Chapter 1

Introduction

The most exciting phrase to hear in science, the one that heralds new discoveries, is not Eureka! It's rather, "hmm... that's funny...".
(Isaac Asimov)

1.1 Introduction to Luminescence

Light is a form of energy. To create light, another form of energy must be supplied. There are two common ways for this to occur, incandescence and luminescence.

Incandescence is light from heat energy. If you heat something to a high enough temperature, it will begin to glow. When an electric stove's heater or metal in a flame begin to glow "red hot", that is incandescence. When the tungsten filament of an ordinary incandescent light bulb is heated still hotter, it glows brightly "white hot" by the same means. The sun and stars glow by incandescence.

Luminescence is "cold light", light from other sources of energy, which can take place at normal and lower temperatures. The word luminescence was first used by a German physicist, in 1888, Eilhardt Wiedemann, in latin 'Lumen' means 'light'. The materials exhibiting this phenomenon are know as 'Luminescent materials' or 'Phosphors' meaning 'light bearer' in Greek. The term phosphor was coined in 17th century by an Italian alchemist named Vincentinus Casciarolo of Bologona. In luminescence, some energy source kicks an electron of an atom out of its "ground" (lowest-energy) state into an "excited" (higher-energy) state; then the electron gives back the energy in the form of light so it can fall back to its "ground" state.

There are several varieties of luminescence, each named according to what the source of energy is, or what the trigger for the luminescence is:-

- Photoluminescence (PL), when the excitation is by electromagnetic radiation/photons, is a less specific term which embraces both fluorescence and phosphorescence;
- Cathodoluminescence, when the excitation is by energetic electrons or cathode rays;
- Electroluminescence is light emission triggered by electric influences;
- Radioluminescence, when the excitation is by high-energy X-rays or γ rays;
- Sonoluminescence, when the excitation is by ultrasonic waves;
- Triboluminescence can occur when a material is mechanical treated, e.g. fractured or polished;
- Chemiluminescence is light emitted during chemical reactions;

- Bioluminescence is chemiluminescence from living organisms;
- Thermoluminescence (TL), also known as thermally stimulated luminescence, is the luminescence activated thermally after initial irradiation by other means such as α, β, γ, UV or X-rays. It is not to be confused with thermal radiation: the thermal excitation only triggers the release of energy from another source.

Each process mentioned above has its own significance and advantage in the field of science and technology. Emphasis in the present work has been given to study the photoluminescence (PL) of phosphors that exhibit strong emission in the visible region. However, before going into the detail it is important to know the procedure leading to luminescence and its various characteristics.

1.2. General characteristics of luminescence

The process of luminescence can be illustrated in figure-1.1

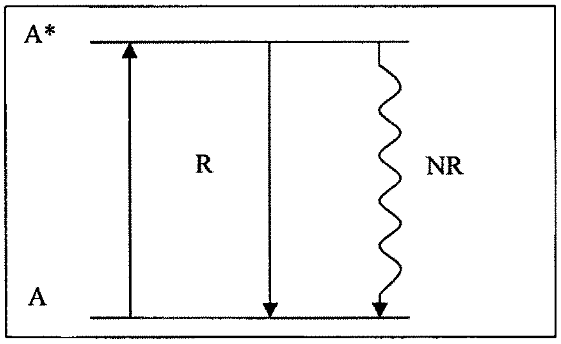


Figure 1.1. Energy level Scheme of the luminescent ion A. The * indicates the excited state , R the radiative return and NR the nonradiative return to the ground state.

The figure depicts two types of return to the ground state, one radiative and the other one non-radiative. The former is the one through which the luminescence process occurs. The other has no role in luminescence yet it occurs with the radiative emission due to the phonons which are converted to lattice vibrations that transport energy in the form of heat. An efficient luminescent material is one in which radiative transitions dominate over the non-radiative ones. Though practically in the luminescent materials the situation is more complex than depicted in figure above, the exciting radiation is not absorbed by the activator but elsewhere. Depending on the duration of the emission, luminescence has further sub classification:

(a) fluorescence: On removal of excitation an exponential afterglow is observed independent of the excitation intensity and of temperature, with lifetime less than 10^{-8} seconds.

(b) phosphorescence: On removal of excitation there exists another phenomenon of afterglow (decay is more slow with complex kinetics), often dependant on intensity of excitation and strongly temperature-dependent, with life time of more than 10^{-8} seconds. Metastable states created by the defect centers, activators, impurities, electron or hole traps present in the lattice may delay the luminescent emission causing this effect. Since thermal activation of the metastable activator or trap is prerequisite to emission.

1.2.1. Photoluminescence

As has been defined earlier, luminescence occurs when some form of energy excites solids and this energy is released in the form of photons. When this solid is excited by short-wavelength light (usually UV radiation), the phenomenon is known as photoluminescence.

Photoluminescence can be classified as either intrinsic or extrinsic luminescence.

1. Intrinsic luminescence: As the name implies, intrinsic luminescence refers to a situation in which the luminescence comes from within a pure material or crystal. It may be grouped into three categories:

a) Band-to-Band Luminescence:

This kind of luminescence occurs due to the recombination of an electron in the conduction band with a hole in the valence band, producing a band-to-band transition. This type of luminescence process can only be observed in very pure materials at relatively high temperatures, but is transformed into exciton luminescence at low temperatures. Examples of such materials are Si, Ge and some IIIb–Vb compounds such as GaAs.

b) Exciton Luminescence:

An exciton is a bound electron-hole pair in which an excited electron is interacting with a hole. As the exciton moves through the crystal, it carries some energy and the electron and hole recombine to produce luminescence. There are two kinds of excitons. The Wannier exciton is composed of an electron in the conduction band and a hole in the valence band bound together by the coulomb interaction and is found primarily in IIIb–Vb and IIb–VIb inorganic semiconductors. The Frenkel exciton exists when the expanse of the electron and hole wavefunctions is smaller than the lattice constant and can be found in organic molecular crystals such as anthracene, inorganic complex salts such as tungstates and vanadates, and in uranyl salts.

c) Cross-Luminescence:

Cross-luminescence is produced when an electron in the valence band recombines with a hole created in the outermost core band. This kind of luminescence is typically observed in alkali and alkaline-earth halides and double halides.

2. Extrinsic Luminescence:

Extrinsic luminescence refers to luminescence caused by intentionally incorporating impurities or defects into a phosphor. In ionic crystals and semiconductors, it may be unlocalized or localized. It is unlocalized when the free electrons in the conduction band and free holes in the valence band of the host lattice also participate in the luminescence. On the other hand, the localized type occurs when the excitation and emission process of the luminescence are constrained within a localized luminescent center.

