

## Luminescence Phenomena: An Introduction

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**Abstract.** Luminescence phenomena have fascinated mankind since the earliest times. The light from the aurora borealis, glow worms, luminescent wood, rotting fish and meat are all examples of naturally occurring luminescence. E. Newton Harvey's 770 page volume, "A History of Luminescence: From the Earliest Times until 1900" published by American Physical Society (1957) is a classic which documents history of luminescence from antiquity to modern times.

The purpose of this review is to highlight the basic concepts of luminescence phenomenon, which has been achieved by a detailed discussion of mechanism of luminescence based on Configuration Co-ordinate model and Jablonski diagrams. There are several varieties of luminescence, each named according to what the source of energy is, or what the trigger for the luminescence is. The phenomenon of luminescence can be classified into various categories depending on the mode of excitation. More importance is given to Photoluminescence (PL) and Thermoluminescence (TL) due to their wide variety of applications. PL, TL, OSL, and PCTL are discussed briefly along with bioluminescence and other luminescence processes. Applications of fluorescence in a variety of fields, and description of phosphors have also been discussed in some detail in this Chapter.

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## 1. Introduction

Luminescence devices, in a day to day life of urban civilization, have become so essential that life can not be imagined without these; which is due to the usage of various types of lamps, TVs, mobile displays, LED lamps, LED TVs, signals, displays, etc.. Light is a form of electromagnetic energy. To create the 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, Eilhardt Wiedemann, in 1888 [1]. In Latin 'Lumen' means 'light'. The materials exhibiting this phenomenon are known 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 Bologna. Casciarolo found a stone which was probably barite ( $\text{BaSO}_4$ ) and fired it with the intention to convert it into a noble metal. Although he did not obtain any metal, he discovered a material which glows (red light) in the dark after exposure to sunlight. In 1866, Theodore Sidot prepared zinc sulfide ( $\text{ZnS}$ ) which was the prototype of phosphor used in the present day cathode ray tubes. In Germany, between late 19th and early 20th centuries, Philip E.A. Lenard and

colleagues worked on phosphors. They used different rare earth ions in addition to heavy metal ions as luminescent ions in different host materials [2].

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 in the visible region, so that it can fall back to its "ground" state. We can observe the luminescence phenomenon in nature like, in glow-worms, fireflies, and in certain sea bacteria and deep-sea animals. This phenomenon has been used in various fields by different scientists all over the world, for example, Archaeology, Geology, Biomedical Engineering, Chemistry, Physics, and various Industrial Applications for Quality Control, Research and Development [3].

**1.1 Luminescence and Stokes Law.** In the process of luminescence, when radiation is incident on a material some of its energy is absorbed and re-emitted as a light of a longer wavelength (Stokes law). In the process of luminescence, wavelength of light emitted is characteristic of a luminescent substance and not of the incident radiation. The light emitted could be visible light, ultra-violet, or infrared light.

This cold emission, i.e. luminescence, that does not include the emission of blackbody radiation, involves two steps: (1) The excitation of electronic system of a solid material to higher energy state, and (2) subsequent emission of photons or simply light.

