

## Luminescence Applications Few Basics

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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'. [Phosphor handbook]. The materials exhibiting this phenomenon are known as 'Luminescent materials' or 'Phosphors' meaning 'light bearer' in Greek. The term phosphor was coined in 17<sup>th</sup> century by an Italian alchemist named Vincentinus Casciarolo of Bologna. 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:-

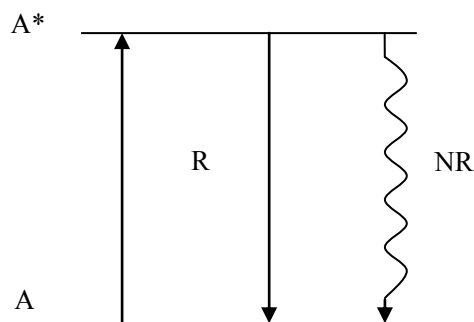
- Photoluminescence, when the excitation is by electromagnetic radiation/photons, is a less specific term which embraces both fluorescence and phosphorescence;
- Cathodoluminescence, when the excitation is by energetic electrons or cathode rays;
- Electroluminescence is light emission triggered by electric influences;
- Radioluminescence, when the excitation is by high-energy X-rays or  $\gamma$  rays;
- Sonoluminescence, when the excitation is by ultrasonic waves;
- Triboluminescence can occur when a material is mechanically treated, e.g. fractured or polished;

- Chemiluminescence is light emitted during chemical reactions;
- Bioluminescence is chemiluminescence from living organisms;
- Thermoluminescence, also known as thermally stimulated luminescence, is the luminescence activated thermally after initial irradiation by other means such as  $\alpha$ ,  $\beta$ ,  $\gamma$ , 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. GENERAL CHARACTERISTICS OF LUMINESCENCE

The process of luminescence can be illustrated in fig. 1.



**Fig. 1: Energy level Scheme of the luminescent ion A. The \* indicates the excited state, R the radiative return and NR the non radiative return to the ground state. (Grabmeir and Blasse Chapter -1).**

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

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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.

## 2. 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.

*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:

### 2.1 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.

### 2.2 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 wave functions 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.

### 2.3 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.

## 3. 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.

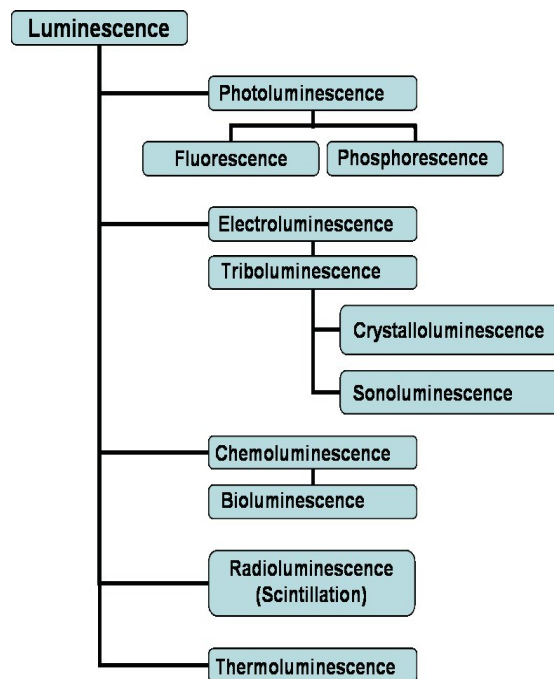
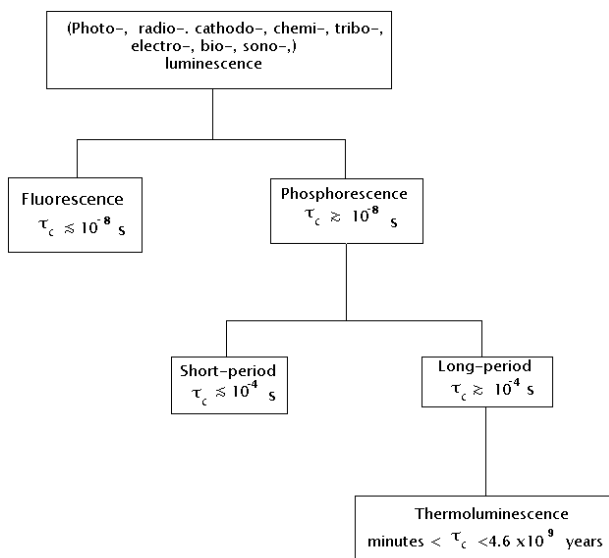


