CHAPTER I

INTRODUCTION

1.1 Solid State Luminescence :

1.1.1 Historical

Luminescence, in a broad sense, is considered as a physical process of absorbing energy in the matter re-emission in visible or and its near visible radiations. It is always interesting to recollect the hisotry of luminescence in solid material. 1603 Tn Cascariolo of Bologna, was first to synthesise luminescent material which emits feeble blue glow at night after exposure to day light; and hence was named as Lapis 1768. Solaris, the sun stone. Later in Canton synthesised a brigher luminescent material by heating calcium carbonate with sulphur. Further in 1866, T. Sidot discovered Zinc Sulphide phosphor which emits green same time, E. Becqueral¹ made light. At about а systematic study of luminescence and laid the foundation for experimental investigation of emission spectrum and duration after glow. It was then followed by the contributions of L. Boisbaudran² and 'P' Lenard and his School³ who studied phosphors doped with various impurities.

In true sence, the term luminescence was first introduced by Widemann⁴ in 1889 for all those phenomenon of light which are not caused solely by rising temperature. The extensive classification of luminescent materials was first made by Nicholas, Howes and Wilbur in U.S.A. at the begining of the 20th century. Mott and Gurney⁵ proposed theories to explain the phenomenon of luminescence in 1940. A novel interest in the field of luminescence arose with the theoretical foundation laid by Randall & Wilkins⁶ in 1945; and Garlick and Gibson⁷ (1948). Since then, there has been a spectacular growth of phosphor studies and novel methods are being devised for the preparation of new luminescent materials for varity of applications.

1.1.2 General

In Luminescence, the excitation may usually be with high energy photons, electrons, electric field , mechanical disruption etc. and accordingly there arises photoluminescence, cathodoluminescence, electroluminescence, mechanoluminescence and so on. The energy derived either from chemical reaction or from biological reaction can also produce a type of process called chemiluminesence or bioluminescence respectively. In thermoluminescence emission occurs only after thermal stimulation. The study of luminescence has motivated many workers to prepare new luminescent materials which have immense use in Radar, Television, Cathod Ray Tube, Infra - Red detectors, fluorescent lamps etc. Recently chemiluminescence has found applications in the laboratory as Chemical lasers. Thus the field of luminescence has been scientific investigation subject of а from both theoretical and practical point of view.

1.1.3 Present Status - Survey of Literature

In recent years considerable interest has been shown in RE (rare earth) doped sulphate phosphors due to their potential use in TL dosimetry^{8,9}. and dignostic X-ray analysis.^{10,11}. The luminescent materials for the visulisation of long wave length radiations are also popularly in use. The importance was attached to the applicability of these phosphors to low level dosimetry such as environmental radiation monitoring and day to day dosimetry measurements. TL dosimators of high sensitivity are useful for monitoring the area near nuclear installation.¹²

Eramakov and Chukichev¹³ have investigated the characteristic radiative recombination involving SЪ in GaP Allsalue low temperature. centers at et al.^{14,15}. have studied X-ray luminescence of activated Ca and Sr sulphates and sulphides under synchrotron radiation. They have shown calcium and strontium sulphate phosphors activated by rare-earth are widely used as dosimeters , since they have high energy yield. They reported that in the samarium doped strontium sulphide, Sm^{3+} ion radily enters in to the host lattice and activation by Sm^{2+} is not complete even under reducing synthesis conditions.

Ushakov et al.¹⁶ have studied luminesence of implanted rare-earth impurities i.e. Pr, Nd and Yb in GaAs and GaP. They found that, observed spectra are due to infra 4F - shell electron transistions at various optical centres, formed on the basis of trivalent rareearth ions. Aslnov et al.¹⁷ made study of spectral luminescence of Nd³⁺ in binary gallium and lanthenide and found that at а low pumping level, the Neodium luminescence is efficiently excited through band-to-band in transistions frequency range, 580 to 700 nm. Yamashita and Arano¹⁸ studied photo luminesence of sm^{3+} ions in MgS, CaS and BaS. The emission spectra of these phosphors, consists of six groups of emission lines located at about 565, 605, 650, 710, 790 and 900 nm at 300 K. Above five groups were assigned to the transisstate to the 6_{H_1} (J = 5/2, 7/2, $4_{G_{5/2}}$ from the tions 9/2, 11/2, 13/2) states and the last group to the $6_{\rm F}$ (J = 1/2, 3/2, 5/2) states in a Sm³⁺ ion.