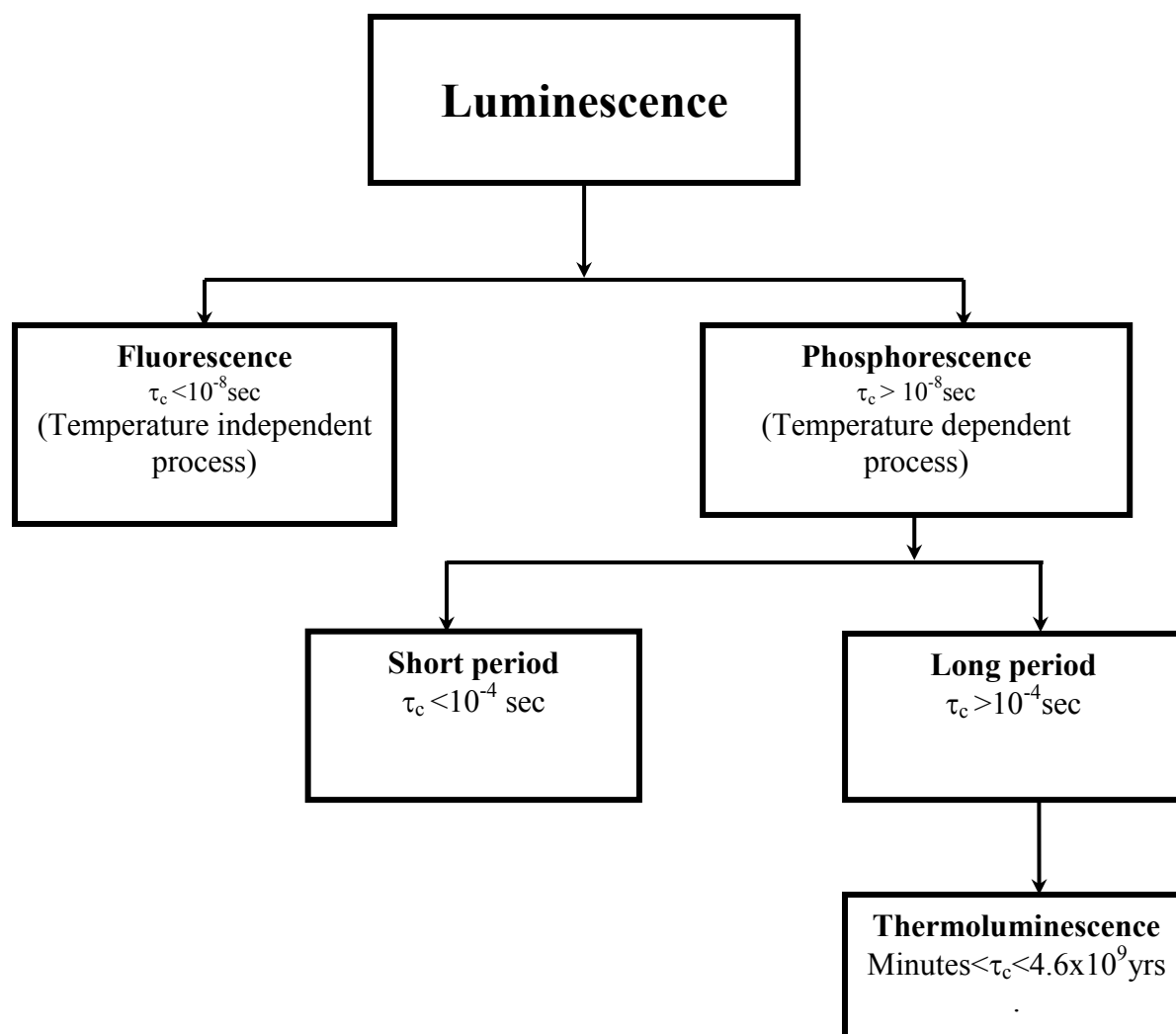
The emission of light takes place at characteristics time ' $\tau_c$ ' after absorption of the radiation, this parameter allows us to sub-classify the process of luminescence into fluorescence and phosphorescence.

Luminescence can be classified on the basis of duration of emission,  $\tau_c$ , in to two parts:

1. Fluorescence where  $\tau_c < 10^{-8}$  s (Temperature independent process), and
2. Phosphorescence where  $\tau_c > 10^{-8}$  s (Temperature dependent process).

The Phosphorescence phenomenon can be further divided into two parts: (a) short period  $\tau_c < 10^{-4}$  s, and (b) long period where  $\tau_c > 10^{-4}$  s is called Thermoluminescence (TL), the emission depends from minutes  $< \tau_c < 4.6 \times 10^9$  years falls under long period category. Each process mentioned above has its own significance and advantage in the field of science and technology [3].

Solids exhibiting property of luminescence are usually referred to as Phosphors. The Fluorescence emission is seen to be spontaneous as ' $\tau_c < 10^{-8}$  s', thus fluorescence emission is seen to be taking place simultaneously with absorption of radiation and stopping immediately as radiation ceases. Phosphorescence on the other hand is characterized by delay between radiation absorption and time ' $t_{\max}$ ' to reach full intensity. Also phosphorescence is seen to continue for some time after the excitation has been removed. If the delay time is much shorter it is more difficult to distinguish between fluorescence and phosphorescence. Hence phosphorescence is subdivided into two main types, namely, short-period ( $\tau_c < 10^{-4}$  s) and long-period ( $\tau_c > 10^{-4}$  s) Phosphorescence. Fluorescence is essentially independent of temperature, whereas decay of phosphorescence exhibits strong temperature dependence. The family tree of luminescence phenomena is shown in Fig. 1.



**Fig. 1** Classification of luminescence on the basis of duration of emission [3]

A large number of substances both organic and inorganic show the property of luminescence, but materials used in various applications of luminescence, involve inorganic solid insulating materials such as alkali and alkaline earth halides, Quartz ( $\text{SiO}_2$ ), Oxides, Phosphates, Borates, and Sulphates, etc..