Fig. 2: Types of Luminescence

## 4. PHOSPHOR CONFIGURATION

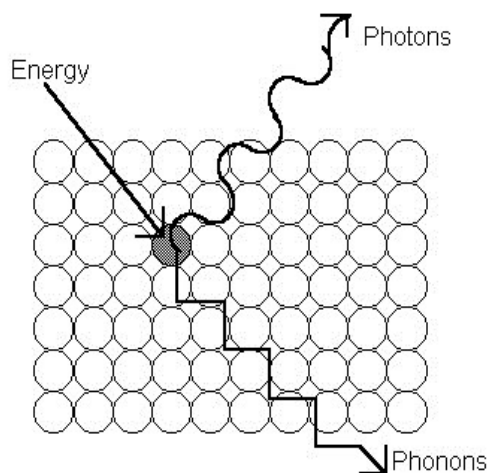
Phosphors, the term coined after the element phosphorous which glowed when in contact with air, basically, consists of an inert imperfect host crystal lattice to which some impurity ions called dopants, are intentionally added.



**Fig. 3: Classification of luminescence on the basis of duration of emission**

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. [Yen]. 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 [2,5]. 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.



**Fig. 4: An illustration of how a phosphor emits light. The dark circle denotes an activator ion which is surrounded 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 nonstoichiometric lattice, the native defects do not have to appear in pairs but some mechanism for preserving charge balance must exist.

### 5. LANTHANIDES / RARE EARTHS

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<sub>2</sub> and 5p<sub>6</sub>

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<sup>3+</sup>), and terbium(III) (Tb<sup>3+</sup>) 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.

The electronic configurations of trivalent rare earth ions in the ground states are shown in the table-1.

As shown in table, Sc<sup>3+</sup> is equivalent to Ar, Y<sup>3+</sup> to Kr and La<sup>3+</sup> to Xe in electronic configuration. The lanthanides from Ce<sup>3+</sup> to Lu<sup>3+</sup> 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<sup>3+</sup>, Y<sup>3+</sup>, La<sup>3+</sup> and Lu<sup>3+</sup>, have no electronic energy levels that can induce excitation and luminescence processes in or near the visible region. In contrast, the ions from Ce<sup>3+</sup> to Yb<sup>3+</sup>, 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 <sup>2S+1</sup>L<sub>J</sub>, 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 <sup>2S+1</sup>L<sub>J</sub> states combined by spin-orbit interaction. For qualitative discussions, however, the principal L state can

**Table 1: Electronic configurations of trivalent rare-earth ions in the ground state**

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

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.

Those transitions are intra configurational 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. Quenching occurs only at higher temperatures or higher activator concentrations. The low absorbance is a drawback for good luminescence but can be bypassed through the antenna effect.

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 is the traditional use for staining glass and ceramics. Nowadays, one can find them 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<sub>4</sub> (yttrium vanadate), giving the red color. Other phosphors also contain rare earths.

The rare earths have also found very place as a thermoluminescent dosimeters. The most famous and globally used thermoluminescent dosimeter, CaSO<sub>4</sub>: Dy,

gives us an idea of the importance of lanthanides in this field. The other examples of rare earth based TLDs are CaSO<sub>4</sub>:Tm, MgB<sub>4</sub>O<sub>7</sub>:Dy, Tm, Mg<sub>2</sub>SiO<sub>4</sub>:Tb, CaF<sub>2</sub>: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.