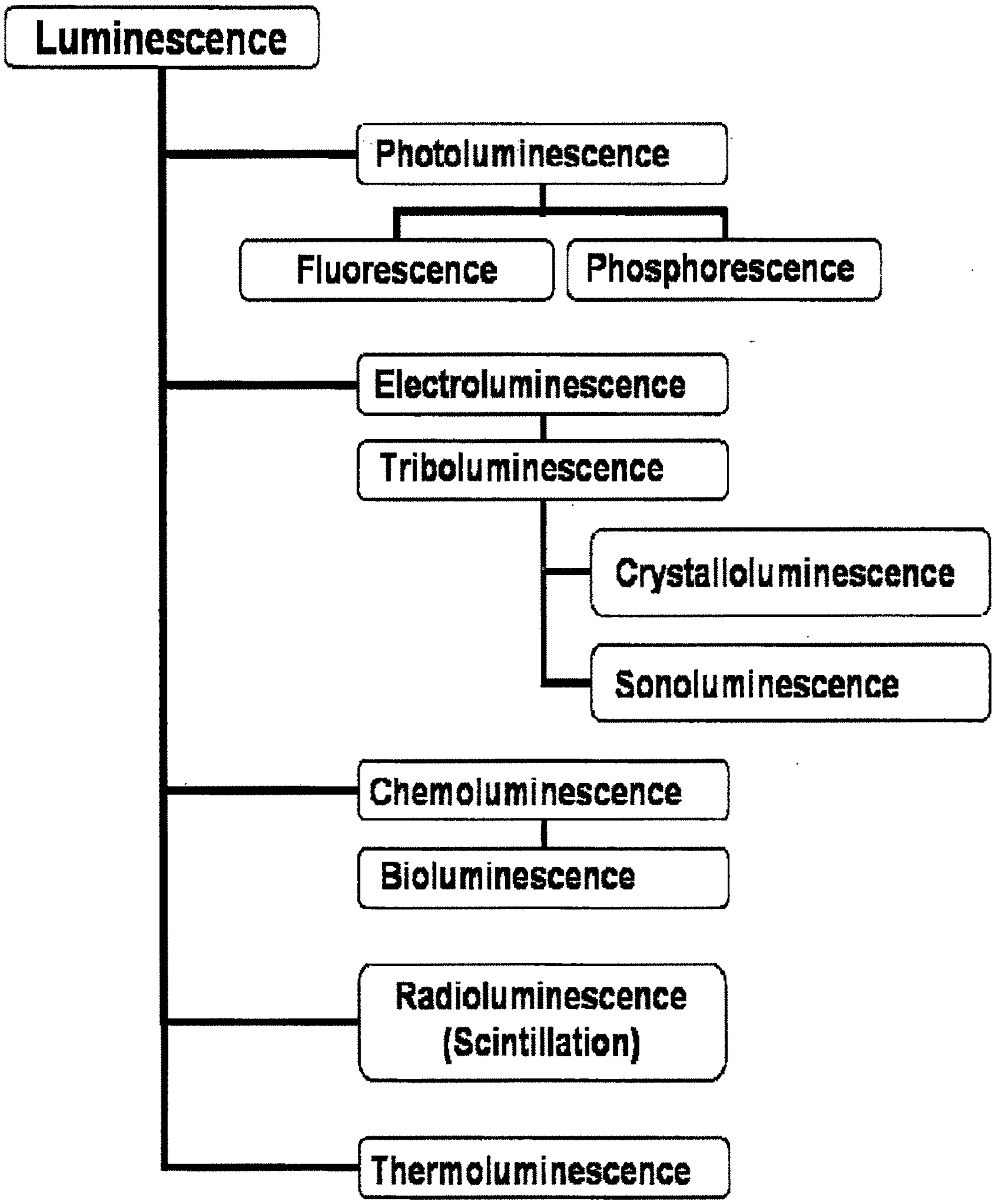


Figure 1.2. Types of Luminescence

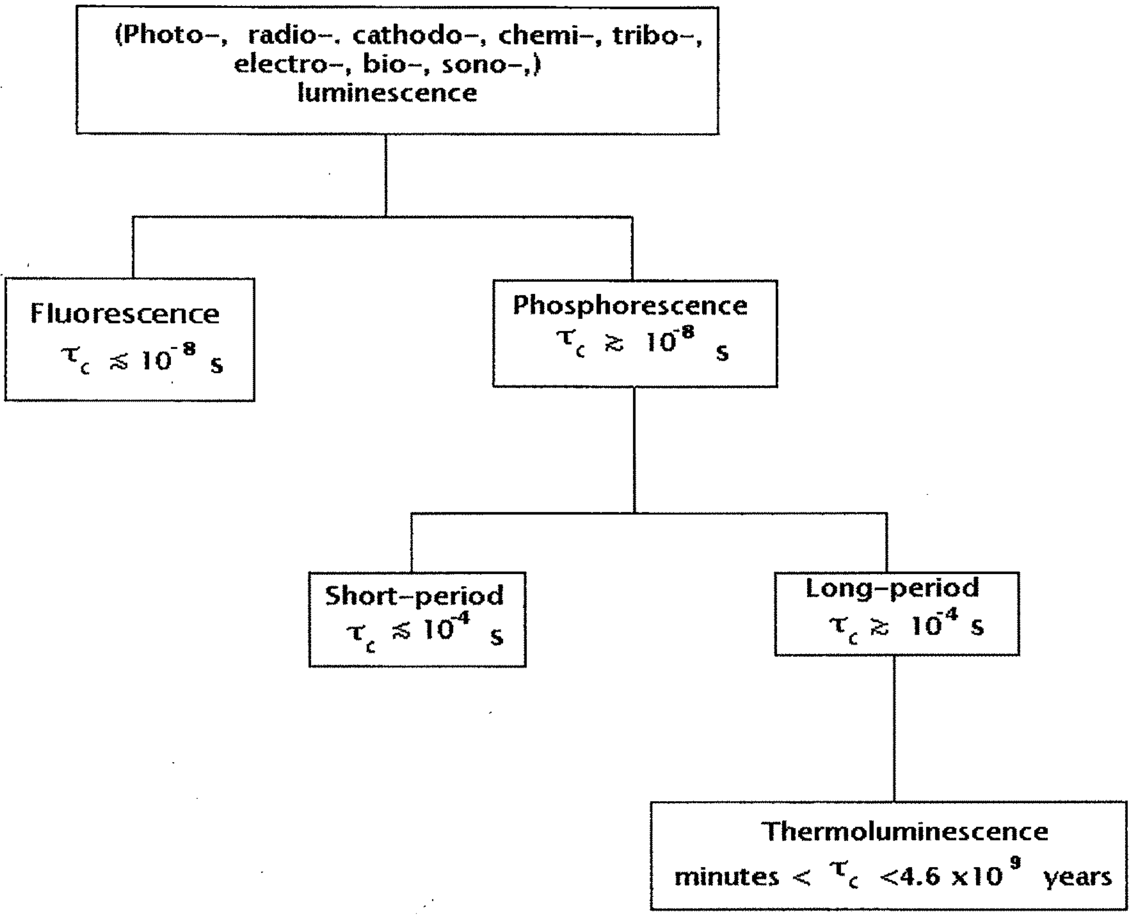


Figure 1.3. Classification of luminescence on the basis of duration of emission

1.3. Phosphor configuration

Phosphors, the term coined after the element phosphorous which glowed when in contact with air, basically, consists of an inert imperfect host crystal lattice to which some impurity ions called dopants, are intentionally added. Their history dates back to more than 100 years when a French chemist Théodore Sidot, (in 1886) accidentally prepared a prototype of ZnS-type phosphor. Since then the research and development of phosphors has undergone a many fold changes with invention and different application of these. Crystal lattice consists of periodic configuration of atoms. There are different kinds of crystals and are classified according to their symmetries, which specify invariant properties for translational and rotational operations. These crystals have closely spaced discrete energy levels, which merge into bands. Based on availability of electrons these bands form different electronic states called electronic energy band that also obey the symmetries of crystals. In these energy bands, the states with lower energies are occupied by electrons originating from bound electrons of atoms and called valence bands. The energy bands having higher energies are not occupied by electrons and are called conduction bands. The materials like rock-salt, zinc-blende etc. that exhibit crystal symmetries, usually, have no electronic state between the top of valence band and the bottom of conduction band. This vacant region between the valence band and conduction band is called forbidden gap or bandgap. Any deviation in a crystal from a perfect periodic lattice or structure is called imperfection. The common imperfections are chemical impurities, vacant lattice sites and interstitial atoms (atoms not in regular lattice positions). A point imperfection is localized at a point in the structure, in contrast, with a line or plane of imperfection. Many important physical properties of solids are controlled as much by imperfections as by the parent atom of the host lattice. The conductivity of some semiconductors is entirely due to the imperfections. A small concentration of point defects may drastically modify the electrical or the optical properties of a solid to make it useful in many industrial applications, such as solid-state electronic circuit element, phosphors for fluorescent lamp, television, solid-state laser and long persistent dark vision display devices. Luminescence of crystals is connected with the presence of impurities. The colour of many crystals arises from imperfection. The chemical and physical properties of the solid are usually controlled by imperfections.

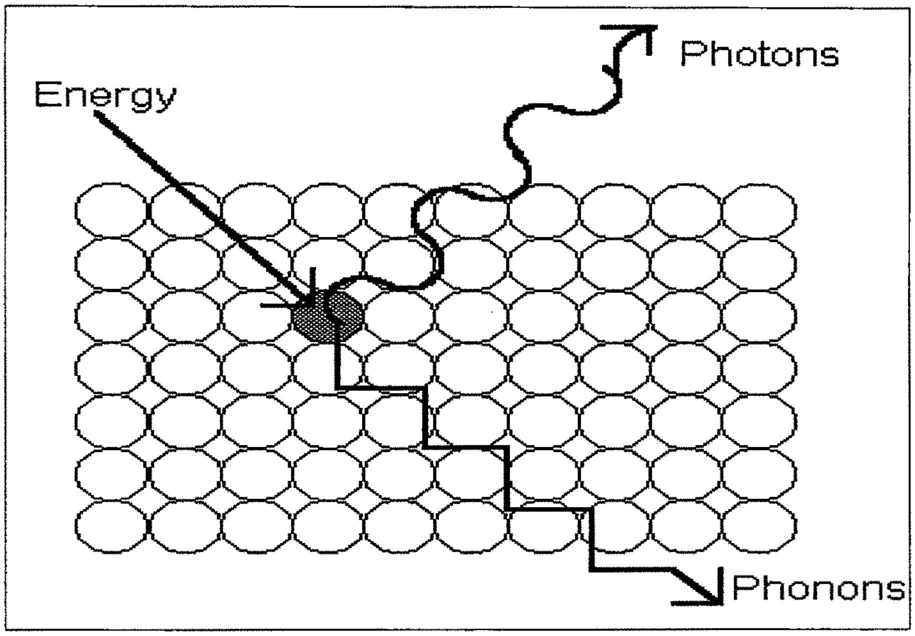


Figure 1.4. An illustration of how a phosphor emits light. The dark circle denotes an activator ion which is surrounding by a host lattice.

The point defects in solids can be classified as native defects and impurity defects. In a stoichiometric lattice, the common types of native defects are:

(a) Frenkel defects – in which either a cation or anion leaves the site and goes into an interstitial position creating a vacancy and interstitial pair.
(b) Schottky defects – in which a cation and an anion vacancy appear together.
(c) Anti Structure – in which a cation and an anion interchange.

In nonstochiometric lattice, the native defects do not have to appear in pairs but some mechanism for preserving charge balance must exist.

To accomplish our main objective or aim the present study revolves around the photoluminescence (PL) and Thermoluminescence (TL) features of the developed lamp phosphors. The emphasis is given in the present study on the role of trivalent rare earths doped in the one of the phase of $SrO.Al_2O_3$ system. But before proceeding further it is necessary to get the brief idea of the lanthanides/ rare earths, lamp phosphors, thermoluminescence, dosemeters, and alkaline earth aluminates.

1.4. Lanthanides / Rare Earths

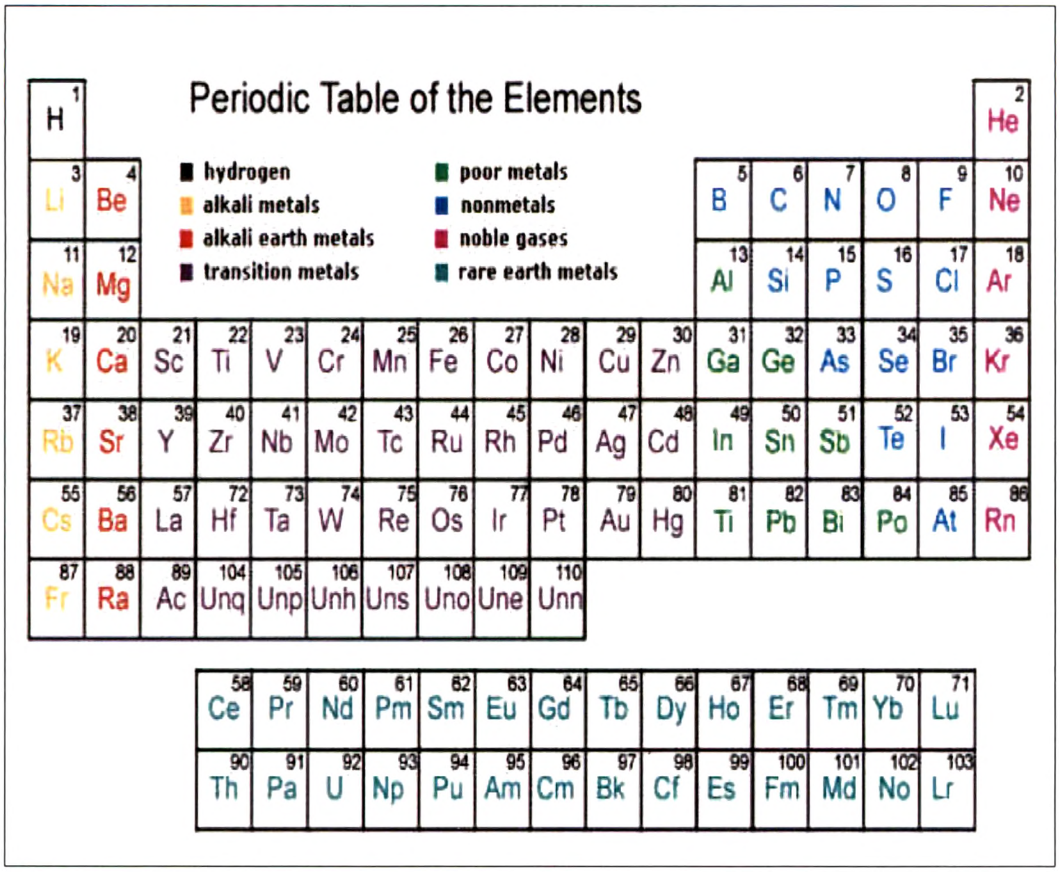


Figure 1.5 Periodic Table

Lanthanides are the series of elements from lanthanum (La, Z = 57) to lutetium (Lu, Z = 71). The 'rare earths' is the traditional name for the group of elements consisting of the lanthanides together with scandium (Sc) and yttrium (Y).

For Mendeleyev, each discovery of a new rare-earth element meant a new puzzle, because each of them showed very similar chemical behavior that made it difficult to assign positions in his periodic table. This unique chemical similarity is due to the shielding of 4f valence electrons by the completely filled $5s_2$ and $5p_6$ orbitals. The beauty of this family of elements is that, although the members are very similar from a chemical point of view, each of them has its own very specific physical properties--including color, luminescent behavior, and nuclear magnetic properties. While exploring the possibilities of the latter for structural analysis, our paths crossed in the 1970s, and the lanthanides appeared to catalyze not only a fruitful professional collaboration but also a personal friendship.

This name -rare earths- is somewhat misleading. The minerals in which they were originally discovered (gadolinite and cerite) are scarce, but the elements are not. Cerium (Ce), the most abundant member of the family, is occurring in about 66 ppm in the earth' s crust (comparable to tin). Thulium (Tm), the least occurring lanthanide is still more abundant than cadmium or silver. In our modern world, lanthanides are becoming more and more important, especially where light emission is involved. Their very high color purity is a major advantage of the lanthanides. The trivalent lanthanide ions are known for their sharp electronic transitions in the ultraviolet, visible and near-infrared spectral regions. This makes emission from lanthanide ions like europium (III) (Eu^{3+}), and terbium(III) (Tb^{3+}) very attractive for application in display devices like luminescent LCDs (Liquid Crystal Displays) and OLEDs (Organic Light- Emitting Diodes). Europium (II and III) and terbium are of interest as activators for getting tricolour lamp phosphors, also.

More possible applications for visible light emitting lanthanides doped in alkaline earth aluminates will be discussed later in this chapter.

The electronic configurations of trivalent rare earth ions in the ground states are shown in the table.

