Summary

Lamp phosphor in a fluorescent lamp or compact fluorescent lamp (CFL) to serve as a radiation monitoring device is a novel concept recently introduced by Murthy et al [1] Since the materials used in the fluorescent lamps are good photo luminescent materials, one can either use the inherent defects present in the phosphor or add suitable modifiers to induce thermoluminescence in these phosphors, the device (fluorescent lamp/ CFL) can then be used as an accident dosemeter. Besides having very good luminescence efficiency, good dosimetric properties of these phosphors render them useful for their use in accidental dosimetry also.

Many materials or phosphors are available for thermoluminescence dosimetry (TLD) for storing information on exposure to radiation zone. Dosimetric applications can be most conveniently divided into several general categories, which include detection of the absorbed dose to people and to the environment. Among the applications of TLD, accident dosimetry is also important. The primary objective of accident dosimetry is to monitor the radiation dose delivered to persons and environment during radiation leak or nuclear explosion with sufficient sensitivity.

The most common fluorescent lamp phosphors used till now are the rare earth doped Barium Magnesium Aluminates, Lanthanum Phosphate and Calcium Halo phosphates [2]. The optical properties along with the thermoluminescence dosimetric properties of the alkaline earth aluminates have not been studied in detail yet. Alkaline earth aluminates for the past few decades have opened a new challenge in the field of phosphor technology by showing their long light persistence property. Researchers around the globe have studied this material as this has potentially replaced the use of ZnS:Cu (in which radioactive element was used as an activator) for long persistence green phosphor with longer decay time compared to that of ZnS:Cu. Moreover the radioactive element used in this compound makes it very harmful [3]. Recent advances in the field have led to an improvement in rare earth based phosphor technology. Alkaline earth aluminates as a host material are being pursued with a great interest. The list of applications of materials having alkaline earth aluminates as host matrix is endless. Almost all phases of alkaline earth aluminates doped with rare earths find applications as refractory oxides in the steel and cement industries [4]. Of these strontium aluminates doped with rare earths are of great interest in material science because of their

phosphorescence. The $SrO-Al_2O_3$ system exists in many phases at different calcining temperature and with proper doping of rare earths has found various applications. The different phases show different optical and luminescence properties [4]. Their bright luminescence has attracted attention in the lamps, cathode ray tubes and plasma display panels (PDP) [5]. A number of important applications such as radiation detectors, sensors for structure damage and temperature, in addition to traditional luminous paints have been investigated and reported [6]. Luminophores of alkaline earth aluminates doped with rare earths are used in projection screens, field emission and plasma displays, scanning systems, etc. Luminophores also find wide applications in other fields such as light sources, passive indicators in road safety devices, fillers for films, in polygraphy (luminescent ink) in diverse systems and electronic control panel [7]. The trivalent rare earth doped alkaline earth aluminates are of great importance due to their potential technological applications as functional photonic materials such as optical fiber amplifiers, lasers and wavelength converting devices. In addition it can also be applied in textile, the dial plates of glow watch, warning signs, etc [8]. The $Sr_3Al_2O_6$ doped with divalent europium and trivalent dysprosium is having an application as mechano-luminescent material which can be utilized in the visualization of stress distribution and other mechano - optical properties [9]. The thrust on research and development studies to find out applications of alkaline earth aluminate system doped with different rare earths is still in progress. In the present work, the material has to serve as an efficient lamp phosphor and also as a suitable dosimeter and thus it has to satisfy some of the basic criteria such as optical absorption in short ultra-violet region, retentivity of luminescent characteristics over long periods of operation at operating temperature of the lamp, etc. The application of this system in the field of dosimetry has not been explored much; so emphasis is given, in the present studies, to find out its suitability as an efficient dosimeter.