## 6. 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<sup>2+</sup>) and transition metal ions (Cu<sup>+</sup>) 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<sup>3+</sup> → Tb<sup>3+</sup> and Eu<sup>2+</sup> → Mn<sup>2+</sup>.

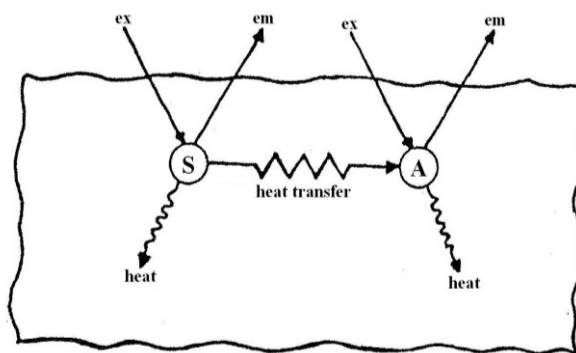
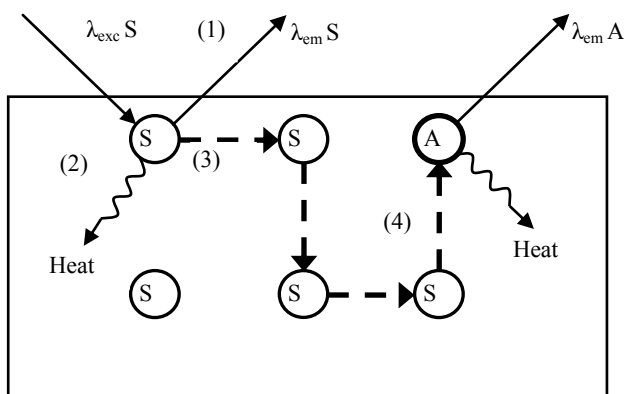


Fig. 6: Schematic representation of luminescence process

**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<sup>3+</sup>, Cl<sup>-</sup>, F<sup>-</sup> 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.

### 7. MODEL FOR A LUMINESCENCE PROCESS TO TAKE PLACE



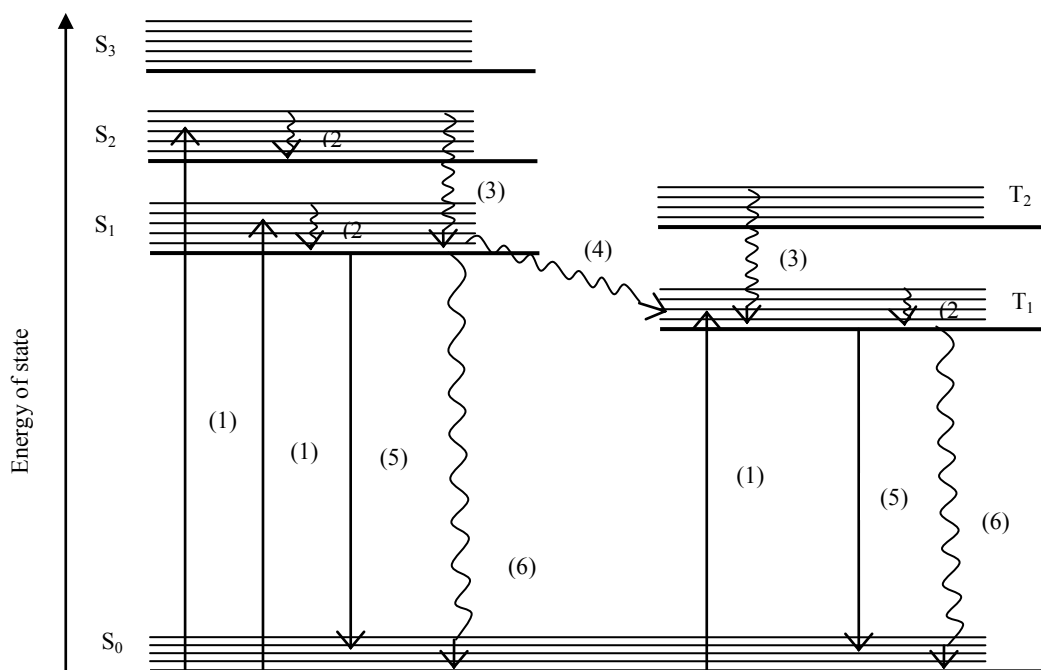
**Fig. 7: Schematic representation of the possible luminescence processes of a crystal system with donor D and acceptor A ions. Following excitation D may: (1) emit radiatively, (2) decay nonradiatively, (3) transfer energy to another D ion, or (4) transfer energy to an A ion. In the last case, energy 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 non radiative 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.