**1.2 Types of Luminescence.** There are several varieties of luminescence [3, 4], each named according to what the source of energy is, or what the trigger for the luminescence is, for example:

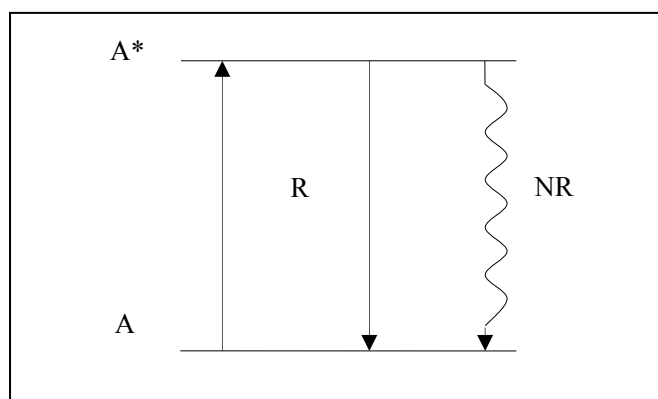
- *Chemiluminescence*: The emission of light by the release of energy from a chemical reaction is called chemiluminescence. The reaction of Luminol ( $\text{C}_8\text{H}_7\text{N}_3\text{O}_2$ ) with an appropriate oxidant results in a striking blue glow.
- *Bioluminescence*: Bioluminescence is also known as “living light” and the most amazing examples of this phenomenon can be found in the deep seas. In the darkness of the oceans where sunlight can not reach, several living organisms produce light as the result of chemical reactions.
- *Triboluminescence*: In this accidentally discovered type of luminescence, light is generated by mechanical energy. Pulling apart, ripping, scratching, crushing, or rubbing can result in the breaking of chemical bonds in the material which triggers light emission like in sugar or silicon crystals. It is also called mechanoluminescence.

- *Cathodoluminescence (CL)*: The light emission is a result of electron beam excitation. Both in the case of cathode ray tube (CRT), televisions or computer screens and a scanning electron microscope (SEM), an electron gun is used for this purpose.
- *Electroluminescence (EL)*: Light is generated in response to an applied electric field on a certain material. The most used electroluminescent devices in daily life are certainly light emitting diodes (LEDs).
- *Photoluminescence (PL)*: Emission of the light is the result of the excitation by electromagnetic radiation/photons. It is a less specific term which embraces both fluorescence and phosphorescence. Photoluminescence has a very broad application area from whitening substances in washing powder to plasma screens for large scale displays. There is a special type of luminescence which has a very slow decay with the emission continuing for minutes or hours. This type of luminescence is called long lasting or persistent luminescence and it is commonly used in road safety and exit marking.
- *Thermoluminescence (TL)*: It is also known as thermally stimulated luminescence (TSL). It 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, imparted to the material from another source of excitation.
- *Radioluminescence (RL)*: It is the phenomenon by which light is produced in a material by bombardment with ionizing radiation such as beta particles, X-rays or gamma rays.
- *Sonoluminescence (SL)*: It is the phenomenon by which light is produced due to the excitation by ultrasonic waves.

Each process mentioned above has its own significance and advantage in the field of science and technology. Emphasis in the present review has been given to study the basic phenomenon of Luminescence and its mechanism, along with 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.

**1.3 General Characteristics of Luminescence.** The process of luminescence can be illustrated in Fig. 2. 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 all the luminescent materials the situation is more complex than depicted in figure 2 below, the exciting radiation is not absorbed by the activator but elsewhere [5, 6].