Tuning of emission colours in a single host lattice is a novel idea, which unfortunately has not received serious thought in the past. Achieving various emission colours from alkaline earth aluminates has created an enormous interest among the researchers of the world [10]. This, in turn, opens up the involvement of various other aspects such as chemical nature, structure, reactivity, stability, etc, that are related to the host lattice. Scientists are also studying the effect of incorporation of trivalent rare earth impurities in the alkaline earth aluminates. Some studies have been reported over the last few years on the effect of doping of the trivalent impurities in the alkaline earth aluminates viz., $CaAl_2O_4:Tb^{3+}$, Ce^{3+} [11], $CaAl_4O_7$: Tb^{3+}, Ce^{3+} [12] and on their optical properties. Moreover, a blue and red emission from different phases of $SrO-Al_2O_3$/ $CaO-Al_2O_3$ systems doped with trivalent rare earths is still under investigation [8].

Formation of the new compound or different phases of the $SrO-Al_2O_3$ system can be achieved by varying the preparative condition, preparation techniques and the type of dopants used. Various synthesis techniques are used to synthesize the alkaline earth aluminates doped with different rare earth ions. Among them the solid state reaction is the most common and easy to use method. But the temperature required for calcining is very high i.e., in the range of 1200°C to 1800°C to get the stable phase of $SrO-Al_2O_3$ system. When the components are mixed and fired at such high temperatures usually in excess of 1300°C solid state diffusion is induced between the components, and the final product also contains unreacted precursors [4]. In addition, solid state reaction is costly and time consuming due to many hours of required firing at high temperature with an expensive high temperature furnace. To reduce the calcining temperature and time, the use of a flux is necessary. [13,14]. Other techniques like hydrothermal method [15], solid state reaction using spray dried amorphous precursors [4], and laser heated pedestal growth technique [11], combustion process [8], floating zone technique [16], are also used to synthesize alkaline earth aluminates. All these techniques, however, do not solve the problem of multiple phases. To overcome the multiphase issue, researchers have tried the various procedures based on the sol-gel technique. The sol-gel process is an efficient technique for the synthesis of phosphors due to the good mixing of starting materials and relatively low reaction temperature resulting in more homogenous products than those obtained by other synthesis techniques. Some of the reported techniques based on sol-gel synthesis are, base catalyzed sol-gel process [5], sol-gel by using organic precursor [17], Pechini method [18] and sol-gel with reflux [3].

Apart from the long persistence property of alkaline earth aluminates, the search for finding their application in the various types of displays is nowadays attracting attention of the researchers. Different aspects of $SrO-Al_2O_3$ system have been studied and reported but the lesser studied and difficult to obtain is single phase $Sr_3Al_2O_6$ ($3SrO-Al_2O_3$) which was not studied much. In this thesis greater emphasis has been given to synthesize this lesser studied phase and to study its photoluminescence (PL) and thermoluminescence (TL) dosimetric properties and also its applicability in fluorescent lamps as well as CFLs. The ratio of $SrO:Al_2O_3$ is 3:1 in $3SrO-Al_2O_3$ system, so there are bright chances of incorporating trivalent dopants at the strontium (Sr^{2+}) sites. Different rare earth dopants with different optical properties have been tried. Morito Akiyama et al have studied $Sr_3Al_2O_6$ phase by doping divalent europium at the strontium sites and using trivalent dysprosium as co-activator [9,13].

Up till now the application of thermoluminescence study of the $SrO-Al_2O_3$ system was done only to find the trap depth or the activation energy so as to correlate the phosphorescence obtained from this system but the TL dosimetric properties of this system were never reported. Our interest lies in developing lamp phosphors which can also act as dosemeter at nuclear installations, so we have also examined whether this system can be used as a dosemeter with various rare earth dopants. Therefore, in the present thesis a systematic study of the new phase, viz., $3SrO-Al_2O_3$ ($Sr_3Al_2O_6$) is carried out and its optical and TL dosimetric characteristics have been discussed at length. The evaluation of the various trap parameters namely Activation energy (E), Frequency factor (s) and Order of kinetics (b) using different methods [19,20] has been carried out and the information on the type and nature of trap has been suggested. To verify that this phosphor can be used as a dosemeter, studies were done to check its linearity, fading, dose dependence etc [21] and conclusions were drawn on them.

All the phosphor materials to be presented in the thesis were prepared using the sol-gel reflux technique.