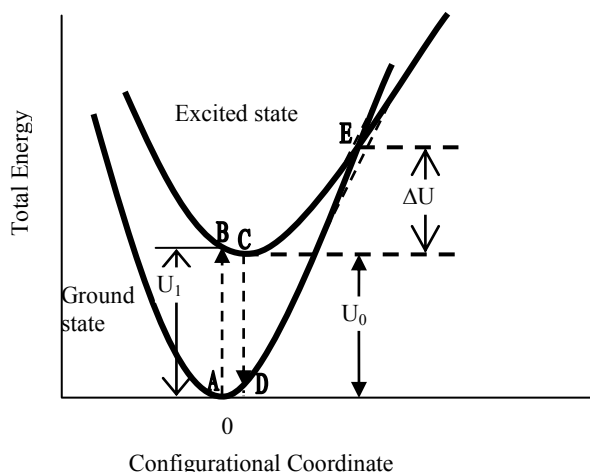
### 8. DECAY PROCESS OF EXCITED STATES

Production and decay processes of excited states are described using an energy state diagram called Jablonski diagram shown in figure-A. 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 from



**Fig. 8: 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) non radiative transition.**

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.



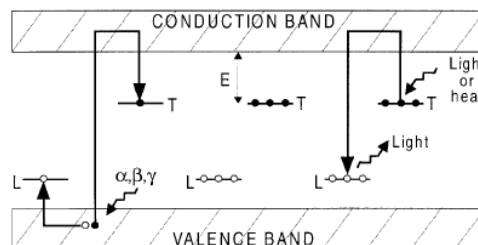
**Fig. 9: Configurational Coordinate diagram (Energy Levels of transitions taking place).**

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 neighbor 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.

### 9. THEORY OF THERMALLY STIMULATED LUMINESCENCE: 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 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

**Fig. 10: 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.

### 10. 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.

### 11. HOW DOES AN ELECTRON TRAPPED AT A DEPTH OF 1 eV GET FREE AT A TEMPERATURE BARELY 100-200 °C?

This question is important, 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-Boltzmann 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  $N/N_0 = e^{-E/kT}$ . For  $E=1\text{eV}$  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.

### 12. HOW DOES THIS HAPPEN?

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

$$P = s \frac{N}{N_0}$$

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

Where,  $s$  = frequency factor.

If  $s=10^{13}$  and  $N/N_0=10^{-13}$ , 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  $E \geq 1\text{eV}$  (i.e.  $10^{-13}$  fraction) have escaped. To visualize the rapidness with which equilibrium is re-established, we need to remember that the particles in equilibrium at room temperature have a velocity of  $2000 \text{ ms}^{-1}$ , which is approximately equivalent to  $2 \times 10^{13}$  lattice distances. This means that in 1 second  $2 \times 10^{13}$

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  $E \geq 1\text{eV}$ . The process of re-establishing equilibrium and escaping (de-trapping) thus sustains (the phonon relaxation time is  $10^{-13}$  second).

### 13. MATHEMATICAL DESCRIPTION

#### 13.1 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  $t$  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,

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

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  $10^{12}$ - $10^{14} \text{ s}^{-1}$ . The rate of release of electrons from the trap is

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

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:

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

where  $C$  is a constant related to luminescence efficiency.