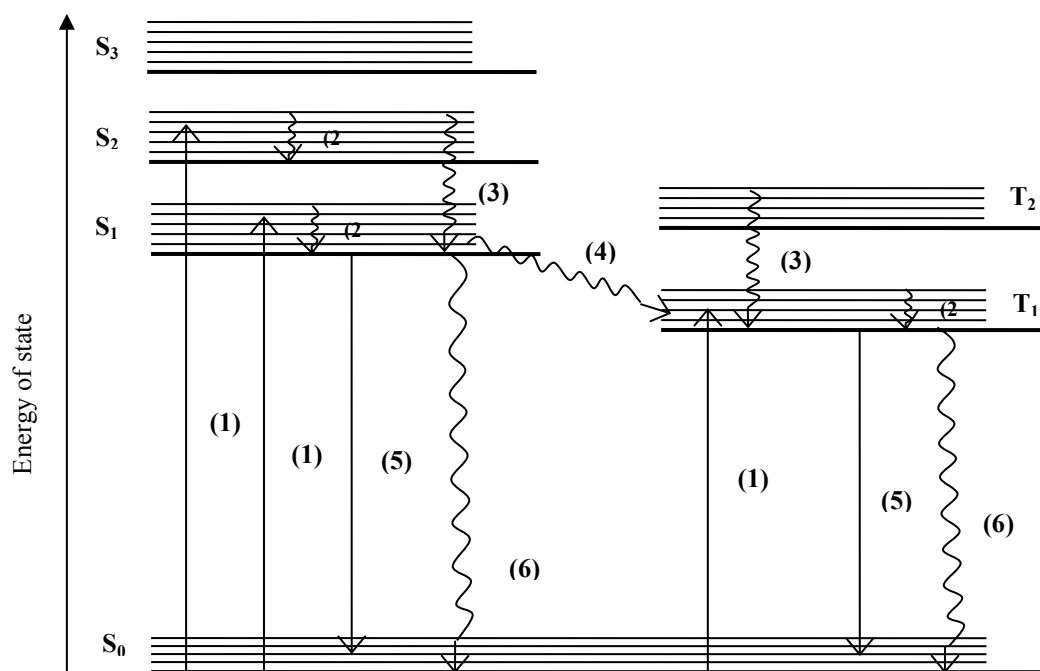
**Fig. 2** Energy level scheme of the luminescent ion A. The \* indicates the excited state, R the radiative return, and NR the non-radiative return to the ground state [6].

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 after glow (decay is more slow with complex kinetics), often dependent 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 pre-requisite to emission.

**1.3.1 Production and Decay Process of Excited States.** Production and decay processes of excited states are described using an energy state diagram called Jablonski diagram. The Jablonski diagram (Fig. 3) describes most of the relaxation mechanisms for excited state molecules. 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 (*highest occupied molecular orbital minus lowest unoccupied molecular orbital*) 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 transition and hence the time scale of the transition is of the order of a few nanoseconds. On the other hand, the time scale of the  $T_1$  to  $S_0$  transition is much longer, ranging from 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 [2, 7, 8].

A detailed description about the Jablonski diagram and various radiative and non-radiative processes is given in the Appendix at the end of this Chapter.



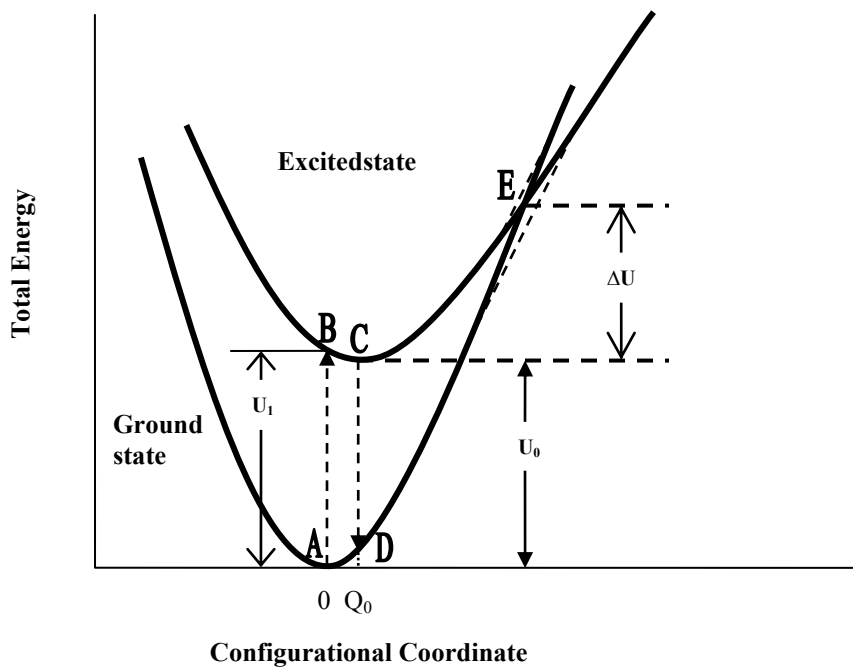
**Fig. 3** The Jablonski diagram, which explains the photophysical processes in molecular systems: (1) photoabsorption; (2) vibrational relaxation; (3) internal conversion; (4) intersystem crossing; (5) radiative transition; and (6) non-radiative transition [adopted from Ref. 8].