Travnikov¹⁹ studied the luminescence in CdS crystal and showed that there exists two new lines in the et al.²⁰ studied emmission spectra. Rao thermaly earth stimulated of alkaline luminescence sulfide phosphors doped with cesium and samarium impurities by the excitation of ultra violet, r and X-rays and reported that trapping centres are responsible for the energy storage. Mulla and Pawar²¹ studied thermoluminescence,

photoluminescence and electroluminesence of CaSO₄ : Dy Phosphors and have explored the effects of charge compensating ions.

Vallabhan²² and studied Pillai electroluminescent spectra of CaS : Sm and CaS : Dy phosphors in which emission bands are well resolved into descrete lines. They have identified site of samarium impurity in CaS by considering crystal field parameter calculations and by using measured line separation. Further they found that CaS: Dy gives five emission bands which are further resolved into lines and the band with maximum intensity at 580 nm is resolved into six lines. Crandall²³ studied electroluminescence in alkaline earth sulfide phosphors and found that voltage wave form gives three light emission peaks, of which two peaks are due to voltage decrease. Crandall and Ling²⁴ observed thin film alkaline earth sulfide electroluminescence under voltage step excitation and there occur unexpected decrease in light output, if the voltage is abruptly increased at some time after the beginning of step.

Pipinys and others²⁵ studied electroluminescence of cadmium fluoride films doped by rare earth elements and they investigated temperature and field relations of the EL brightness. The rise in the EL brightness with the increase of the temperature and

applied voltage have been explained on the basis of dependance of the rate of generation of free charge Rennie and Sweet²⁶ reported results of EL carriers. output of doped CaS phosphor under A.C. excitation, and frequency dependance at various voltages and the voltage dependance at various frequencies are presented for phosphors with different dopant species and dopant concentrations. Gour²⁷ studied, EL of calcium sulfide phosphors activated with manganese and found the power law relation to hold good between EL brightness and the applied voltage. Further he observed the frequency dependance to be linear at low frequencies and the wave form of brightness was found to consist of two major peaks per cycle of the applied sinusoidal voltage. Bhand et al.²⁸ synthesised Cu, Bi activated ZnO phosphors and studied mechanism and spectral distribution of EL emission, and conclued that addition of Sulphur to the phosphor mixture enhanced the EL brightness of the Ghosh²⁹ Pandey and reported compositae phosphor. prelimary results of the A.C. electroluminescence in poly crystalline CaS:Ce phosphors.

Maheshwari and Tripathi³⁰ studied brightness waves for CdS : Sm and CdS : Cu, Sm phosphors at frequencies 500Hz, 1 KHz and 5 KHz, in each half period of the applied sinusoidal field. They observed one primary and one secondary peak. Further they have

reported that EL emission spectra shows peaks at 600 & 650 nm CdS : Sm phosphors and at 600 nm for CdS : Cu, Sm Pathak³¹ R investigated EL Maheshwari phosphors. characteristics of ZnS : Cu, Yb phosphor under high A.C. field. They have reported that the plot of voltage and frequency variations of EL brightness are in good agreement with the collision excitation mechanism and there exist a Schottky barrier at the metal semiconductor Chandra³² Bushan and investigated interface. Luminescence Spectra of CaS : Cu phosphor which shows three peaks in the visible region and dependance of 'B' on voltage have been explained on the basis of transport process of Schottky emission type. Singh and Singh³³ investigated EL of ZnS : Cu, Mn (H) phosphors under the simultaneous action of AC, DC fields, and they have reported that D.C. luminescence is governed essentially by the Mn²⁺ Centres.