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

Equation (2) becomes,

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

On integration, we get



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

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),

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

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,

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

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.

### 13.2 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 concentration, and thus, we have a “second-order” reaction. Here we have

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

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,

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

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).

### 13.3 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

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

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,

$$I(T) = s^n n_0 \exp\left(\frac{-E}{kT}\right) \times \left[1 + (b-1) \frac{s^n}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{kT}\right)dT\right]^{-b/(b-1)} \quad (12)$$

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  $b \rightarrow 1$ . 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.

### 14. DETERMINATION OF 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.  $\beta = dT/dt =$

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.

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, Parfianovitch, 1954, Halperin and Braner, 1960, Chen 1969a)
4. Isothermal decay method (Randall and Wilkins, 1945b, May and Partridge, 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).

## 15. 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.

## 16. 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 availability 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.

Few important applications of TL dosimetry has been in the field of medical physics for their application in radio diagnosis, radiotherapy and nuclear medicine. In fact, TL dosimetry system has become an integral part of the medical physics departments in most of major radiotherapy centres. However the following are other important Dosimetry applications.

Environmental Dosimetry, Measurement of External Radiation Exposure in High Background Radiation Area (HBRA) in Kerala, India, Environmental Gamma Radiation Monitoring around Nuclear Power Plants, Personnel Monitoring of Radiation Workers, Quality Assurance of Thermoluminescence based Individual Monitoring System for External Radiations, Estimation of absorbed dose and energy in high-energy photon beams, Beta Dosimetry, Neutron Dosimetry, Thermal Neutron Dosimetr, Fast Neutron Dosimetry, High LET Dosimetry: Charged Particle Dosimetry, Ultraviolet (UV) Dosimetry, High Level Gamma-Ray Dosimetry, Retrospective Dosimetry, Dosimetry at Elevated Temperatures, TL and OSL Dating Studies, Optically Stimulated Luminescence, Nanophosphors for Radiation Dosimetry, Radiophotoluminescence (RPL)