**1.3.2 The Configurational Coordinate Model.** Most of the luminescent materials consist of a transparent host crystal and a luminescent ion called an activator. The activator consists of a very small amount of impurity atoms which are deliberately added into the host crystal. Most of the time emission and excitation features of the luminescent material are determined by the activator. Luminescent properties of activators such as  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  are explained by the configurational coordinate model [2, 6, 7].

Although the activator is responsible for the luminescence properties of the phosphor, the surrounding atoms' vibrations also have an effect on optical properties. The configurational coordinate model is used to explain this fact by selecting a luminescent ion and its nearest neighbour sites like an isolated molecule which is called the *luminescent center*. 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. These normal coordinates are called the *configurational coordinates*,  $Q$ . 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 coordinates. Here the total energy means the sum of the electron energy and the ion energy. For simplicity, the vibrational frequencies of the ground and the excited states are often assumed to be the same.

The Configurational co-ordinate model provides very useful information such as:

- Stokes' shift; the energy difference between absorption and emission.
- The temperature dependence and the widths of absorption and emission bands.
- Thermal quenching of luminescence. This model gives only a qualitative explanation of thermal quenching. It is necessary to use a multidimensional model for quantitative explanation.



**Fig. 4** A schematic illustration of a Configurational co-ordinate model: Transitions between ground state and excited state are shown with broken arrows  $A \rightarrow B$  (the absorption of light) and  $C \rightarrow D$  (the emission of light) [adopted from Ref. 5].

The parabolic shape of curves is inherited from the vibration motion of the bonds between the luminescent ion and a nearest-neighbor ion which is assumed to be harmonic and it is expressed by Hooke's law. The larger value of  $Q_0$  induces a larger Stokes' shift and broader absorption and emission bands.

The optical absorption and emission processes are indicated in Fig. 4. It is assumed that these processes occur at 0 K and the nucleus of the luminescent ion does not change its position during the absorption (the Franck Condon principle). The absorption from the lowest vibrational level of the ground state is shown by the arrow  $A \rightarrow B$ . The wave functions of the levels are known and in the lowest vibrational level, the highest probability of finding the system is near the equilibrium position. Nevertheless, for higher vibrational levels the highest probability position is at the edges of the parabolas. The transition from state B to the equilibrium position C is relaxation since in the same state the probability of losing energy by light emission is about  $10^5$  times lower than by the generation of lattice vibrations. Spontaneously, emission occurs ( $C \rightarrow D$ ) and the cycle is completed by the second relaxation from a high vibrational level in the ground state D to the equilibrium position A. In other words, after absorption ( $A \rightarrow B$ ), the luminescent center expands to a new equilibrium position  $Q_0$  at higher energy ( $B \rightarrow C$ ). Then a large part of the energy is lost by emission ( $C \rightarrow D$ ). By the relaxation process ( $D \rightarrow A$ ) to the equilibrium position of the ground state, the luminescent center contracts again.

As shown in Fig. 4, when two parabolas intersect, an electron in the excited state can non-radiatively turn back to the ground state through the intersection E over a thermal barrier. The non-radiative transition probability,  $W_{NR}$ , exponentially depends on the activation energy  $\Delta U$  which is required to excite the electron from the equilibrium position of the excited state to the intersection E of the parabolas:

$$W_{NR} = s. \exp(-\Delta U/kT)$$



Where  $k$  is the Boltzmann constant and  $s$  is the frequency factor.  $\Delta U$  is a thermal energy. At higher temperatures, the non-radiative transition probability is higher due to the exponential dependence on  $T$ . The case, which is explained above, is not the only possible way for the non-radiative transition. The non-radiative decay process may be observed when the equilibrium position of the excited state is placed outside the configurational coordinate curve of the ground state. In this case, the excited state intersects the ground state in relaxing from B to C. Although  $W_{NR}$  is usually governed by thermal relaxation processes, it can be increased by the resonant energy transfer between two luminescent ions.

**1.3.3 The Mechanism of Luminescence.** The production of luminescence from a solid material can be understood from the band theory for solids [3-7]. An isolated atom carries its collection of electrons in its orbitals surrounding the nucleus. These orbitals are analogous to the orbits of the planets around the Sun, although in that case gravity binds the system instead of the electromagnetic force as in an atom. The electrons can only occupy discrete orbits that allow them to orbit without losing energy. These allowed orbits may be determined from the laws of quantum mechanics. Also, owing to the fact that electrons can share their orbitals with at most one other electron of the opposite spin (the Pauli Exclusion Principle), some electrons must occupy orbitals far from the nucleus because the lower energy orbitals closer to the nucleus are already occupied.