Recently considerable efforts have been made by various workers to study TL of alkaline earth Sulphate phosphors. Bull³⁴ has discussed theoratical and practical aspects of TL phenomenon, and its application to radiation dosimetry, archeological dating and metrosite research. Furetta³⁵ have studied thermoluminescent properties of $CaSO_4$: Dy Phosphor in the form of pellets and showed that the new product can be very well useful in the enviromental dosimetry. Sunta³⁶ has taken review

of TL properties of Calcium based fluoride, Sulphate and Carbonate phosphors and pointed out that in calcium fluoride main emitter of TL is a 'Ce' impurity. Further by using TL emission spectra he could distinguish two types of Ce^{3+} Centers, those associated with O^{2-} compensating ion and those which have either no local compensator or are associated with F Interstitial ion at the adjescent Vecant body centre position. He found that in calcium carbonate Mn^{2+} can be used as an efficient dopant for TL emission; and co-dopant like Ce^{3+} enhances the luminescence yeild.

Sweet et al.³⁷ studied TL of pure Ca single crystal in the temperature range 8-500 K and estimated the activation energies by using method of Hoogenstraatn. Laxmanan et al.³⁸ made comparitive study of some CaSO₄ phosphors for radiation dosimetry. They used variety of activators such as Dy, Mn:Pb, Mn:Ag, Mn:Zi, Mn, Ti, Zr and Dy.; of these only, Dy gives high sensitivity as dosimetor Drazic and Trotenlj³⁹ have shown the order of kinetics to be biomolecular in CaSO₄ : Dy dosimator and reported that the glow curve of sintered CaSO₄ : Dy dosimators are formed during the sintering process; and are probably located near grain boundries in the sintered material. Komor and Osvay⁴⁰ have studied photon energy dependance of Phosphors LiF:Mg, Ti, MgB₄O₇ : Dy, CaF₂ : Mn Al₂O₃ : MgY ; by using X-ray radiation (48-205 Kev) and a 60_{r0} source and investigated relative sensitivity, linearity, fading and uv-light induced TL signal, in the dose range from several mGy to Several Gy. Srivastav and Supe⁴¹ have reported the effect of r-rays and radiation damage of CaSO₄:Dy Phosphors and the mechanism of emission of light in this phosphors. Hasan et al. 42 studied thermoluminescence of $CaSO_{\Delta}$: Dy to reveal the dosage dependance of TL output. Morgan and Stoetre 43 have reported TL mechanism in CaSO₄ : Dy single crystals, and the results of their E.S.R. study show that, in addition to usual intrinsic defects in sulphate phosphors four new paramagnetic centers have been formed, namely sulphate ion, calcium vacancy, hole associated with sulphate ion, electron trapping site with structure similar to calcium vacancy.

Tan & Sapru⁴⁴ made the analysis of TL glow peaks and reported the fractional order of kinetics of TL glow peak in contrast to the usually accepted values i.e. (1) for the first order kinetics and (2) for 2nd order of kinetics. Furetta⁴⁵ reviewed critically the methods for determining parameters in TL processes namely activation energy, trap depth and order of kinetics. Delunas et al.⁴⁶ have used initial rise method and isothermal decay method for calculating activation energies and the values so obtained were critically compaired, and they have arrived at doubtful conclusion about thermal

quenching or high temperature quartz glow peak. 47,48,49. have determined the Christodoulides trap parameters by using different methods and have described the procedure for linearising peaks of TL or after thermally simulated processes with hyperbolic heating for general order kinetics. Chaubey and Tripathi⁵⁰ studied thermoluminescence in ZnS: (Cu, Ce), ZnS: (Ag, Ce), ZnS:(Mn, Ce), ZnS:(Cu, Tb), ZnS:(Ag, Tb) and ZnS:(Mn, Tb) Phosphors and obtained values of trap depth and escape frequency factor.

Yeh⁵¹ obtained activation energy for TLD CaSO₄ : Dy Phosphor and reported the avarage activation energy of about 0.87 ev., the symmetry factor as 0.52 and the kinetics order equal to 1.88. Joshi et al.⁵² studied thermal glow curves of NaCl : Sr phosphors, using suitable filters, and reported that the 340 K peak is associated with impurity vacancy dipoles and 380 K glow peak is related to isolated Sr⁺⁺ ions. Reddy et al.⁵³ examined the TL glow spectra of undoped NaYF4 and Gd doped NaYF_{Δ} and showed that the permitted motion of the dislocations and multiplication which is conductive to the generation of centers which are responsible for the 130°C glow peak. The survey of literature shows that the structure of starting material, SrSO, is Orthorhombic⁵⁴. A projection on a face of the atomic contents of the orthorhombic unit of SrSO, is shown in figure 1.1B. The crystallographic axes ao, bo and co coincides with the X, Y and Z axes. In the same figure 1.1A the packing drawing of the atoms of SrSo₄ is shown. The line shaded spheres are strontium ions, sulphur atoms are completely hidden within their surroundings oxygen tetrahedra.