## **17. 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) × (natural dose rate)

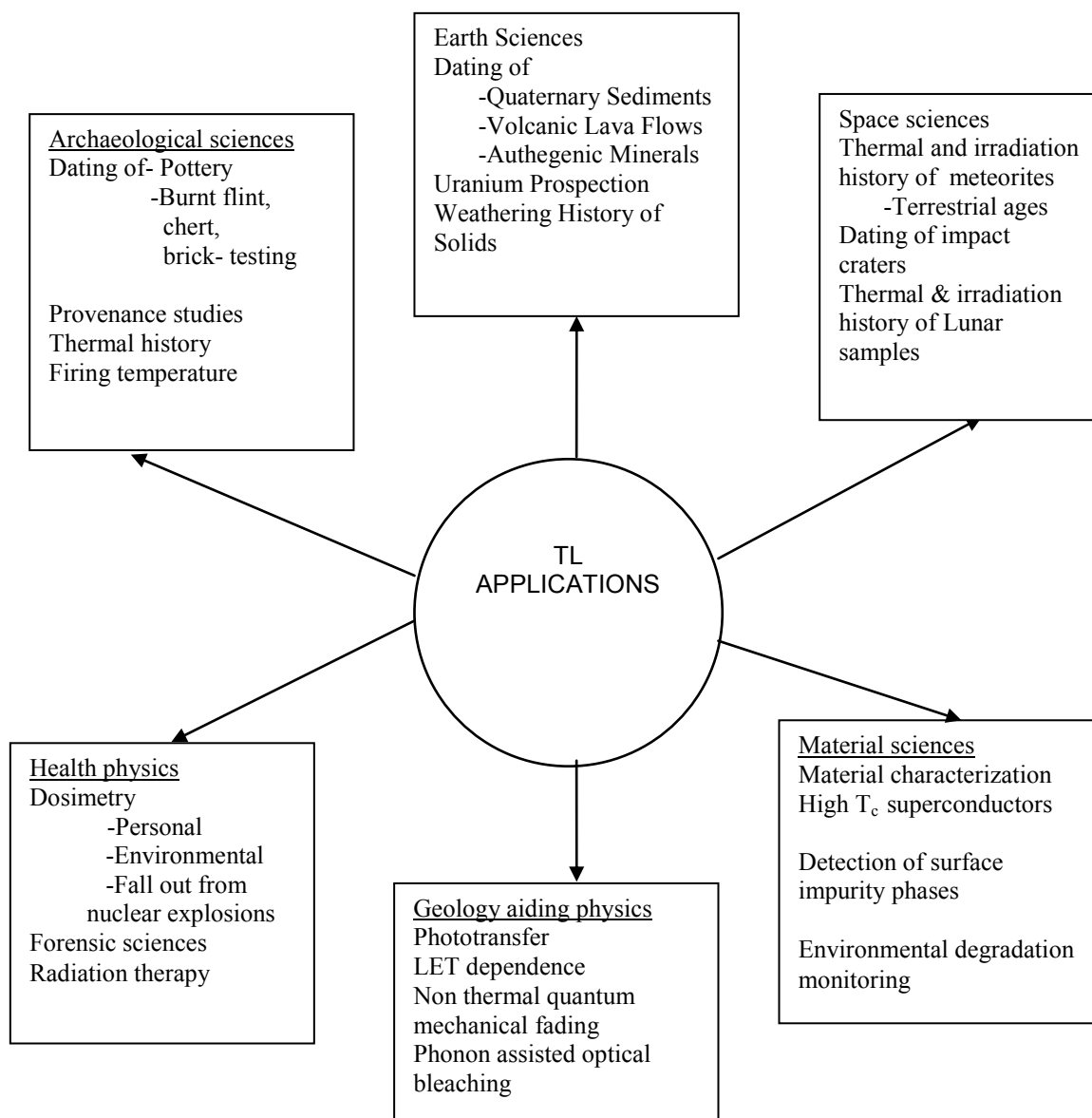
Thus, age assessment consists of measurement of the natural TSL, calibrating the TSL signal from the material to determine the TSL per unit dose, and measurement of the natural dose rate in the location of the find (Aitken, 1974). Strictly, the “age” being determined is the time since the TSL signal 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).

## **18. 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 (Sears, 1993), source identification for various minerals, radioactive ore, and oil and gas well prospecting (McKeever, 1985).

## **19. APPLICATIONS OF THERMOLUMINESCENCE**

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 dosimeter. 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



**Fig. 11: Schematic representation of Applications of TL**

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.

**Light emitting diodes (LED)** are one of the most efficient solid state lighting sources. For lighting applications, white light LEDs are very comparable to sunlight spectrum. Currently, white light LEDs can be achieved by combining blue, green, and red LEDs, or by coating the three colour phosphors to a UV LED or green and red phosphors to a blue LED. Most of the LED phosphors are from the traditional lamp phosphors with absorption at the LED emissions. For example, a blue LED emitting at 460

nm in combination with  $Ce^{3+}$  doped yttrium aluminium garnet ( $YAG:Ce^{3+}$ ), a yellow emitting phosphor, is one of the best white light LED systems. Alkali earth sulfide phosphors are good candidates for LED applications because all of them have strong absorption in the blue region that is suitable to blue LED pumping. Nowadays, alkaline earth sulfide doped with rare earth ions such as  $CaS:Eu^{2+}$  has been reported as a red phosphor source,  $CaS:Ce^{3+}$  as green,  $SrS:Ce^{3+}$  as blue and  $SrS:Eu^{2+}$  as orange phosphors. Sulfide phosphors have been ignored for a long time because they are not chemically stable. When sulphides exposed to moisture they decomposed to carbonates or sulphates that eliminate the original luminescence. Sulfide phosphors may also degrade under high energy UV or electron beam strike. However, sulfide phosphors fit well for LED applications with adhesive seal and blue excitation.