Vacancies can be created in occupied orbitals by dislodging the occupied electron with a pulse of radiation such as from a photon, a fast electron or some other process. When this occurs, an electron from an outer level will fall down to reoccupy the inner, lower energy, level. The excess energy is radiated away as a photon. For some transitions, this photon can be within the visible spectrum. Gases in discharge tubes that are bombarded by currents of electricity can display a spectrum characteristic of the transitions between the allowed energy levels in the solitary gas atoms.

In a solid, the situation is more complicated. When individual atoms are joined together to make a solid, the atoms must be pushed relatively close together. When this happens, the outer electron orbitals begin to overlap. Since no more than two electrons can occupy the same level, the energy levels begin to split into sub-levels. If six atoms are joined together to make a small lump of material (crystallite), the orbital of the outermost electron overlaps with the adjacent atoms and splits into six orbitals to accommodate all the electrons. These new orbitals are associated with the entire lump, rather than just a single atom. Millions of atoms are joined together to make a sizable lump of material. The outer orbitals overlap and split into a number of sub-levels, all with slightly differing energies. In practice, the energy levels are so close together, and there are so many of them, we can speak of the orbital now consisting of an energy band. On a small scale, the solid consists of a crystal with all atoms occupying lattice sites. Some normal solids, of interest here, consist of large assemblages of microscopic crystals. The luminescent properties of the solids depend on the properties of the crystal structure.

The formation of energy bands occurs regardless of whether the energy levels are occupied by electrons or not. Therefore, in a typical material, the outermost electrons occupy a band called the valence band, above which is the next higher energy band called the conduction band. The energy difference between the highest energy (top) of the valence band and the lowest energy (bottom) of the conduction band is called the band gap energy. If the valence band is completely full of electrons and conduction band is completely empty, the material is an insulator, since to conduct electricity the electrons must pick up energy and move to a slightly higher level. Since all available levels in the valence band are full, they cannot do this, and the material is an insulator.

If the valence band is only partially occupied, then the material is an electrical conductor since there are free energy levels available for the electrons to carry the electric current. Owing to the fact that the valence band is formed from the outermost occupied orbitals of the atoms, which can contain

either one electron or two electrons of opposite spins, the valence band in any material is always either entirely full (insulators), or just half full (conductors).

In some materials, the gap between the fully occupied valence band and the empty conduction band is very narrow. So narrow in fact that ordinary heat energy at room temperature can promote electrons from the valence band into the conduction band. Such materials are semiconductors. These are generally poor conductors compared to metals.

The various types of luminescence phenomena are discussed briefly in the following sections, depending on their application potential.

## 2. Photoluminescence

As has been defined earlier, luminescence occurs when some form of energy excites solids and energy is released in the form of photons. When 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 [4, 5].

**2.1 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 [2, 5].

**b) 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 [5].

**c) 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 [4, 5].

**2.2 Extrinsic Luminescence.** Extrinsic luminescence refers to luminescence caused by intentionally incorporating impurities or defects into a phosphor and 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 emissions. On the other hand, the localized type occurs when the excitation and emission process of the luminescence are constrained within a localized luminescent center.

The spontaneous emission of light upon electronic excitation (e.g. excitation by ultraviolet radiation) is called photoluminescence. Luminescence is a common phenomenon among inorganic

and organic as well as in semi-conductors. However, non-radiative relaxation processes may also be predominant in some compounds. In those cases where spontaneous emission of light does occur, its spectral and temporal characteristics carry a lot of important information about the metastable emitting state and its relation to the ground state. Luminescence spectroscopy is thus a valuable tool to explore these properties. By studying the luminescence properties we can gain insight not only into the light emission process itself, but also into the competing non-radiative photophysical and photochemical processes [6].

Luminescence is the emission of optical radiation (infrared, visible, or ultraviolet light) by matter. This phenomenon is to be distinguished from incandescence, which is the emission of radiation by a substance by virtue of it being at a high temperature (blackbody radiation). Luminescence can occur in a wide variety of matter and under many different circumstances. Thus, atoms, polymers, inorganic, organic or organo-metallic molecules, organic or inorganic crystals, and amorphous substances all emit luminescence under appropriate conditions. The various luminescence phenomena are given their names, which reflect the type of radiation used to excite and to get the emission.