As shown in table, Sc^{3+} is equivalent to Ar, Y^{3+} to Kr and La^{3+} to Xe in electronic configuration. The lanthanides from Ce^{3+} to Lu^{3+} have one to fourteen 4f electrons added to their inner shell configuration, which is equivalent to Xe. Ions with no 4f electrons i.e., Sc^{3+}, Y^{3+}, La^{3+} and Lu^{3+}, have no electronic energy levels that can induce excitation and luminescence processes in or near the visible region. In contrast, the ions from Ce^{3+} to Yb^{3+}, which have partially filled 4f orbitals, have energy levels characteristics of each ion and show a variety of luminescence properties around the visible region.

The azimuthal quantum number (l) of 4f orbitals is 3, giving rise to 7 ($=2l+1$) orbitals, each of which can accommodate two electrons. In the ground state, electrons are distributed so as to provide the maximum combined spin angular momentum S. The spin angular momentum s is further combined with the orbital angular momentum (L) to give the total angular momentum (J) as follows:-

$J = L - S$, when the number of 4f electrons is smaller than 7.

$J = L + S$, when the number of 4f electrons is greater than 7.

As electronic state is indicated by notation $^{2S+1}L_J$, where L represents S,P,D,F,G,H, I, K,L,M,…………., corresponding to L = 0,1,2,3,4,5,6,7,8,9,……….., respectively. More accurately, as an intermediate coupling state, which can be described as a mixed state of several $^{2S+1}L_J$ states combined by spin-orbit interaction. For qualitative discussions, however, the principal L state can be taken to represent the actual state. The mixing due to spin-orbit interaction is small for the levels near ground states, while it is considerable for excited state that have neighboring states with similar J numbers. The effect of mixing is relatively small on the energy of levels, but can be large on their optical transition probabilities.

Table 1.1: Electronic configurations of trivalent rare-earth ions in the ground state

Atomic Number	Ions	Corresponding element	4f electron	S	L	J
				s	l	Σ (L+S)
21	Sc^{3+}	Ar		0	0	0
39	Y^{3+}	Kr		0	0	0
57	La^{3+}			0	0	0
58	Ce^{3+}	Xe	↑	1/2	3	5/2
59	Pr^{3+}	Xe	↑↑	1	5	4
60	Nd^{3+}	Xe	↑ ↑↑	3/2	6	9/2
61	Pm^{3+}	Xe	↑ ↑ ↑↑	2	6	4
62	Sm^{3+}	Xe	↑ ↑ ↑ ↑ ↑	5/2	5	5/2
63	Eu^{3+}	Xe	↑ ↑ ↑↑↑ ↑	3	3	0
64	Gd^{3+}	Xe	↑ ↑ ↑ ↑ ↑ ↑↑	7/2	0	7/2
65	Tb^{3+}	Xe	↑↓ ↑ ↑ ↑ ↑ ↑ ↑	3	3	6
66	Dy^{3+}	Xe	↑↓ ↑↓ ↑ ↑ ↑ ↑ ↑	5/2	5	15/2
67	Ho^{3+}	Xe	↑↓ ↑↓ ↑↓ ↑ ↑ ↑ ↑	2	6	8
68	Er^{3+}	Xe	↑↓ ↑↓ ↑↓ ↑↓ ↑ ↑ ↑	3/2	6	15/2
69	Tm^{3+}	Xe	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑ ↑	1	5	6
70	Yb^{3+}	Xe	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑	½	3	7/2
71	Lu^{3+}	Xe	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	0	0	0

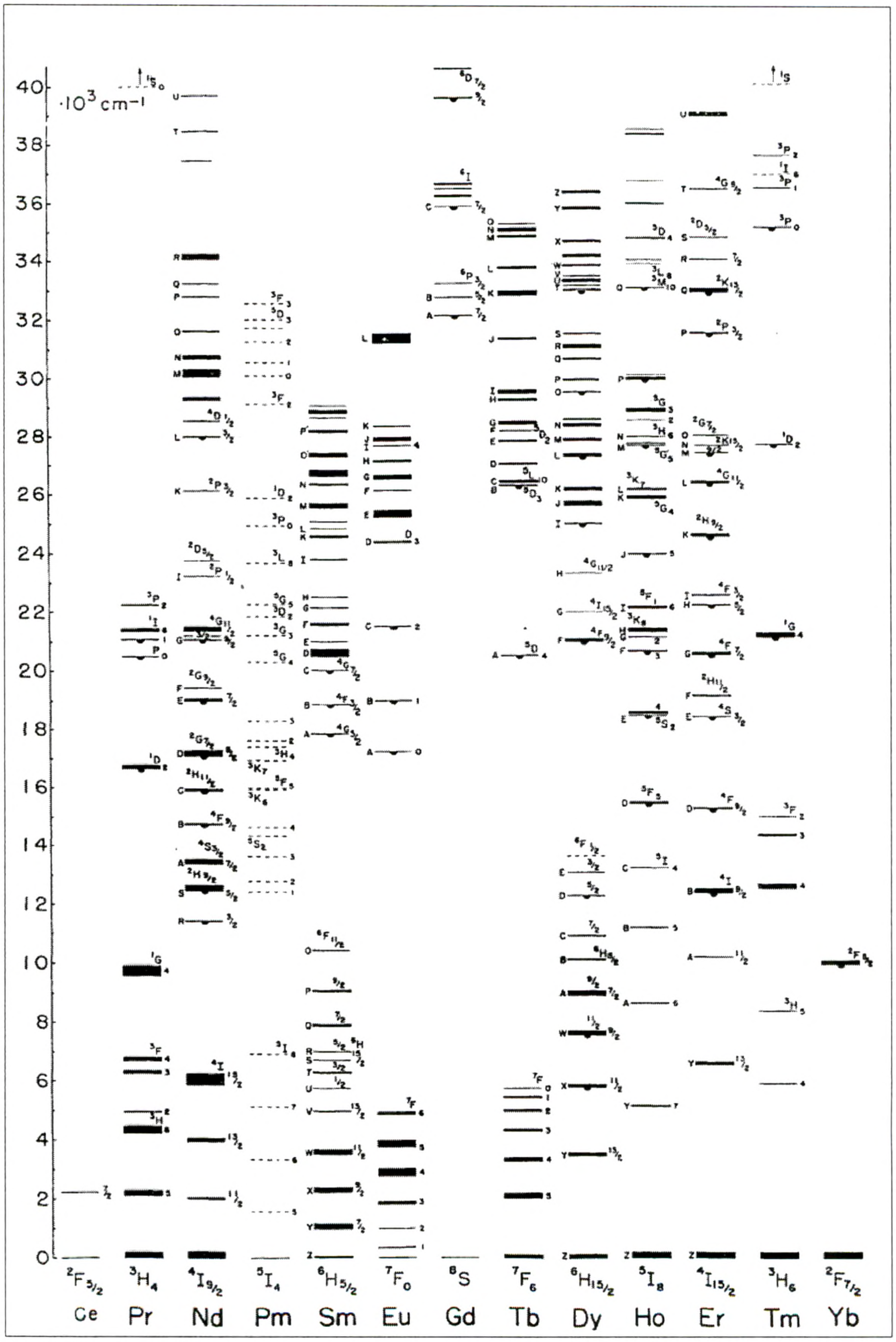


Figure 1.6. Observed energy levels of the trivalent rare-earth ions.

Those transitions are intraconfigurational 4f-4f transitions. Usually, two kinds of transitions can be observed in the spectrum of a lanthanide ion. Most of the transitions are induced electric dipole transitions (ED) which are forbidden by the Laporte selection rule, because these transitions occur within one (4f) configuration. Some transitions are magnetic dipole transitions (MD). In both cases, the intensity of the transitions is low. Because of rather efficient shielding by the filled 5s and 5p shells, the 4f shell experiences very little influence from the environment in which the trivalent lanthanide ion is embedded. Therefore the transitions appear as sharp lines, in contrast to the broad bands often observed for transition metals. This also results in a longer decay time of the excited state and therefore trivalent lanthanides show strong luminescence with high color purity.

absorbance is a drawback for good luminescence but can be bypassed through the antenna effect.

The applications of lanthanides are numerous, but we have presented only a small and quite personal selection, which is required in this thesis. We expect that many new and exciting applications will emerge in the future. There is, however, no need to worry that these elements will be depleted in the near future.

The luminescent properties of the lanthanides also have been utilized in medical diagnosis. A variety of luminescent bioassays and sensors have been developed that take advantage of the unique luminescent properties of these elements, such as a relatively long-lived emission.

The lanthanides have played an important role in our lives. They initiated our collaboration and friendship, and they helped us in our careers, during which the lanthanides have gained significantly in importance and will undoubtedly continue to do so.

Most applications of lanthanides are based on their physical properties. First of all, there

everywhere. The TV screens and computer monitors that we use for our communication across the ocean have lanthanide phosphors. The glass fibers used for data transport contain lanthanides, and our offices and houses are illuminated with energy-saving tricolor lanthanide-based luminescent lamps. As an example of the metallurgical uses, rare earths elements were used in the steel alloy for the Alaska crude oil pipeline. The cathode ray tube phosphor is Eu-doped YVO (yttrium vanadate), giving the red color. Many phosphors also contain rare earths in single or double dopant form.

The rare earths have also found very place as a thermoluminescent dosimeters. The most

the importance of lanthanides in this field. The other examples of rare earth based TLDs

$_4$:Tm, MgB_4O_7:Dy, Tm, Mg_2SiO_4:Tb, CaF_2:Dy, etc.

The rare earth doped alkaline earth aluminates have also found its application in the various filed of display devices which are described in the next chapter.

1.5. Types of dopants

The dopants play different roles in different host lattices depending upon their electronic configuration, solubility and structure of the host lattices. Furthermore, dopants have been classified into various categories on the basis of their function in host lattices.

Activator: When an electron from dopant ion jumps to the excited state after absorption of excitation energy and emits the energy in the form of radiation while returning to ground state, it is known as activator (A) or luminescent center. For example, rare-earth (Eu^{2+}) and transition metal ions (Cu^{+}) in crystal lattice of alkaline earth aluminates, and sulfides, respectively act as activators.

Sensitizer: In case of two dopants in a crystal lattice, one is known as sensitizer (S) and another is A. The 'S' absorbs most of the energy and transfers it to the 'A' for the process of emission as seen in Figure 1.3. The metal ions, for example, forming sensitizer → activator pairs are $Ce^{3+} \rightarrow Tb^{3+}$ and $Eu^{2+} \rightarrow Mn^{2+}$.

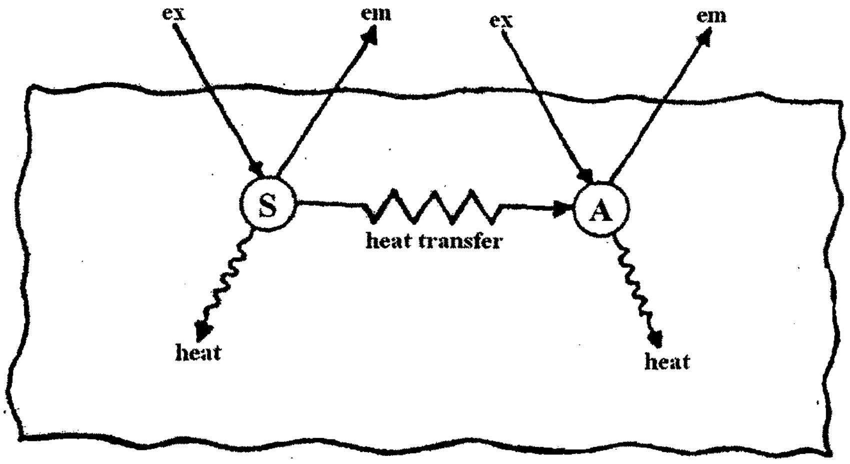


Figure 1.7. Schematic representation of luminescence process

Co-activator: The dopant ion that does not luminescence but help in the process of luminescence by acting as charge compensator or by creating hole/electron-traps is known as co-activator. For example, Al^{3+}, Cl^-, F^- in ZnS lattice.