In this direction the Display Materials Laboratory, Applied Physics Department, The M. S. University of Baroda, India is working since more than a five decades headed by Prof. R V Joshi till 1985, T R Joshi till 2000 followed by K V R Murthy since 1993 with a number of publications on various luminescence applications and also synthesized phosphors for Thermoluminescence dosimetry, TL of minerals, Lamp Phosphors and LED phosphors. Our laboratory is helping the students and researchers from all over India for luminescence measurements. More than 100 students from different groups got their work done [Ph.D] from Display Materials Laboratory, Applied Physics Department, Faculty of Technology and Engineering, The M. S. University of Baroda

**Dedication**— This paper and talk is dedicated to our beloved teacher and LSI member Late Prof. R.V Joshi who did his Ph.D in Leeds University, UK in 1962 and started luminescence research at Baroda.

#### ACKNOWLEDGEMENTS

The author is thankful to all his research students A.S.Sai Prasad, M.C.Parmar, Rahul Ghildiyal, K.Suresh and Pallavi Page for excellent collection of literature. Most of the write up of this paper is from my students Ph.D thesis of Mrs. Pallavi Page, 2010, M S University of Baroda. The visiting fellowship at AERIAL CRT, France by late Prof. Louis Rey, Switzerland to work on Low Temperature Thermoluminescence is greatly acknowledged. The funding for the research activities from AICTE, New Delhi and DAE/BRNS is acknowledged. The co-operation extended since 30 years from M. S. University of Baroda to work on luminescence and applications is greatly acknowledged.

As a President Luminescence Society of India, I thank the UNISCO for declaring the year 2015 as **Year of Light**.

#### REFERENCES

- [1] S. Shionoya, W. Yen, Phosphor Handbook, CRC Press, Boca Raton, (1999).
- [2] M.H.V. Werts, Science Progress, 88, (2), (2005), 101–131.
- [3] S.W.S McKeever, Thermoluminescence of solids, Cambridge University, Cambridge, (1985).
- [4] G. Blasse, B.C. Grabmaier, Luminescent Materials, Springer Verlag, Berlin, (1994).
- [5] G. Blasse, Materials Chemistry and Physics, 16, (1987), 201.
- [6] R. Chen, D.J. Lockwood, Journal of The Electrochemical Society, 149, (9), (2002), S69-S78.
- [7] C.R. Ronda, T. Justel, H. Nikol, Journal of Alloys and Compounds, 275–277, (1998), 669–676.
- [8] R.P. Rao, J. Electrochem. Soc., 143, (1), (1996), 189–96.
- [9] K.V.R. Murthy, Y.S. Patel, A.S. Sai Prasad, V. Natarajan, A.G. Page, Radia. Meas., 36, (2003), 483.
- [10] V. Natarajan, K.V.R. Murthy, M.L. Jayanth Kumar, Solid State Communication, 134, (2005), 261-264.
- [11] K.V.R. Murthy, S.P. Pallavi, R. Ghildiyal, M.C. Parmar, Y.S. Patel, V. Ravi Kumar, A.S. Sai Prasad, V. Natarajan, A.G. Page, Radia. Protec. Dosim., 120, (2006), 238.
- [12] K. V. R. Murthy, S. P. Pallavi, R. Ghildiyal, Y. S. Patel, A. S. Sai Prasad, D. Elangovan, Radia. Protec. Dosim., 119, (2006), 350–352.
- [13] P. Page, R. Ghildiyal, K.V.R. Murthy, Materials Research Bulletin, 41, (2006), 1854-1860.
- [14] R. Ghildiyal, P. Page, K.V.R. Murthy, Journal of Luminescence, 124, (2007), 217–220.
- [15] P. Page, R. Ghildiyal, K.V.R. Murthy, Materials Research Bulletin, (2007).E. Danielson, M. Devenney, D. Giaquinta, J.H. Golden, R.C. Haushalter, W. McFarland, D.M. Poojary, C.M. Reaves, W.H. Weinberg, X.D. Wu, Science, 279, (1998), 837.
- [16] From J.D. Graybeal, Molecular Spectroscopy (1988), McGraw-Hill Book Co., New York City.
- [17] Mahesh, K., Weng, P.S. and Furetta, C. Thermoluminescence in Solids and Its Applications. Ashford, Kent: Nuclear Technology Publishing (1989).
- [18] B.C Bhatt, International Journal of Luminescence and Applications, Vol.2(III) (17-43)2012
- [19] Theory of Thermoluminescence and related phenomena, By – Chen & S.W.S. Mc Keever, 1997
- [20] C. Furetta, Hand Book of Thermoluminescence, World Scientific Pub. Co. Pte. Ltd, 2003.
- [21] Proceedings of National Seminar on TL and its Applications, Feb. Ed. K.V.R.Murthy et al., Pub. TaTa McGraw Hill Co., 1992.
- [22] J.R. Cameron, N. Sutharlingam and G.N. Kenney, (1968) “Thermoluminescence Dosimetry”, Univ. of Wisconsin Press, Madison.
- [23] K.V.R. Murthy, Y.S. Patel, A.S. Sai Prasad, V. Natarajan, A.G. Page, Radiat. Measurements 36 (2003) 483.
- [24] S.W.S.McKeever, M. Moscovitch and P.D.Townsend (1995) “Thermoluminescence Dosimetry Materials: Properties and Uses”, Nuclear Technology Publishing. England.
- [25] Murthy,K.V.R and Reddy,J.N. Thermoluminescence basic theory, application and experiment, Feb.2008, Pub. Nucleonix, Hyderabad.
- [26] C.M.Sunta and S. Watanabe, J. Phys. D: Appl. Phys.2, 1271(1976).