1.2 Concentration Quenching of Luminescence :

Johnson and Williams⁵⁵ have derived theoretical equation to represent the concentration quenching in luminescent phosphors considering by the capture cross-section of the luminescent centres; and host atoms. Ewles and Lee⁵⁶ have derived some what different expression taking into account the role played by structure luminescence centres centres which acts as or as quenching centres. The concentration quenching of rare earth ion fluorescence has been discussed by Blasse⁵⁷.

Quenching of Luminescence can further be explained on the basis of interaction between dissimilar There are a number of possible ways of dividing ions. the excess energy of an excited rate-earth ion with one in the ground state and the host lattice 58, 59. If M⁺ is the rare-earth ion in excited state and M, rare-earth ion in ground state, then there are four different ways of transfer of energy from M^{\dagger} to M and these are shown in fig. 1.2. In fig. 1.2a, the excited rare-earth ion (M^+) returns to the ground state non-radiatively giving its energy to the neighbouring rare-earth ion in the ground state (M), so that M goes to the excited state. As the excited energy state of M is lower in energy, the difference in energy is transferred to the matrix as heat. In fig. 1.2b similar situation is depicted except that the M⁺ comes to the lower lying metastable level rather than the ground level. In fig. 1.2c, M⁺ comes to the ground state through successive energy transfers Δ_1 and Δ_2 which is subsequently followed by a non-radiative transition of energy Δ_3 . This energy Δ_3 is given to the neighbouring ion M taking it in the excited level of energy Δ_4 . In this case $\Delta_3 > \Delta_4 \simeq \Delta_1 \simeq \Delta_2$. In Fig. 1.2d, the mechanism is similar to 1.2c except that the energy Δ_4 is sufficient to excite the ground state ion to a higher level of a multicomponent ground manifold.

1.3 Scope of Present Work :

Survey of literature shows that, in the recent years there has been a marked revival of interest in the old and long neglected alkaline earth sulphate phosphors. Applications of these phosphors in the radiation dosimetry has attracted the attention of many workers, because of there better efficiency comparable with commercial grade phosphors and some what easy laboratory preparation technique. In the last few years a large number of papers has appeared in the literature on calcium sulphate phosphors doped with RE elements. A lot

of work has also been done in understanding and interpreating the luminescence process as regards to nature of trap, energy storage, luminescence centres and the basic mechanism involved in the luminescence process. However a relatively little efforts has gone into the study of electroluminescence response of SrSO₄ phosphors activated with Dy, and Tb . Further it is hard to find any reference on the role of charge compensator on the EL. efficiency of these phosphors are few to date as far as author is aware of. Further little efforts have gone into investigation to understand the structure of SrSO₄ phosphor prepared with and without charge compensator.

Hence present work is undertaken with the view, (1) to investigate the crystal structure of RE (Dy, and Tb) doped $SrSO_4$ phosphor with and without charge compensator, (2) to reveal the role of charge compensator (Na_2SO_4) in the luminescence as well as structural, electrical and magnetic properties of these phosphors and (3) to understand the basic mechanism involved in the emission of light.

In order to achieve this, the present work is conveniently divided into three parts as detailed below.

1. <u>Preparation of Phosphors</u>

The luminescent phosphors studied in the present work were prepared from SrSO₄ (A.R. grade)

following closely the method described by Nambi⁶⁰. Strontium sulphate is doped with Dy, Tb, in varying concentrations. The Na_2SO_4 is also added in some phosphors to investigate the role of charge compensating ion Na^+ in the luminescence, electric and magnetic properties of these phosphors. In all thirty four phosphors have been prepared and studied in the present investigation.