Quenchers or Killers: The dopant ion that is responsible for decrease or complete disappearance of luminescence is known as quencher. When energy is transferred from an emitting center in a nonradiative manner with evolution of heat it causes quenching of luminescence. For example, Fe, Co and Ni in ZnS act as nonradiative centers thus called quenchers.

1.6. Model for a Luminescence Process to take place

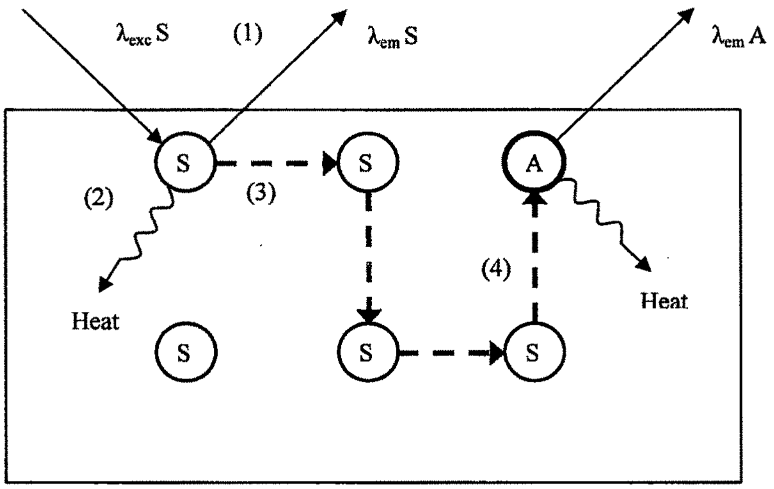


Figure 1.8. Schematic representation of the possible luminescence processes of a crystal system with donor D and acceptor A ions. Following excitation D may: (1) emit radiatively, (2) decay nonradiatively, (3)transfer energy to another D ion, or (4) transfer energy to an A ion. in the last case, energy transfer to A is followed by either radiative or nonradiative decay.

In the host lattice the ion which absorbs the radiation is referred to as the donor, and the ion which excitation energy is transferred is the acceptor. From the schematic presented in Figure, four different processes following excitation of D can be distinguished: (1) D may luminesce, (2) D may decay nonradiatively producing heat, (3) D may transfer energy to another D type ion, or (4) D may transfer energy to an A type ion. If energy transfer to A is followed by nonradiative decay, A is referred to as a killer site, because it acts to quench luminescence. Commonly the nature of the transfer mechanism is inferred by examining how the luminescence decay of an ensemble of "equivalent" ions within a host lattice depends on their concentration and temperature. Figure shows a schematic of the possible luminescence processes which can occur when ion within a larger ensemble is excited.

1.6.1. Decay process of Excited states

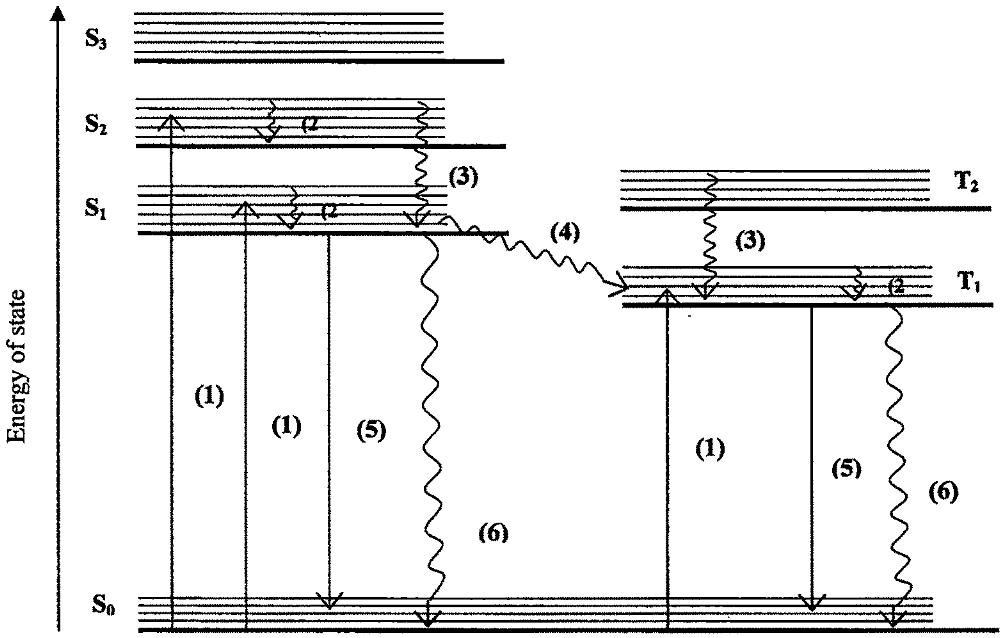


Figure 1.9. The Jablonski diagram, which explains the photophysical processes in molecular systems. (1) photoabsorption; (2) vibrational relaxation; (3) internal conversion; (4) intersystem crossing; (5) radiative transition; and (6) nonradiative transition.

Production and decay processes of excited states are described using an energy state diagram called Jablonski diagram. The ground state S_0 and lowest singlet and triplet states, S_1 and T_1 are composed of multiple vibrational states due to the presence of vibronic motions of atoms that make up a molecule. When energy larger than the HOMO-LUMO energy difference is introduced into a molecule, either a higher vibronic state within S_1 states, or higher singlet excited states S_2 and S_3 are produced. The higher vibronic states of S_1 relax to the lowest vibronic state of S_1 within a time scale of picoseconds. The higher energy singlet states such as S_2 and S_3 relax to the S_1 state via nonradiative internal conversion (IC) processes. Triplets states are usually produced via an intersystem crossing (ISC) processes from $S_1 \rightarrow T_1$. Thus, radiative transitions take place as the electronic transition from the lowest excited states of S_1 or T_1 to the ground state S_0. the radiative transition from S_1 to S_0 is classified as a spin-allowed transitions and hence the time scale of the transition is of the order of a few nanoseconds. On the other hand the time scale T_1 to S_0 transition is much longer ranging form micro- to milliseconds because the process is spin-forbidden. Thus, an emission spectrum looks like the mirror image of the absorption spectrum of the molecule.

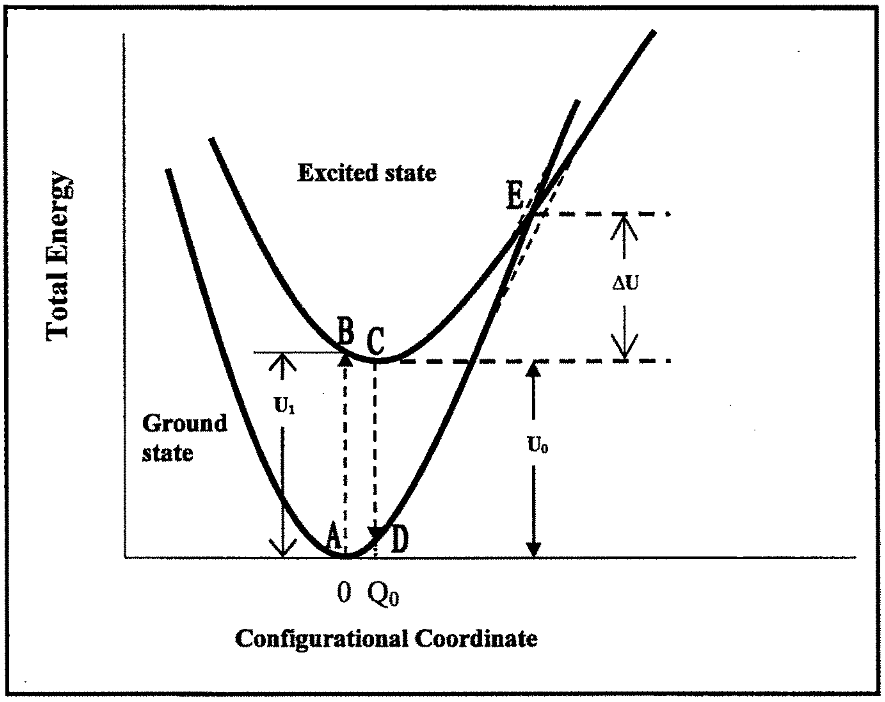


Figure 1.10. Configurational Coordinate diagram (Energy Levels of transitions taking place).

The configurational coordinate model is often used to explain optical properties, particularly the effect of lattice vibrations, of a localized center and have been shown in figure-1. In this model a luminescent ion and the ions at its nearest neighbour sites are selected for simplicity. In most cases, one can regard these ions as an isolated molecule by neglecting the effects of other distinct ions. In this way, the huge number of actual vibrational modes of the lattice can be approximated by a small number or a combination of specific normal coordinates. This normal coordinates are called the configurational coordinates. The configurational coordinate model explains optical properties of a localized center on the basis of potential curves, each of which represents the total energy of the molecule in its ground or excited state as function of the configurational coordinate. Here the total energy means the sum of the electron energy and ion energy.

1.7. Introduction to Thermoluminescence

1.7.1. Historical Background of Thermoluminescence phenomenon:

Historically, thermoluminescence (TL), or more appropriately Thermally Stimulated Luminescence (TSL) may be said to have its beginning in 1663 with Robert Boyle who reported to the Royal Society of London (Boyle, 1664) his observation "Eleventhely, I also brought it some kind of glimmering light by taking it (natural diamond) into bed with me and holding it a good while upon a warm part of my naked body." Not much later Elsholtz (1676) observed similar effect in fluorspar (Encylopedia Britannica). However, experimental and radiation induced TSL under its modern name in a wide variety of natural and synthetic materials was probably first reported by Wiedemann and Schmidt (1895) of Germany in an article entitled "On Luminescence" in a then widely read and highly regarded scientific journal. Wiedemann and Schmidt were probably the first to report the TSL of at least two of the modern materials widely used viz. fluorite and CaF_2:Mn. They also spoke of the possibilities of TSL of glasses and borates. Then in 1904 Marie Curie's dissertation was perhaps the first dissertation on TSL, viz. in rocks, minerals and synthetic crystals has been studied by an ever increasing number of workers. But the real boost can be said to have been given in the late 1940s and early 1950s by the pioneering work of Farrington Daniels and his group at the Universities of Wisconsin (USA).

Farrington Daniels and his group first suggested the use of TSL as a technique in radiation dosimetry (Daniels et al., 1953) through studies on LiF as a TSL material. Lithium fluoride was used to measure radiation dose after a bomb test. Soon the idea of using TSL in dosimetry caught on and many groups started working in the field of thermoluminescent dosimetry (TLD). It became evident that in LiF the desirable properties of the material were the result of the interplay between the complex defects present within the material resulting from the presence of the Mg and Ti. This realization emerged from the work of Cameron and colleagues (Cameron et al., 1963, 1968) and this work led eventually to the patenting of TLD-100 by the Harshaw Chemical Company in 1963. In last few decades there has been tremendous research in this field. Thermoluminescence (TL), as an experiment technique, finds application in diverse scientific disciplines, such as radiation dosimetry, archaeology, geology, medicine, solid state physics, biology and organic chemistry. In the last four decades, many new and dosimetrically useful TLD materials were reported. $Li_2BV_4O_7$:Mn (Schulman et al., 1965), CaF_2:Dy (Binder et al.,1968), $CaSO_4$:Dy and $CaSO_4$:Tm (Yamashita et al., 1968,1971), BeO (Tochilin et al., 1969), Al_2O_3:Mg,Y(Janas et al., 1976) and Al_2O_3:Si,Ti (Mehta et al., 1976), CaF_2:Tm (Lucas et al., 1977), LiF:Mg, Cu, P (Nakajima et al., 1978), $Li_2B_4O_7$:Cu (Takenaga et al., 1980) and MgB_4O_7:Dy or Tm (Prokic, 1980), Al_2O_3:C (Akselrod et al., 1990a, 1990b). Subsequently, a large number of laboratories have also been successful in preparing LiF:Mg,Cu,P, BeO, $CaSO_4$:Dy or Tm and some other TLD phosphors.

