may
cause either activation or poisoning. Therefore, the
substance, materials and chemicals should be at
least luminescencent pure (L.P.) i.e. 99.9999%
purity. Very clean laboratory as well as cleaness
throughout the various stages of synthesis of
phosphors are essensial[7].

b.   <u>Reaction vessels</u> - The selection of reaction vessel
(crucibles) is performed on the basis of their
chemical inertness, purity, high refractoriness and
ability to withstand thermal and mechanical shocks.

c.   <u>Firing temperature and its duration</u> - To obtain a
maximum brightness, the phosphor is required to be
fired for suitable time at an appropriate
temperature[14]. Also the temperature within the
heating chember of the furnace must be uniform and
constant. And any changes in temperature of furnace
may change crystal structure of phosphor,
consequently final product is affected as regards
the structural homogenity of the final product[20,21,22].

d.   <u>Atmosphere of firing</u> - The atmosphere in which
phosphor ingradients are fired has pronounced effect

on the character of the phosphor[23]. eg. hexagonal CdS when fired in the natural atmosphere, emits in the infrared region while it emits, in the green region after being heated in H_2S atmosphere[24].

e. <u>Grain size of ingradients</u> - The grain size of the basic ingradients required for phosphor makes striking effect on the rate of solid state reaction and also on the quality of phosphor. The solid state reaction must be contineous and uniform. This has been achieved by taking particles of very fine size and having large surface to volume ratio[20,25,26].

f. <u>Rate of cooling</u> - Rate of cooling strongly influences normally luminescent emission, brightness, absorption & phosphorescence decay rate. The rapid cooling preserves the valance states prevalent at high temperature and often changes the colour of fluorescence. On the other hand slow cooling helps in uniform distribution of defects throughout the phosphor.

g. <u>Size of charge</u> - Homogenity of the final product is affected by the size of charge[26]. Preparation of phosphor in large quantities may involves different rates of heating due to poor conductivity of charge. The mixture just contact with the walls of its container will attain furnace temperature earlier

than the central portion; forming a temperature gradient within it. The effect may be minimised by taking small quantity of mixture each time.

2.4   Preparation of $SrSO_4$ Phosphor :

In the present investigation $SrSO_4$ is used as a host material due to its large band gap which is greater than 1.5 ev. The required purity of the host material is 99.9999%.

2.4.1   Preparation of stock solution

A predetermined quantity of Dy_2O_3 on the basis of gram-mole was completely dissolved in double distilled water. The solution so obtained was collected in a round bottom flask which was named as a stock solution. Similarly stock solution of Tb_2O_3 was prepared.

2.4.2   Preparation cf charge

In the present studies $SrSO_4$:Dy, $SrSO_4$:Tb phosphors were prepared with and without Na_2SO_4 following closely the method used by Nambi[27].

Ten grams of purified $SrSO_4$ powder was taken in a corning glass beaker. The concentrated H_2SO_4 was added to it till powder gets completely dissolved. A batch of twenty such beakers was arranged on the table. A fixed quantity of stock solution was added to the beaker as per required activator concentration. To prepare some

phosphors charge compensator is added in some beakers. The charge so obtained was thoroughly stirred and batch of twenty beakers was kept ready for firing and it was fired at an appropriate temperature for suitable time.

The beakers containing the charge were inserted in a specially prepared double storeyed metalic box with lid, provided with a nozzle at the front as shown in the figure 2.1. The temperature inside the heating chamber was fairly uniform and constant. Ten beakers were kept in lower half and ten in upper half. And the beakers were covered with a glass plate taking care to leave a small gap for H_2SO_4 fumes to escape. The double storeyed box was inserted in the muffle furnace capable of attaining temperature of $1200^{\circ}C$ with automatic control ($\pm 10^{\circ}C$). A long glass tube with downword bend at the rear side was inserted in the hole of lid in order to give an outlet for H_2SO_4 fumes formed during firing. The double storeyed metalic box was used to avoid the reaction of H_2SO_4 fumes with coil of muffle furnace. And because of long glass tube used for outlet of H_2SO_4 fumes in the laboratory, and creating health hazard, was reduced to certain extent.

The charge was kept for evaporation at $300^{\circ}C$ for eight hours. The dried residue obtained after the treatment was washed repeatedly with distilled water in order to remove the traces of undesirable soluble

sulphates and to wash off unused amount of Na_2SO_4. The charge was then dried and heated to $600^{\circ}C$ for two hours followed by rapid quenching to room temperature. Finally samples were crushed in an agate mortar, so that size of each grain must be nearly same and sieved out through 120 mesh. And latter on it was collected in clean, dry test tubes and sealed. In all 34 phosphors were prepared and the list of phosphors prepared with and without charge compensator is given in table 2.1.