The objective of the present investigation of the $Sr_3Al_2O_6:Ln^{3+}$ phase is two fold. The first goal is to achieve strongly light emitting single phase phosphor doped with trivalent rare earth dopants and to get the required photoluminescence emission which is useful in the fluorescent lamps and compact fluorescent lamps (CFL). The second goal is to study the thermoluminescence properties of $Sr_3Al_2O_6:Ln^{3+}$ phosphors which emit good PL in the required range, and to find out its applicability as TL dosimetric material.

This thesis has been divided into six chapters in which all the information related to the present work has been discussed in detail.

The first chapter throws light on the introduction to luminescence and its applications in today's world. The objective and need for this work with a brief introduction to the alkaline earth aluminates has also been discussed. The applications of different phases of alkaline earth aluminates, and the effect of different rare earth dopants in this system with appropriate references are presented.

The second chapter is divided in two parts. The first part describes the experimental techniques and instrumentation used, such as high temperature furnace, X-ray diffractometer, spectrofluorophotometer, thermoluminescence glow curve recorder, etc. and the second part of this chapter deals with the preparation of alkaline earth aluminate, $SrO-Al_2O_3$ system, the fundamental knowledge of structure of $Sr_3Al_2O_6$ phase, its structure and chemistry. A detailed description, with references, about the phase formation at respective calcining temperature is discussed in this chapter.

Chapter three describes photoluminescence and thermoluminescence characteristics of $Sr_3Al_2O_6$ doped with trivalent europium. The concentration of europium was varied from 0.5 mol% to 2 mol% in equal interval of 0.5 mol%. The photoluminescence characteristics of trivalent dysprosium, with different concentration of Dy^{3+} doped in $Sr_3Al_2O_6$ is also studied. The effect of trivalent europium and dysprosium as activator and co-activator respectively in $Sr_3Al_2O_6$ is discussed in this chapter. The effect of the dysprosium, as co-activator, on the luminescent properties of $Sr_3Al_2O_6:Eu^{3+}$ is studied and discussed in this chapter. The europium concentration was kept constant at 1 mol% whereas the concentration of dysprosium was varied from 0.1 mole % to 2 mole %. The thermoluminescence study of the plain $Sr_3Al_2O_6$, $Sr_3Al_2O_6:Eu^{3+}$ and $Sr_3Al_2O_6$: Eu^{3+}, Dy^{3+} is studied and discussed in detail in this chapter. The trap parameters (E, s, b) have also been evaluated using the Chen's equation followed by conclusions and references.

Chapter four mainly covers the photoluminescence and thermoluminescence study of $Sr_3Al_2O_6$ doped with terbium. Terbium was doped in different mole percentages with respect to strontium from 0.025 mol% to 2 mol%. The XRD of this phosphor confirms the formation of the single phase of the compound. The photoluminescence study of this phosphor shows characteristic emission at 545 nm, in the green region of the visible spectrum, showing the stabilization of terbium in trivalent state. The effect of beta irradiation on the trap formation and relaxation is studied by recording the thermoluminescence (TL) glow curve of the phosphor. The thermoluminescence glow curve of samples shows peaks around 120°C, 164°C and around 360°C with variation in the intensity. The doped $Sr_3Al_2O_6$:Tb (0.5%) sample showed the highest TL peak intensity in the glow curve. The fading effect of $Sr_3Al_2O_6$:Tb (1.0%) was studied for beta irradiations and their results are discussed in detail in this chapter. The dose response on beta irradiation of the $Sr_3Al_2O_6$:Tb (1%) was also studied to see the linearity. The concentration quenching in the thermoluminescence intensity was also studied by taking TL of $Sr_3Al_2O_6$ doped with different terbium concentrations.

The chapter five discusses the photoluminescence study of $Sr_3Al_2O_6:Tb^{3+}$, Ce^{3+} phosphor. The concentration of the terbium was kept constant at 0.025% while the concentration for cerium was varied. In this chapter the effect of flux viz. Boric acid on the photoluminescence intensity enhancement was also studied for different $Sr_3Al_2O_6$ compounds doped with Eu^{3+}, Tb^{3+},Ce^{3+}, Tb^{3+} and Ce^{3+}. The effect of various concentrations of flux on the different dopants is discussed at length in this chapter with references.

Chapter six is the concluding chapter of this thesis in which the summary of the thesis and the future scope of the work are presented.