With the progress in crystal growing techniques, artificially doped samples were grown in the laboratory. Wiedemann developed the first artificially activated $CaSO_4$:Mn phosphor. Extensive work of Cameron et al. (1963, 1968) of LiF powder supplied by Harshaw Chemical Co., U.S.A., has led to development of now well-known dosimetric phosphor LiF:Mg, Ti. This phosphor is being manufactured by Harshaw Chemical Co. under the trade names of TLD-100, TLD-600 and TLD-700. These phosphors have been extensively studied for its thermoluminescent properties relevant to radiation dosimetry. The presence of rare-earth ions in the natural fluorite (CaF_2) as efficient emission centers, led to the development and study of rare earth doped phosphors such as CaF_2:Dy, CaF_2:Tm, $CaSO_4$:Dy, $CaSO_4$:Tm and Mg_2SiO_4:Tb. These phosphors have proved to be more sensitive in comparison to LiF:Mg,Ti phosphor. Many of these phosphors have now become commercially available.

In the case of Phosphor development, it started with the development of $CaSO_4$:Mn, which was used, by Wiedemann and Schmidt (1895) in late nineteenth century, for TSL studies and for radiation detection. In early 1950s Farrington Daniels successfully used LiF for radiation dosimetry during atomic bomb testing. The late nineteenth-early twentieth century was dominated by studies on natural minerals. Natural CaF_2 was used by Marie Curie to detect radiations from radium source. X-ray induced TSL was examined by many workers like Lind and Bardwell (1923). The study of the TSL properties of synthetic materials also gained momentum at this time with $CaSO_4$:Mn phosphor being the particular interest. The use of TSL in UV dosimetry using $CaSO_4$:Mn was actively being examined during this period. Even though, TSL studies on $CaSO_4$:Mn were carried out by Wiedemann and Schmidt (1895), its use as a possible TSL dosimeter was demonstrated by Watanabe in 1951. Search for new materials for specific applications started in early 1950s. Outcome of efforts of Daniels et al. (1950, 1953) in this direction was development of promising material LiF. But the study of complex behavior of this material by Cameron and colleagues (1963,1968) led to the patenting of TLD-100 by the Harshaw Chemical Company in 1963. Despaired with unpredictable properties of LiF, Daniels group turned their attention to the next material, Al_2O_3 (Rieke and Daniels, 1957). Al_2O_3 in the form of sapphire, was high grade optical material, but due to lack of sensitivity, lost its credibility. In 1957, two new materials BeO (Moore, 1957) and CaF_2:Mn (Ginther and Kirk, 1957) made their appearance. CaF_2:Mn had major impact in this field due to its excellent sensitivity and simple glow curve structure. It is the first TLD material in this field and still never went back seat any time (McKeever et al., 1995).

In 1960s several new materials like $CaSO_4$:Sm (Kraysnaya et al., 1961), $Li_2B_4O_7$:Mn (Schulman, et al., 1965), CaF_2:Dy (Binder, et al., 1968), $CaSO_4$:Tm and $CaSO_4$:Dy (Yamashita, et al., 1968) entered into the field. Natural CaF_2 (Kozlowitz et al., 1965) made its appearance again along with tissue equivalent and promising material, LiF:Mg, Ti (Cameron et al., 1963 and 1968). Thomas and Houstan's (1964) MgO was another addition to this family.

In 1970s, Al_2O_3 reappeared in new form as Al_2O_3:Mg, Y (Janas et al., 1976) and Al_2O_3:Si,Ti (Mehta et al., 1976). Another form of CaF_2, namely, CaF_2:Tm (Lucas et al., 1977) was reported during this period. Two new materials, namely, $Li_2B_4O_7$:Cu (Takenaga et al.., 1980) and MgB_4O_7:Dy or Tm (Prokic, 1980), were reported during 6th International Conference on Luminescence at Toulouse, France, MfB_4O_7:Mn (Prokic, 1993) was latter addition to this group.

Another remarkable newcomer was LiF:Mg,Cu,P (Nakajima et al., 1978), but remained unnoticed until the group at Solid Dosimetric and Detector Laboratory in Beijing reported the manufacture of a LiF:Mg,Cu, P TLD material (Wang et al.., 1986), known as GR-200, in 1986. This is reported as an ultra sensitive material with sensitivity as high as 50 times that of TLD-100. This is followed by even more sensitive material, Al_2O_3:C (Akselrod et al., 1990). These two materials are now dominating the field of TLD material research. At the 12th International Conference on Solid State Dosimetry, it was reported (Nam et al., 1999) that LiF:Mg,Cu,Na,Si has a similar glow curve shape to that of LiF:Mg,Cu,P but the relative TSL sensitivity is about 2 times that of LiF:Mg,Cu,P.

Around 1940s clear picture of general processes involved in TSL had been developed. Randall and Wilkins (1945a, 1945b) and Garlick and Gibson (1948) gave a theoretical basis to this phenomenon. The TSL was used for the first time by Daniels (1950) to make quantitative measurements of radiation exposure. Their main interest was in TSL of geological specimen and in TSL properties of alkali halides. Since that time TSL dosimetry has found wide application particularly in radiation dosimetry. Daniels et al.(1953) suggested some more possible applications of TSL in archeological and geological dating, including radiation dosimetry. A lot of progress has taken place during 1960s and 1970s in this field and now TSL phenomenon is used in many fields with improved sophisticated techniques.

Thermally Stimulated Luminescence (TSL) is the emission of light (in excess of thermal radiation) from an insulator (or semiconductor) when the TSL material is heated (stimulation), following an initial irradiation (excitation) of the TSL material. This latter component (i.e. radiation absorption) is an essential feature of TSL phenomenon. The light emitted from the TSL material is proportional to the amount of radiation absorbed by the TSL material and hence this process can be used to estimate the dose (energy absorbed per unit mass of the material) absorbed in the material. The TSL phenomenon has a very high sensitivity of detecting the presence of defect centers which are responsible for the TL process. Townsend and Kelly (1993) estimated that the technique is capable of detecting as few as 10^9 defects levels in the material.

This high sensitivity of the process allows the determination of very low radiation doses. On the other hand this high sensitivity hampers the investigation of the relation between the TSL and the defects involved the TSL process. This is because a very small change in the defect concentration responsible for TSL will give rise to an appreciable change in TSL output and this small variation in the defect concentrations is very difficult to detect by other techniques such as Optical Absorption (OA) and Electron Spin Resonance (ESR). TSL is one of a family of processes collectively known as thermally stimulated phenomenon. Other members of the family are thermally stimulated conductivity (TSC), thermally stimulated capacitance (TSCap), thermally stimulated polarization (TSPC) and depolarization currents (TSDC), including ionic thermocurrents (ITC), deep level transient spectroscopy (DLTS), thermo gravimetry (TG), and several more (Chen and Kirsh, 1981). Each of these phenomenons may be described by two fundamental stages: Stage I, the perturbation of the system from equilibrium into a metastable state; and stage II, the thermally stimulated relaxation of the system back to equilibrium. In each of the above techniques one monitors the nonisothermal change of a particular property of the material (e.g., luminescence, conductivity, capacitance, etc.) as the system returns to equilibrium during stage II.

In the case of TSL, stage I necessitates the absorption of energy, normally from ionizing radiation, in order to perturb the material into a nonequilibrium state. Energy storage occurs through the processes of electron-hole pair production, exciton creation, and/or direct displacement damage, followed by charge localization (trapping) at defects within the host lattice of the irradiation material.

During stage II, the stored energy is released as the temperature of the sample is increases, and a fraction of the released energy is in the form of luminescence. The luminescence originates from electron-hole recombination or vacancy-interstitial recombination. In either case, electrons undergo de-excitation from metastable excited states to the ground state, thereby restoring equilibrium. The simplest manner in which this can be achieved is via electron – hole recombination of thermally freed charges (although the discussion could just as well proceed on the basis that it is holes that are thermally liberated). The process is initiated when phonon coupling between the trapped electron and the lattice results in the absorption of an amount of thermal energy by the electron. The probability per second that the amount of energy is enough to release the trapped electron from its localized state (i.e. to overcome the energy barrier E and undergo a transition into the conduction band is given by

$$p = s\exp\left(\frac{-E}{kT}\right)$$

where, 's' is frequency factor and is related to the local lattice vibration frequency and the entropy change associated with the charge release. Thus, once the temperature is high enough, the electron will be released into conduction band and will then be free either to get retrapped (either in same or different localized states) or to recombine with trapped holes. The recombination process results in the emission of phonons (nonradiative recombination) or photons (radiative recombination). It is the latter that are monitored when recording the emission. Thus, we have the thermally stimulated return of the system from its metastable state to equilibrium, with a portion of the excess energy being liberated as light (McKeever, 1997).

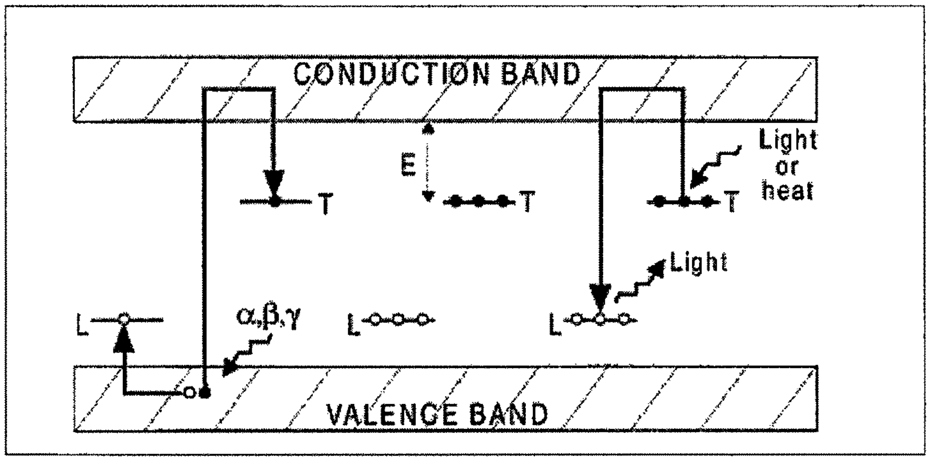
1.8. Theory of Thermally Stimulated Luminescence

1.8.1. Basic Phenomenon

The phenomenon underlying the TSL process is usually explained on the basis of band structure of electronic transition in an insulating material exhibiting TSL. The figure 1.1

shows the simplest process one can visualize that can occur in the phosphor during and after exposure of ionizing radiation.

TL is usually observed by heating a sample at a constant rate to some temperature (e.g. 500°C) and recording the luminescence emitted as function of temperature. The TL signal is characterised by a so-called "glow curve", with distinct peaks occurring at different temperatures, which relate to the electron traps present in the sample. Defects in the lattice structure are responsible for these traps. A typical defect may be created by the dislocation of a negative ion, providing a negative ion vacancy that acts as an electron trap. Once trapped, an electron will eventually be evicted by thermal vibrations of the lattice. As the temperature is raised these vibrations get stronger, and the probability of eviction increases so rapidly that within a narrow temperature range trapped electrons are quickly liberated. Some electrons then give rise to radiative recombinations with trapped "holes", resulting in emission of light (TL). Although a TL glow curve may look like a smooth continuum, it is composed of a number of overlapping peaks derived from the thermal release of electrons from traps of different stabilities.