The main characteristic of luminescence is that the emitted light is an attribute of the object itself, and the light emission is stimulated by some internal or external process. This process is quite different to the incandescence seen in an ordinary light bulb filament. In this case, the energy from a current of electricity is transferred directly to the metal atoms of the wire. This causes them to vibrate and hence heat up. The wire can then glow white hot, as in an incandescent light bulb. A characteristic of this type of light is that it is accompanied with a great deal of heat. The electrical energy is converted into radiation with an efficiency of about 80%, but the visible light being emitted is less than 10% of the total radiation. The remaining radiation is mainly in the form of infra-red region or heat. The spectrum of radiation emitted from a hot wire, or any other object, is not sensitive to the attributes of the object. All hot objects emit light and heat with very similar characteristics and this is well described by models based on a generic blackbody [5, 6].

### 3. Fluorescence

Fluorescence is the emission of light, with a characteristic time  $t_c < 10^{-8}$  s, in which emission takes place from an excited singlet state, and the phosphorescence ( $t_c > 10^{-8}$  s), in which emission occurs from an excited triplet state. To clarify difference between fluorescence and phosphorescence is to study the effect of temperature upon the decay of the luminescence. Fluorescence is essentially independent of temperature; whereas the decay of phosphorescence exhibits strong temperature dependence.

Several types of luminescence can be recognized. Some objects, when illuminated by light of one color, are stimulated to emit light of another color. This is called fluorescence. A common example is the chemical residue left behind in clothes by some types of washing powders. These powders emit visible light when stimulated by invisible ultra-violet (UV) light found in sunlight. Thus the clothes containing the residues appear brighter because of the combined effect of the reflected visible sunlight and the fluorescence from the washing powder residues. Another example is the fluorescent chemicals that coat the inside of fluorescent tubes. In these tubes the UV light (253.7nm) comes from excited mercury vapour inside the tube. The energetic UV light excites electrons in the fluorescent powder phosphor which then emit visible light (with a small amount of heat) upon decaying back to their original states. The term photoluminescence is sometimes also applied to this type of luminescence which is stimulated by light of another colour [6].

Another example of fluorescence is in the modern machines for producing medical X-ray images; a screen that produces a lot of visible light called fluorescence when irradiated with X-rays is used to

form an image which can then be photographed with films which are sensitive to visible light. This process is more sensitive than using the film to record the X-rays directly, thus minimizing the dose of X-rays to the patient. The following are few important applications of fluorescence [9].

**3.1 Applications of Fluorescence.** The substances emitting the luminescence are called phosphors. Some phosphors are basically semiconductor describable in terms of energy band model. These are in biological forms. They may be in micro or macro forms. Professionals have examined the PL of different materials and developed many macro and microscopic luminescence based devices. The brief account of applications of fluorescence is given below:

**3.1.1 Biological Application.** Plants contain fluorescent compounds in small concentration and distributed in specific locations. The examination of the fluorescence pattern of these compounds and their careful analysis leads to new technique to detect fungus in specimen, individual fluorescent chemical compound of biological origin. In addition to this it has helped to study phenomena of photosynthesis by inspecting the variation of chloro- fluorescent at the beginning and end of period of the exposure of the plant material to light. The measurements of fluorescence polarization under various conditions lead to determine along the rotation of diffusion constant of proteins.

**3.1.2 Fluorometry.** In this technique, emitted visible emission from the material is analyzed critically, which gives information about the material and which is a very good technique. It is used in many fields. (a) Impurity analysis is done through comparison of PL spectra of specimen with that of standard spectra. This technique is widely used in tablet industry in medical field. (b) The detection and assessment of several fluorescing compounds in the same solution is also possible. (c) Fluorometry is also useful in biology and medicine. It gives idea regarding vitamin deficiency, estimation of blood, urine and concentration of hormones. In chromatographic separation; it is used for detection of poison and identification of strain, i.e. pus, blood and urine.

**3.1.3 Fluorescent Microscopy.** The microscopic components of the specimen exhibit PL on the interaction with UV or blue light. Fluorescence microscopes have been developed on this premise to examine and locate fine structure of such substances.

**3.1.4 Fluorescent Lamp/Compact Fluorescent Lamps (CFLs).** The phosphors are pasted on inside wall of the lamp. UV light of 253.7 nm is generated through electric discharge. The phosphor absorbs the UV and through fluorescence emission it converts it in to visible light. The emission color of fluorescent lamp depends on nature of phosphor used in the lamp. Many varieties of fluorescent lamps are now available in market.

**3.1.5 Fluorescent Screen.** Different luminescent materials under exposure of ionizing radiations; such as invisible alpha particles, electrons, ultraviolet light etc. display visible emission of different colors. If the screen is prepared with luminescent material, it can be used to detect the presence of radiation field. This property of phosphors has been utilized in TV screen picture tubes, watch dials, etc..