- [28] K.S. V. Nambi, V.N. Bapat and A.K. Ganguly, *J.Phys. C: Sol. St. Phys.*7, 4403(1974).
- [29] I.K. Kaul, In: *Thermoluminescence of Geological Materials*, Proc. of a NATO Advanced Research Institute on Applications of Thermoluminescence to Geological Problems, McDougall( Ed.), Academic Press, London and New York (1968).
- [30] A.K.Singhvi and K.S.V.Nambi. *Bull. Radiat. Prot.* Vol. 2 (No. 4), 89 (1979).
- [31] D. Curie, *Luminescence in Crystals*, 3<sup>rd</sup> Ed., John Wiley & Sons Inc, New York (1963).
- [32] M.J. Aitken, D. W. Zimmermann and S.J. Fleming, *Nature* 219, 442(1968)
- [33] *Thermoluminescence of Geological Materials*, Proc. of a NATO Advanced Research Institute on Applications of Thermoluminescence to Geological Problems, McDougall ( Ed.), Academic Press, London and New York(1968).
- [34] P.G. Benny, B.C. Bhatt, *Appl. Radiat. Isot.* 56(2002)891.
- [35] J. K. Srivastava,B.C. Bhatt, S.J. Supe, In: *Proc. National Seminar on Luminescence and its Applications*, Feb. 7-9, 1991, M.S. University of Baroda (1991) 169.
- [36] A.S. Pradhan, R.K. Kher, R.C. Bhatt, *Int. J. Appl. Radiat. Isot.* 29(1978)329.
- [37] A.R. Lakshmanan, S.S. Shinde, R.C. Bhatt, *Phys. Med. Biol.* 23(1978)952.
- [38] S.S. Sanaye, V.K. Shirva, S.S. Shinde,B.C. Bhatt, In: *Proc. Natl. Seminar on Luminescence and its Applications*, NSLA-2001(2001)144-150.
- [39] K.Suresh, K.V.R Murthy, Ch.AtchyuthaRao, N.V.Poornachandrarao, *ISRN Condensed Matter Physics*, volume -1(2) 2011.
- [40] *Synthesis and Characterization of SrS: Eu, Ga PHOSPHOR* Ch. Kishore Babu, K.V.R.Murthy, B.Subba Rao and P.Sujita, *IJSID*, 2012, 2 (3), 386-392