(i) Ionisation **(ii) Storage** **(iii) Eviction**

Where, T = Electron Trap, L = Luminescence Center

Figure 1.11. Energy-level representation of TL process

(i) *Ionisation due to exposure to nuclear radiation with trapping of electrons and holes at defects T and L, respectively.*

(ii) *Storage of radiation energy during time; if leakage is negligible the lifetime of the electrons in the traps needs to be much longer than the storage time of the* *sample. This lifetime is dependent on the energy depth E of the trap below the conduction band.*

(iii) *By heating the sample, electrons are evicted from the electron traps and some of these reach luminescence centres (L); if so, light (i.e. TL) is emitted as a result of the process of recombining into these centres.*

1.8.2. Dynamics of Detrapping (Trap Emptying Process)

Release of the charge carrier, i.e., the trapped electron or the hole from its trapped position is the most important step in the emission of TL. The release of the charge carrier can be achieved in two ways:

- Optical stimulation
- Thermal stimulation

In optical stimulation, an optical photon of energy greater than the binding energy of the charge carrier can knock out it from its trap by direct hit. In contrast to this the thermal stimulation process consists of multiple hits. The energy required for the release of the charge carrier is called the thermal activation energy. It is observed that thermal activation energy is always smaller than the optical activation energy. This arises due to the change in the configuration co-ordinates of the trap in the excited state than in the normal state.

An electron trapped at a depth of 1 eV get free at a temperature barely 100-200 °C, this is because the average thermal energy available at 200 °C is= 3/2 (273+200) = 0.04 eV only, which is much smaller compared to 1eV (the activation energy). The Maxwell-Boaltzmann distribution for a system in equilibrium at temperature T tells that the fraction of the particles having thermal energy of 1eV above the ground level is N/No= e - E/kT. For E=1eV and sample temperature, T=200 °C, this fraction would be about 10^{-13}. It is only this fraction which is capable of escaping from the trap. This however, is an incredibly small fraction to make an impact on the total population of the charge carriers in the traps. Yet the traps get emptied in 'no time' when the sample temperature is raised quickly to the peak temperature of the glow curve.

Two factors are reasonable for this:

The few energetic electrons ($E \geq 1$ eV) make an attempt to escape into the conduction band at an incredibly fast rate. The attempt frequency is as high as 10^{13} second (vibrational frequency) this is called 'frequency factor' or more precisely 'attempt to escape frequency'. How does an electron or a hole make an attempt? –It is by jumping and knocking around randomly. Some knocks may push it backward from the 'mouth' of the trap.

Probability for escaping from the traps is given as

$$P = s \cdot \frac{N}{N_o}$$

$$P = s \cdot e^{\frac{-E}{kT}}$$

Where, s=frequency factor.

If $s=10^{13}$ and $N/N0=10^{-13}$, then P=1 per second.

This means, 100 % probability for escaping from the traps. Apparently only an insignificant fraction i.e., 10^{-13}, is able to escape at any point of time when the glow peak is being emitted.

The second factor which helps to empty the traps quickly is the rapidness with which thermal equilibrium (Maxwell-Boltzmann distribution) is re-established after the charge carriers with $E \geq 1$eV (i.e. 10^{-13} fraction) have escaped. To visualize the rapines with which equilibrium is re-established, we need to remember that the particles in equilibrium at room temperature have a velocity of 2000 ms^{-1}, which is approximately equivalent to 2×10^{13} lattice distances. This means that in 1 second 2×10^{13} knocks are exchanged by a single particle. Due to such a high frequency of collisions, the equilibrium is re-established quickly. Thus once again we have particles with energy $E \geq 1$eV. The process of re-establishing equilibrium and escaping (de-trapping) thus sustains (the phonon relaxation time is 10^{-13} second).

1.9. Mathematical Description

1.9.1. First Order Kinetics

The most simplified mathematical model which describes the above process was first given by Randall and Wilkins (1945 a,b).

Consider a material containing defects which give rise to a single electron trap level, having trap depth or activation energy E containing n electrons at time r and at temperature T (in kelvin). The energy distribution of electrons within the trap will be described by Boltzmann distribution, and hence the probability p of release of an electron from the trap is given by the Arrhenius equation,

$$p = s\exp\left(\frac{-E}{kT}\right) \text{-----------------}(1)$$

Where, k is Boltzmann's constant and s is a frequency factor or attempt to escape factor having value in the order of the lattice vibration frequency, namely 10^{12}-$10^{14}s^{-1}$. The rate of release of electrons from the trap is

$$-\left(\frac{dn}{dt}\right) = ns\exp\left(\frac{-E}{kT}\right) \text{-----------------}(2)$$

Randall and Wilkins assumed that all electrons released from traps undergo TSL transitions, i.e., there is no retrapping. This leads to the concept that the rate of release is proportional to the trapped charge concentration, and thus termed a "first-order" reaction. The intensity of the TSL glow, I(t) depends on the rate of release of electrons from traps and their rate of arrival at luminescence centers:

$$I(t) = -C\left(\frac{dn}{dt}\right) = Cns\exp\left(\frac{-E}{kT}\right) \text{--------------------}(3)$$

where C is a constant related to luminescence efficiency.

$$\beta = \frac{dT}{dt} \text{-----------------------}(4)$$

Equation (2) becomes,

$$\left(\frac{dn}{dT}\right) = -\left(1/\beta\right)ns\exp\left(\frac{-E}{kT}\right) \text{-----------------}(5)$$

On integration, we get

$$\ln\left(\frac{n}{n_0}\right) = -\int\left(\frac{1}{\beta}\right)s\exp\left(\frac{-E}{kT}\right)dT \text{------------------}(6)$$

where n_0 is the number of electrons present in the trap at time t_0 and temperature T_0. Finally, substituting for n in equation (3),

$$I(T) = n_0 s \exp\left\{{-E}/{kT}\right\} \exp\left\{\frac{-s}{\beta}\int_{T_0}^{T} \exp\left(-{E}/{kT}\right)dT\right\} \text{-----------}(7)$$

This is the expression for the glow intensity I from electrons trap at a single trapping level E. It is a Randall and Wilkins expression for first order (monomolecular) kinetics. The plot of I against T is termed as glow curve. The glow curve has a characteristics asymmetric shape being wider on the low temperature side than on the high temperature side. The condition of maximum intensity can be found by differentiating equation (7) with respect to T and equating the derivative to zero (i.e. $(dI/dT)_{T=T_m} = 0$) which yields,

$$\frac{\beta E}{kT_m^2} = s\exp\left(\frac{-E}{kT_m}\right) \text{----------------}(8)$$

where T_m is glow peak temperature.

From equation (1) and (8) it is concluded that greater the value of E and smaller the value of s, the greater is the thermal stability of the trapped electrons and hence the higher is the temperature of the glow peak.

1.9.2. Second Order Kinetics

A modification of this view was presented by Garlick and Gibson (1948), who used this same one-trap, one-recombination center model but who included the concept of significant retrapping of the released charges. This leads to the rate of the reaction being proportional to the square of the trapped charge concenetrtion, and thus, we have a "second-order" reaction. Here we have

$$\frac{dn}{dt} = -n^2 s' \exp\left(\frac{-E}{kT}\right) \text{------------ }(9)$$

where, s` = s/N, and N is the total concentration of available electron traps. This leads to the Garlick-Gibson equation for TSL under second-order kinetics,

$$I(T) = \frac{n_0^2 s' \exp\left[-E/kT\right]}{\left[1 + \frac{n_0 s'}{\beta} \int_{T_0}^{T} \exp\left(\frac{-E}{kT}\right) dT\right]^2} \text{-------------(10)}$$

The main feature of this equations is that the glow is nearly symmetric, with the high temperature half of the curve slightly broader than the low temperature half. This can be understood from the consideration of the fact that in the second order reaction, significant concentrations of released electrons are retrapped before they recombine in this way giving rise to a delay in the TSL and spreading out of the emission over a wider temperature range (Bos, 2001).

1.9.3. General Order Kinetics

The Randall-Wilkins and Garlick-Gibson forms of TSL equation have been derived with the use of specific assumptions concerning the relative values of the retrapping and recombination probabilities. However, when these simplifying assumptions do not hold, the TSL peak will fit neither first- nor the second order kinetics. May and Partridge (1964) gave the following empirical expression for general order TSL kinetics

$$I(t) = -\frac{dn}{dt} = n^b s' \exp\left(\frac{-E}{kT}\right) \text{---------------(11)}$$

Where, s` has the dimension of $m^{3(b-1)}s^{-1}$ and b is defined as the general-order parameter and is not necessarily 1 or 2. Integration of the above equation for $b \neq 1$ yields,

$$I(T) = s'' n_0 \exp\left(\frac{-E}{kT}\right) \times \left[1 + (b-1)\frac{s''}{\beta} \int_{T_0}^{T} \exp\left(\frac{-E}{kT}\right) dT\right]^{-b/(b-1)} \text{--------------(12)}$$

Where, s`` = $s`n_0^{b-1}$ with units $s^{-1}$. The above equation includes the second-order case (b=2) and reduces to equation (7) when b → 1. It should be noted that the dimensions of s` is $m^{3(b-1)}s^{-1}$ which means that the dimension changes with the order of kinetics b. Thus, it is difficult to interpret s` physically.

The theoretical mechanism discussed above is related only to electrons trapped at a single trapping level. In real phosphors many different trapping levels will be present, each one due to a particular lattice defect or complex of defects. Each trapping level will give rise to an associated glow peak maximum, which may or may not be resolved during readout. The area and peak height of each glow peak depends on number of associated electron traps present. This in turn depends on the number of lattice defects and, for real phosphors, on the type and amount of impurity atoms present, as well as on the thermal history and treatment of the material.

1.10. Determination of Thermally Stimulated Luminescence (TSL) parameters

During the process of TSL, part of energy, absorbed by the phosphor crystals, is re-emitted during subsequent heating, in the form of light. The plot of the TSL intensity (light output) as a function of rising temperature (at a constant rate of increase in temperature i.e. β = dT/dt = constant) exhibits one or more peaks and is called a glow curve.

The glow curve provides a useful tool for studying the traps and trapping parameters (such as trap depth E, kinetic order b and frequency factors, etc.). Number of methods based on different models that explain the TSL behavior of different phosphor systems, have been developed (Braunlich, 1968, Chen 1969 a,b)) for determination of trapping parameters utilizing the glow curve technique. All the models are statistical in nature and describe the distribution of electron traps over the level in the forbidden band, which takes place during the warming up of the phosphor. Based on these models different expressions have been derived for calculation of electron or hole trap depths from conduction or valence band respectively, using different experimental methods such as shape of the glow curve, glow peak maxima and change in the maximum peak temperature and different heating rate and isothermal decay method. Hoogenstraten (1958), Nicholas and Woods (1964), Braunlich (1968), Chen and Krish (1981), Shalgaonkar and Narlikar (1972), Nambi (1977), Kivits and Hagebeuk (1977), McKeever (1985), Mahesh et al. (1989) and Azorin and Nito (1990) have made a critical review of all these methods.

The values of trap depths for the same material by different methods are found to be somewhat different and also discrepancies in the results are observed when the same material is used by different workers for the calculation of trapping parameters (Kelly, 1970). These discrepancies are because of different approximations and models used by different workers, different levels of impurities present in the sample and various experimental conditions employed. However, the study of trapping parameters gives definite information regarding the order of kinetics, trap (energy) distribution and frequency factor.

These methods can broadly be divided in the following categories.

1. Empirical method (Urbach's method) (Urbach, 1930)
2. Initial rise method (Garlic and Gibson, 1948)
3. Variable heating rate method (Bohum, 1954, Booth, 1954, Parfianovitvh, 1954, Halperin and Braner, 1960, Chem 1969a)
4. Isothermal decay method (Randall and Wilkins, 1945b, May and Partrigdge, 1964)
5. Peak shape methods (Grossweiner, 1953, Halperin and Braner, 1960, Chen, 1969 a,b)
6. Numerical curve fitting method (Mohan & Chen 1970)

All these methods require reliable temperature control and separation of glow peaks is a necessity in most of the glow curves as these methods mainly use peak resolution technique. However, in complex glow curves it may not be that easy.