TABLE NO - 2.1

Details of the $SrSO_4$: Dy and $SrSO_4$: Tb Phosphors prepared for study.

Phosphors activated with Dy			Phosphors activated with Tb		
SR. NO.	Phosphor No.	Wt.%Dy	SR. NO.	Phosphor No.	Wt.%Tb
1.	SC_{03}	0.1	17.	SC_{11}	0.1
2.	SC_{04}	0.2	18.	SC_{12}	0.2
3.	SC_{05}	0.3	19.	SC_{13}	0.3
4.	SC_{06}	0.01	20.	SC_{14}	0.01
5.	SC_{07}	0.03	21.	SC_{15}	0.03
6.	SC_{08}	0.08	22.	SC_{16}	0.0001
7.	SC_{09}	0.001	23.	SC_{17}	0.001
8.	SC_{10}	0.0001	24.	SC_{18}	0.08
9.	SC_{*30}	0.1	25.	SC_{*38}	0.1
10.	SC_{*31}	0.2	26.	SC_{*39}	0.2
11.	SC_{*32}	0.3	27.	SC_{*40}	0.3
12.	SC_{*33}	0.01	28.	SC_{*41}	0.01
13.	SC_{*34}	0.03	29.	SC_{*42}	0.03
14.	SC_{*35}	0.08	30.	SC_{*43}	0.0001
15.	SC_{*36}	0.001	31.	SC_{*44}	0.001
16.	SC_{37}	0.0001	32.	SC_{45}	0.08

33.	SC_{00}	Original $SrSO_4$
34.	SC_{*01}	Heat treated $SrSO_4$
35.	SC_{02}	Heat treated $SrSO_4$

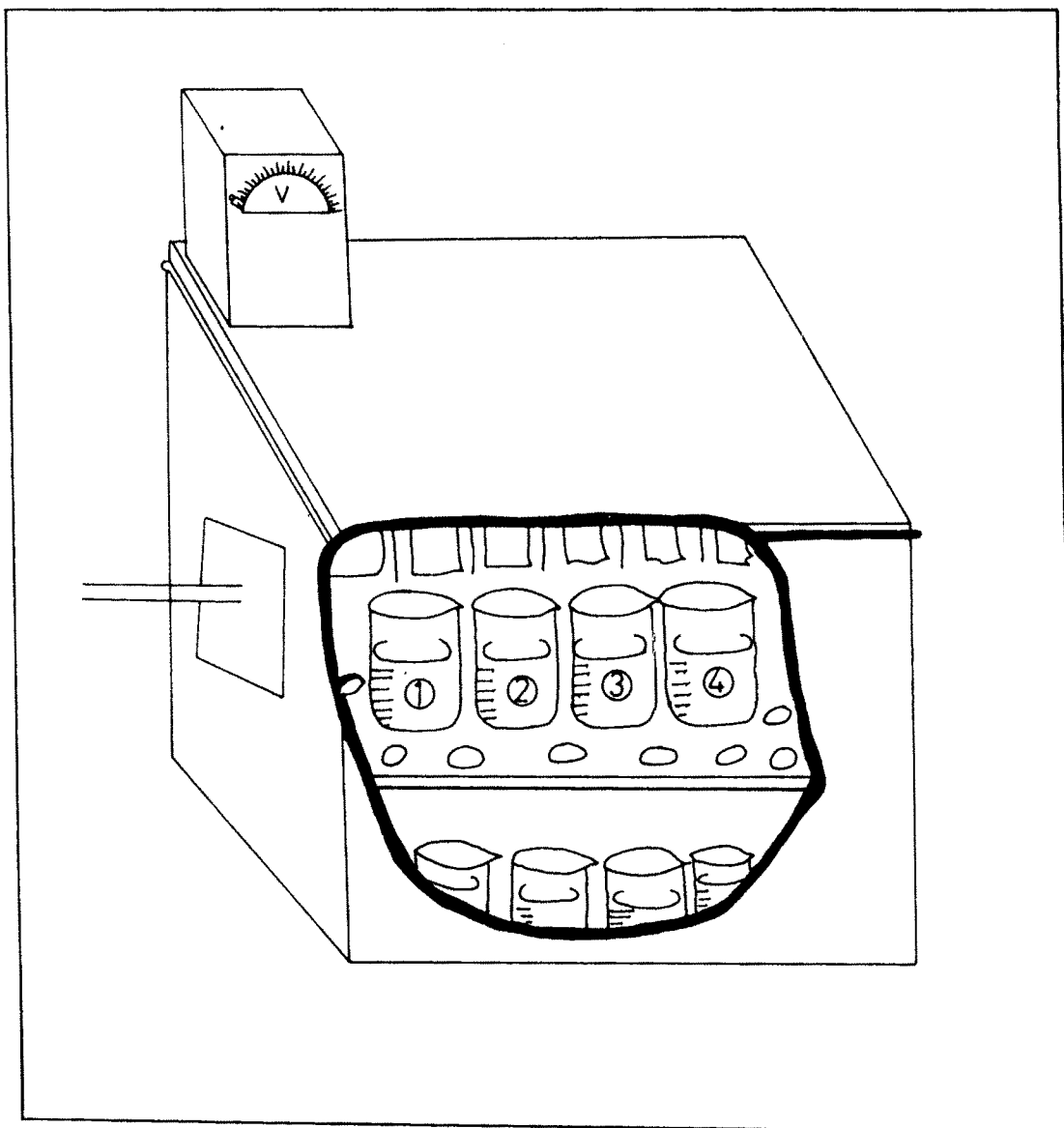Starred phosphors are prepared with the addition of Na_2SO_4.