2. Characterisation of Phosphors

Before undertaking any luminescence studies, the characterisation of phosphors becomes indispensable. In the present work this has been done on the basis of structural, electrical, magnetic and optical properties of these phosphors.

3. Electroluminescence Study

In the present investigation EL measurements of the phosphors are carried out under the action of Sinusoidal Voltage and an attempt is made to propose possible mechanism in the EL process. To achieve this the dependance of brightness voltage, frequency on and concentration investigated activator is and the appropriate explanations are given.

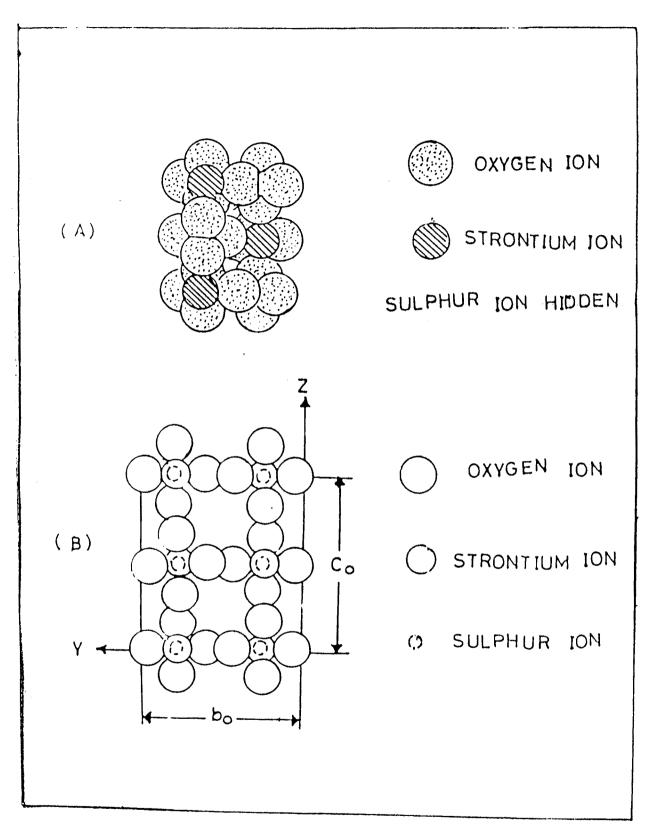
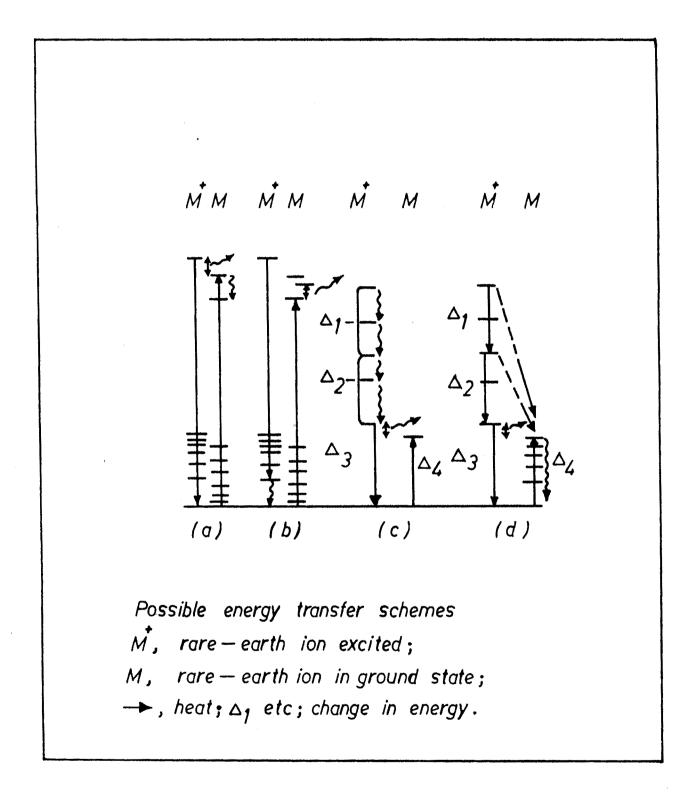


FIG. NO. 1.1 Atomic Structure of SrS0₄



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Fig. 1.2

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