The isothermal decay method, for determination of thermal activation energy, is the only method, which is not affected by temperature and emission spectra and allows estimation of the order of kinetics b for general order case. For the first-order kinetics, the TSL will decay exponentially with time and a plot of ln (I/I_0) vs. t will give a straight line of slope $m = s \exp(-E/kT)$. If the decay is monitored at several different temperatures a plot of ln(m) vs. 1/T will give a straight line of slope E/k from which E can be calculated. The intercept will give ln(s). The general order feature of the isothermal decay of TSL can be demonstrated if a plot of $I^{(1-b)/b}$ vs. t yields a straight line. Since the value of b is not known before hand, a straight line will only be obtained when correct value of b is inserted.

The initial rise method is a widely used method for calculating trapping parameters (E & s) and is independent of order of kinetics. However, it is affected by satellite peaks and by thermal quenching (McKeever, 1985).

1.11. Applications

The applications of the phenomenon of TSL to the measurement of dose have progressed a great deal since the initial work by Daniels and Colleagues (1953). Several thermoluminescent phosphors are now used routinely in many dosimetric applications for environmental monitoring, personnel dosimetry and medical applications. For dosimetric applications, it is always desirable to use TLD phosphors in various physical forms, as routine measurements with loose powder are quite cumbersome due to associated weighing of individual powder samples. A large number of dosimetry phosphors are now available in various physical forms such as single crystals, extruded ribbons (chips) in different thickness (0.15 to 0.8mm), microrods, sintered pellets and as thin substrates for beta and charged particle dosimetry.

However, among the large number of thermoluminescent materials investigated and described in the literature (Prokic and Botter-Jensen, 1993), only a few have been found to be attractive for dosimetry purposes, especially for applications in connection with personnel and environmental dosimetry.

1.11.1. TSL Dosimetry

In TSL dosimetry the relationship between the TSL signal and the absorbed dose to be measured must be determined by an appropriate calibration. Thermoluminescent Dosimeters (TLDs) have found increasing application with the progress made in the development of solid thermoluminescent dosimeters and instrumentation for reading them. Many TLD based systems are now commercially available, and are widely used in routine personal dosimetry, environmental monitoring and clinical radiation dosimetry. The extreme sensitivity of TSL for detecting the presence of defects, as few as 10^9 within a specimen is beneficial for detecting low radiation levels which are encountered in personal and environmental monitoring. General characteristics of some commonly used TSL phosphor are shown in Table 1.1

Thermoluminescent Dosimeters (TLDs) are increasingly accepted for radiation dosimetry for the following reasons:

a. The existence of nearly tissue equivalent thermoluminescent materials;

b. Sufficiently high sensitivity and accuracy for both personal and environmental monitoring;
c. Commercial availabitility as small sized solid detectors adaptable for both manual and automatic processing;
d. Suitability for skin and extremity dosimetry;
e. Availability of materials with excellent long-term stability under varying environmental conditions;
f. Ease of processing;
g. Reusability;
h. Linearity of response with dose and dose rate over a large range.

1.11.2. Personnel Dosimetry

The primary objective of personnel dosimetry is the monitoring of radiation dose delivered to personnel during routine occupational exposure. Examples include workers in nuclear industry, hospital medical physicist and radiotherapy technicians, workers in industrial radiography and high intensity gamma irradiators and naval personnel on nuclear powered vessels. By means of such monitoring it is hoped to limit the exposure of such personnel to within prescribed safety limits, which are based on recommendations of the International Commission of Radiological Protection, publication 60 (ICRP 60).
Clearly, a major requirement of any TLD to be used in these applications is that it is tissue equivalent. The dose equivalent range of interest in this field is from 10^{-5} Sv to 10^{-1} Sv, with a required uncertainty in the calculated dose of ± 10-20% (McKeever, 1985).

1.11.3. Environmental Dosimetry

In recent years regulatory authorities in many countries have become more acutely aware of the increasing concern demonstrated by the public with regard to the potential environmental impact of “man-made” radiation exposure, controlled releases of gaseous radionuclides from nuclear power stations during day-to-day operations, low-level waste disposal, nuclear fuels reprocessing, incidents of nuclear power station accidents and activities connected with nuclear power industry have led to widespread public concern about possible detrimental effects to the public.

In many countries TLD systems are in place near nuclear installations for the purpose of monitoring pre-operational levels (background levels) as well as levels above the natural background, which can be linked with the operation of these facilities. Tissue equivalence is not an issue. However, since exposure levels are low (with a dose equivalent of typically, 10^{-2} mSv) long exposure times are required, and thus, long-term stability becomes vitally important, along with extreme sensitivity. Gamma emitters are the main radiation sources of interest (McKeever, 1985).

1.11.4. Clinical Dosimetry

The small size of TLD materials has long been exploited in clinical studies by inserting the TLDs (with proper covering and encapsulations) into appropriate openings on the human body before exposing the patient to ionizing radiations during diagnosis and/or therapy. The exposed TLDs are then retrieved and analyzed. In this way physicians are able to determine actual doses delivered to critical internal organs during these procedures and from such information are able to prescribe necessary additional treatments. Such utility is generally not possible with any other form of radiation dosimeter/detector.

The two areas of use for clinical radiation exposure of humans are diagnosists radiology (e.g. X-ray exposure in mammography, dentistry and general health screening) and radiotherapy. Radiation types include X rays (as low as 10 keV), gamma rays (from ^{137}Cs or ^{60}Co), high energy photon beams up to 25 MV, electrons (up to 40 MeV), heavy charges particle and neutrons. Range of doses varies from 10^{-5} to 10^{-2} Gy in radiology, and up to 20-60 Gy in radiotherapy. For radiation therapy dose estimation accuracy of better than ±3% is aimed for since errors greater than this can adversely affect the outcome of the treatment.

Clearly, the foremost, requirement of a TLD material to be used in this fashion is tissue equivalency. High sensitivity is desirable so that TLD sizes can be kept as small as possible for *in vivo* measurements. Furthermore, since the doses used can be quite in radiotherapy a linear dose response over a wide dose range is an advantageous property (McKeever, 1985).

1.11.5. High Dose

The use of TLDs in monitoring high dose radiation (for example, from 10^2 Gy up to 10^6 Gy) is a further example of one of the mainstream uses of the technology. Such high doses may be found, for example, inside nuclear reactors, or during food sterilization and materials testing. The use of conventional TLDs in these dose regimes can be somewhat limited, however, due to the onset of sublinearity (saturation) of the TLD response. Some high temperature peaks in some TLD material (e.g. CaSO4:Dy and LiF:Mg,Ti) have been used for these purposes since these appear to saturate at higher dose levels (McKeever, 1985).

1.11.6. Retrospective Dosimetry

Worldwide, interest is growing in the development of new and improved methods for retrospectively assessing the radiation dose in accidentally contaminated areas. For a number of years TSL techniques have been used with some success in this application. Examples include Chernobyl (Byelorussia and Ukraine) and the Techa River (Russia), along with similar efforts at Hiroshima and Nagasaki (Japan) and the Nevada bomb test (United States). The thrust has been to use commonly available materials, located at the actual sites. Example TSL materials that are proving to be useful in this context are pottery, the porcelain, and other ceramic objects. From these materials quartz and feldspar can extract, and the absorbed dose to these components is determined by TSL dosimetry techniques (McKeever, 1997).

1.11.7. Archeological Dating

The accumulated dose absorbed by ceramic artifacts over their archeological or geological lifetime can be appreciable, and this dose lends itself to determination of its age using TSL. The materials of interest are ceramics containing luminescent materials – particularly quartz and feldspar that, when heated after irradiation exposure, emit TSL proportional to the time of their exposure. The radiation originates from cosmic rays and from gamma, beta and alpha irradiation from the local surroundings (due to traces of uranium, thorium and potassium). The “natural” signal is thus related to the age of the specimen by

Age = Natural TSL/ (TSL per unit dose) x (natural dose rate)

Thus, age assessment consists of measurement of the natural TSL, calibrating the TSL signal from the material to determine the TSL per unit dose, and measurement of the natural dose rate in the location of the find (Aitken, 1974). Strictly, the "age" being determined is the time since the TSL signal was last reset to zero. Thus, a "zeroing" event – such as high temperature heating (e.g. in the manufacture of pottery) or optical bleaching (e.g., during the deposition of sediments) – must have occurred in order for the method to be applicable. Otherwise, a TSL signal related to the geological age of the component mineral will be determined instead (McKeever, 1985).

1.11.8. Other Applications

Age determination and radiation dosimetry are the two most extensive applications of TSL. It is also used in solid state physics as a tool for detecting the presence of defects and for establishing such parameters as the trap depth and capture cross sections, along with information regarding the dynamics of the various charge recombination kinetics (McKeever, 1997).

The TSL has also found use in both terrestrial and extraterrestrial geology for mineral identification and for determining the classification and the irradiation and thermal histories of meteorites, source identification for various minerals, radioactive ore, and oil and gas well prospecting (McKeever, 1985).

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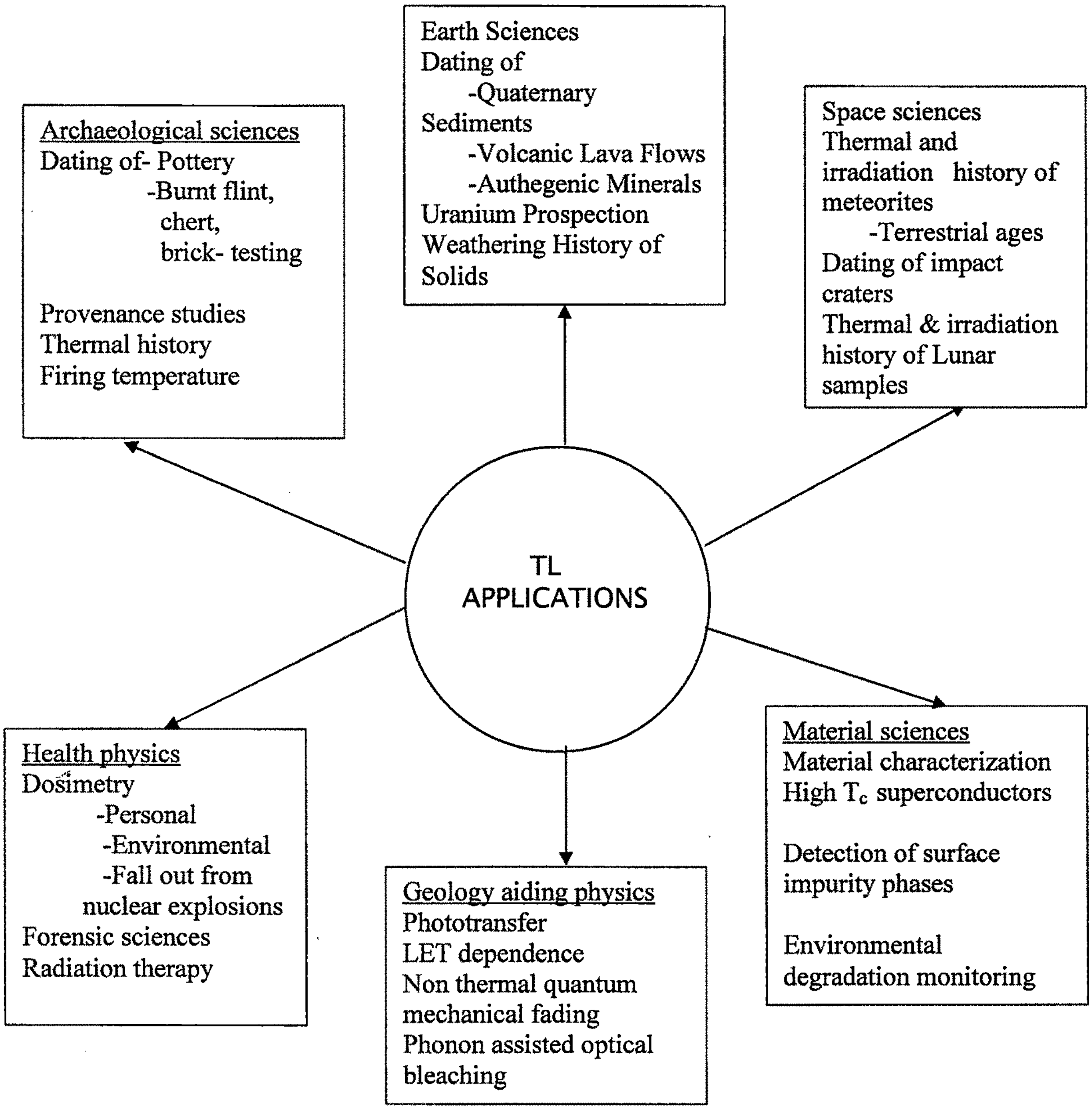