FIG:2·1

REFERENCES

1. "The Harper Encyclopedia of Solids" ediated by James R. Newman Vol. III (Harper and Row Publishers, New York, Washington. D.C., 910 (1963).

2. Garlic G.F.J. "Luminescent Materials", (Oxford, Clarendon Press, 1949).

3. Symposia on diamond, Proc., Indian Acad. Sci., A 19, 189 (1944).

4. Townsend P.D., and Kelly J.C., Coloured centers and imperfections in insulators and semiconductors, published by chatto and winds for Sussex University Press (1973).

5. Dearnaley, G. Rep. Progr. Phys. 32, 495 (1969).

6. Wesch L. 'Method of incorporating an activator in pre-formed crystal by electrolysis' U.S. Pat. 2, 245, 843 (1941).

7. Leverentz H.W. 'An introduction to luminescence of solids' J. Willey and Sons, New York (1950).

8. Matoss, F. Nudelman, S. 'Methods of Experimental Physics'.

9. Kroger, F.A. and Hellingmann,, J.E. J. Electro. Chem. Soc. 95, 68 (1948).

10. Kroger F.A. and Dikoff, J. Physics, 16, 297 (1950).

11. Dubinin, V.G. and Trapezhikova, A.A. Optics and spectrose (U.S.A.), 19, 245, (1960).

12. Krembheller A., and Faria S.T., Electrochem. Soc. 107, 891 (1960).

13. Ward Ronald, J. Electrochem. Soc. 93, 102, (1948).

14. Chakravarti, A.K., Mor. S.L. and Ranade, J.D., Indian J. Pure and applied Phys. 12, 603-7 (1974).

15. Mulla, M.R., AND Pawar, S.H., Pramana, 12, 6, 593 (1979).

16. Awasthi, M.C. and Thakar, J.L., Indian J. of pure and Appl. Phys., Vol. 24, 98-100 (1986).

17. Ward. R. "Cornell Symposium" P-146, (John Wiley, New York, 1948).

18. Tunitskaya V.F., Dokl., Akad. Nauk, SSSR. 91, 507, (1952).

19. Smith, A.L., J. Electrochem. Soc. 75 (1949).

20. Leverentz, H.W., 'An introduction to the luminescence of Solids', 59-80 (J. Wiey and Sons, New York) (1950).

21. Nagy, R. and Chungk Wafluj, J. Opt. Soc. Amr. 37, (1947).

22. Leverentz , H.W. and Seits, F.J. Applied Physics 10, 479 (1939).

23. Kroger F.A. Brit, J. App. Physics, 5, 11, (1955).

24. Kroger. F.A. 'Some aspects of luminescence of Solids' (Elsvei, New York, 1940).

25. Levy L.A. and West D.W., Trans. Fard, Soc. 35, 128 (1939).

26. Froelich, H.C. 'Corness Symposium' (John Wiley and Sons, Inc. New York, 1948).

27. Nambi, K.S.V.Ph.D. Thesis, Gujarat University Ahmedabad (India)(1973).