Figure 1.12. Schematic representation of Applications of TL

1.12. Phosphor Research: Past and Present

Research and Technology in phosphors require a unique combination of interdisciplinary methods and techniques. Synthesis and preparation of inorganic phosphors are based on physical and inorganic chemistry. Luminescence mechanisms are interpreted and elucidated on the basis of solid-state physics. The research and development of major applications of phosphors belong to the field of illuminating engineering, electronics and image engineering. Research on phosphors has a long history. A Prototype phosphor the ZnS-type phosphor for TV tube was first prepared by Theodore Sidot a young French chemist in 1886. This marked the beginning of scientific research and synthesis of phosphors.

In early 20th century Leonard and co-workers in Germany performed active and extensive research on the phosphors. They prepared various kinds of phosphors based on alkaline earth chalcogenides and investigated their luminescence properties. Early lamp phosphors were natural fluorescing minerals, e.g. Willemite, Mn-activated Zinc orthosilicate, that were grinded to a powder and empirically blended together so as to obtain an approximately white field from fluorescent lamp. P.W. Pohl and co-workers in Germany investigated Tl^+ activated alkali halide phosphors in details in the late 1920s and 1930s. A major turning point follows the development in 1940s with synthesis of Sb-Mn co-activated halophosphate phosphors. In a single material blue emission from the Sb^{3+} activator and the orange emission from Mn^{2+} co-activator can be adjusted such that they can produce white field corresponding to wide range of color temperature.

Homboltz and co-workers at Radio corporation of America (RCA) also investigated many phosphor for application in TV tubes. Their achievements are compiled in Leverenz's book. Data on the emission spectra in the book remains useful even today. After World War II, the advances in the optical spectroscopy of solids, especially those of transition metal ions help to evolve research on phosphor and solid state luminescence. In 1960 efficient rare earth activated phosphors were developed for use in color TV (Tb^{3+}- green, Eu^{3+} -red and Dy^{3+} -yellow). In 1970 tricolor lamp was introduced. Blue emission from Eu^{2+}, red emission from Eu^{3+} and green emission from Ce^{3+} - Tb^{3+} pair was used in tricolor lamp. At present a combination of halophosphate and tri-band phosphor blend is used in many lamps as a compromise between performance, phosphor cost and the lamp making cost. In recent years the Plasma Display Panels (PDP) are replacing the conventional Color televisions. In phosphor area today top priority is the replacement of the high performance, but very expensive rare earth activated phosphors with cheaper materials. This essentially means replacing the rare earth ions with transition metal ions or post transition ions. Nowadays phosphors are used in various fields. The applications of phosphors can be classified as follows. Recently Dr. Murthy enlists the Phosphor available globally.

1.12.1. Fluorescent Lamp Phosphors

Luminescence, the emission of light by a material after it has been exposed to ultraviolet-infrared radiation, electron bombardment, X-rays, or some other method of excitation, has fascinated people since ancient times. Even as late as the early 1900s, Thomas Edison and E. L. Nichols concluded that ''unless someone discovers a means of making luminescent bodies that are vastly brighter than the best known now, luminescence may be excluded altogether as a factor in artificial lighting.'' However, in the mid-1930s a small group of innovative engineers at the General Electric Company ~GE! coated linear incandescent lamp tubes with a ground-up mineral phosphor, willemite, evacuted the tubes, dosed them with a small amount of mercury, filled them with a few Torr of argon, and sealed the ends with electrodes. In 1933 GE introduced the first commercial mercury fluorescent lamps. Today fluorescent lamps use synthetically made phosphors; due to their high efficiency, fluorescent lamps produce more light by far than all other lamp types.

In the fluorescent lamp, phosphor materials convert UV radiation into visible radiation. Lamp phosphors are mostly white in colour and they should not absorb the visible radiation. Fluorescent lamp is made of glass tube sealed with two ends in which noble gas and Hg vapor are present in 400 and 0.8 Pa pressure, respectively. About 11.5 mg of Hg is used in fluorescent lamp of diameter 30 mm. In the electric discharge Hg atoms are excited to higher energy levels. When they return to ground state it emits 85% 254 nm wavelength, 12% 185 nm and 3% in the visible radiation. Phosphor materials coated inside the tube essentially convert 254 and 185 nm wavelengths into visible radiation. Thickness of phosphor materials coated inside the tube is in the order of 20–40 μm. Since phosphors have direct contact with Hg, potential phosphors such as ZnS can not be used because of reaction between Hg and ZnS. Therefore, oxides are used as the hosts for fluorescent lamps.

Commonly used lamp phosphor in linear fluorescent lamp is Sb^{3+} and Mn^{2+} doped calcium halophosphate, $Ca_5(PO_4)_3(F,Cl):Sb,Mn$. After the discovery of rare-earth activators, compact fluorescent lamps with various sizes and shapes have began to replace linear fluorescent lamp since rare-earth phosphors show better lumen output, higher color rendering index and greater radiation stability over conventional halophosphate phosphor. Also, compact fluorescent lamp comprising rare-earth phosphors is energy efficient.

There are three types of fluorescent lamps available currently and these are halophosphate lamp, tricolour lamp and special deluxe lamp. Among them, tricolour lamp phosphors form a special group. The tricolour lamp phosphors are 60 wt.% $Y_2O_3:Eu^{3+}$, 30 wt.% $CeMgAl_{11}O_{19}:Tb^{3+}$ and 10 wt.% $BaMgAl_{10}O_{17}:Eu^{2+}$, where, Eu^{3+}, Eu^{2+} and Tb^{3+} are activators. In the case of green, non-radiative energy, transfer goes directly from Ce^{3+} to Tb^{3+} and hence, lot of cerium and terbium oxides are required. Therefore, this green phosphor has been replaced by other two green phosphors, viz. $(La,Ce)PO_4:Tb^{3+}$ and $(Ce,Gd)MgB_5O_{10}:Tb^{3+}$. In these newly developed phosphors, Tb^{3+} is activated via energy migration in the Ce^{3+} and Gd^{3+} sublattice, respectively. Thus, concentration of terbium oxide is reduced and hence, cost of the phosphor is improved. Because of improved lumen output and greater radiation stability of tricolour lamp phosphors over conventional lamp phosphor (linear fluorescent), diameter of the fluorescent lamp could be reduced to 10mm from 38 mm. This innovation results in Hi-Tech compact fluorescent lamps with various sizes and shapes.

The thrust on research and development for the formation of new lamp phosphors is still in progress. Scientists and academicians all over the world are trying their best of efforts to improve the output and efficiency of the phosphors. Their research work has been moving at a pace and gaining momentum, research in this field, till today, is becoming more and more active. The motivation of the present study is to find out the alkaline earth based phosphor, activated with different rare earths, which has dual properties of emitting radiations in the visible region when excited with UV light and also find its application in the field of radiation monitoring.

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. 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.

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. 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+}, $CaAl_4O_7$: Tb^{3+}, Ce^{3+} 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. In this direction the Display Materials Laboratory at Applied Physics Department, The M. S. University of Baroda, India is working since more than a decade with a number of publications on various applications of the synthesized phosphor.

1.13. Scope and objectives of the present study

Alkaline earth aluminates are known for its long persistence phosphorescence, 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 devices.

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.

The SrO-Al_2O_3 system is well known for its long persistence phosphorescence. Many researchers have studied its long properties in blue, green and red color. Almost all the phases of SrO-Al_2O_3 system shows long persistence glow ranging from few seconds to several hours. But none of the above studies, as per our knowledge, shows applicability of this system in the accidental TL dosimetry field. Mostly the trapping levels of SrO-Al_2O_3 system consists of shallow traps which are responsible for the long persistence, but for dosimetric purpose one requires traps in the temperature range of 150-250 °C. Formation of the single phase phosphor having dosimetric traps was a challenge in this system.

Various synthesis techniques were followed and after that, the sol-gel reflux technique is chosen to prepare the phosphor. The $Sr_3Al_2O_6$ phase, doped with trivalent rare earths, shows the trap formation in the temperature range of 150-250 °C. The thermoluminescence glow peaks also shows ability to store traps for more than twenty weeks. Moreover, all the rare earths doped in this system stabilize in the trivalent form. The $Sr_3Al_2O_6$:Eu^{3+},Dy^{3+} shows fluorescence emission in the red region as well as the thermoluminescence peak around 190 °C. The synthesis as well as the basic luminescence study of $Sr_3Al_2O_6$:Eu^{3+} and $Sr_3Al_2O_6$:Eu^{3+},Dy^{3+} phosphor is described in the chapter 3 of thesis.

The $Sr_3Al_2O_6$:Tb^{3+} phosphor, prepared in the laboratory, shows excellent photoluminescence emission in the green region which can be used as lamp phosphor. The thermoluminescence glow curve of this phosphor shows peaks around 120, 164 and 350 °C, where the peak around 164 °C shows its applicability for dosimetric peak. The energy transfer phenomenon between Tb^{3+} and Eu^{3+} in the $Sr_3Al_2O_6$ system is observed and its photoluminescence and thermoluminescence changes reported in the chapter-4.

The bluish green emission was observed when the synthesized $Sr_3Al_2O_6$:Tb^{3+} system codoped with Ce^{3+}. The $Sr_3Al_2O_6$:Tb,Ce also shows good TL response. The addition of flux, in the $Sr_3Al_2O_6$:Tb system, also shows emission in the bluish green region.

To observe the lower temperature traps in the $Sr_3Al_2O_6$:Eu^{3+} codoped system the low temperature TL of this phosphor is also studied. All these studies are discussed in detail in the fifth chapter of the thesis.

B.C. Chakoumakos et al. and A. K. Prodjosantoso et al. had performed the refinement and structural studied of $Sr_3Al_2O_6$ phase. Whereas recently the Chai Yuesheng et al. had studied the red long after glow property of $Sr_3Al_2O_6$:Eu^{2+},Dy^{3+}. Citirc acid precursor synthesis technique was also reported by Yebin Xu et al in 2007. Morito Akiyama et al had already studied in detail the mechanoluminscent property of $Sr_3Al_2O_6$:Eu^{2+},Dy^{3+}. Song et al and L. Liu et al. also reported about this phase occurring at low firing temperature but they have mentioned this phase as intermediate phase during the formation of $SrAl_2O_4$ phase.

This work has thrown some light on the luminescence characteristics of $Sr_3Al_2O_6$ doped with trivalent rare earth.

The sixth chapter of the thesis conspires the conclusion of the studies performed on synthesized phosphor materials studied for this thesis. Also the future aspects related to these materials are presented.

----------x----------x----------x----------

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