**3.1.6 Forensic Science.** Luminous emission from material is highly sensitive to nature, structure and impurity (or defect) present in the specimen. PL spectrum is as good as fingerprint of the specimen. Therefore, the comparison of the PL pattern of the ideal specimen with that of specimen with defect or in different condition provides lot of information. These facts are utilized in forensic science to detect and for prosecution of criminals, etc. It also evaluates physico-chemical condition of the specimen. It can be used for identification of substance in forensic science.

**3.1.7 Fluorescence in Chemical Analysis.** If the different elements in the sample emit their characteristics lines by electron or X-ray bombardment, then these elements may be identified by analyzing the emitted radiation. Measurement of coating thickness on one chemical to another can be made by studying intensity and characteristic emission from the material; chemical behavior of liquids can also be studied by fluorescence emission method.

**3.1.8 Luminescent Devices in Radiation Services.** It includes indicator lamps, data punched type reader, position indicator, optomechanical programming, recondition equipments, thermo-chrome motor controllers, advertisements, etc..

**3.1.9 Medical Applications.** Fluorescence is widely used in analytical work of various compounds present in cells of liver, kidney, etc. The sensitivity and selectivity of PL in many micro systems facilitates the professionals to estimate amino acids, proteins and nucleic acid in medico-legal works. Many blood tests are using luminescence technique to determine and quantify the bacteria, and viruses.

**3.1.10 Mechanical behavior of Materials through Luminescence.** Luminescence is a structure sensitive phenomenon, which is very sensitive to detect pattern inside the lattice of the materials. One may find out defect patterns in host matrix by examining fluorescence spectra.

**3.1.11 Fluorescence in Gemology.** Gemstones are basically categorized based on their crystal structure, specific gravity, refractive index, and other optical properties, such as pleochroism. The physical property of "hardness" is defined by the non-linear Mohs scale of mineral hardness. Gemologists study these factors while valuing or appraising cut and polished gemstones. Gemological microscopic study of the internal structure is used to determine whether a gem is synthetic or natural by revealing natural fluid inclusions, and included partially melted exogenous crystals to demonstrate evidence of heat treatment to enhance colour [10].

One test to determine the gem's identity is to measure the refraction of light in the gem. Every material has a critical angle, at which point light is reflected back internally. This can be measured and thus used to determine the gem's identity. Typically, this is measured using a refractometer although it is possible to measure it using a microscope.

Identification by spectroscopy, this method uses a similar principle to how a prism works to separate white light into its component colors. A gemological spectroscope is employed to analyze the selective absorption of light in the gem material. Essentially, when light passes from one medium to another, it bends. Blue light bends more than red light. Depending on the gem material, it will adjust how much this light bends. Coloring agents or chromophores show bands in the spectroscope and indicate which element is responsible for the gem's color using fluorescence technique [11-13].

**3.1.12 Light Emitting Diode (LED).** Light emitting diode (LED) is 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 [14]. 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  $\text{Ce}^{3+}$  doped yttrium aluminium garnet ( $\text{YAG}:\text{Ce}^{3+}$ ), 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  $\text{CaS}:\text{Eu}^{2+}$  has been reported as a red phosphor source,  $\text{CaS}:\text{Ce}^{3+}$  as green,  $\text{SrS}:\text{Ce}^{3+}$  as blue and  $\text{SrS}:\text{Eu}^{2+}$  as orange phosphors. Sulfide

phosphors have been ignored for a long time because they are not chemically stable. When sulfides were 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 [14]. However, sulfide phosphors fit well for LED applications with adhesive seal and blue excitation (450-470nm).

#### **4. Phosphorescence**

In some materials, electrons excited by the original radiation can take some time to decay back to their ground states. The decay can take as long as few hours to few days. This type of fluorescence is called phosphorescence and the material continues to emit visible light for a while after the original radiation has been switched off. If the duration is very short, around  $10^{-4}$ s, then the material is a short persistence phosphor. If it lasts for seconds or longer it is a long persistence phosphor. Objects displaying phosphorescence are sometimes said to be luminous. Most luminous toys, stickers, exit signs in malls, aeroplanes and watch dials are coated with long persistence or long decay phosphors [9].

#### **5. Bioluminescence.**

It is the result of certain oxidation processes (usually enzymatic) in biological systems like fireflies, glow worms, jellyfishes, etc. Bioluminescence is the production and emission of light by a living organism. Bioluminescence occurs widely in marine vertebrates and invertebrates, as well as in some fungi, microorganisms and terrestrial invertebrates. Some symbiotic organisms carried within larger organisms produce light.

The French pharmacologist, Raphaël Dubois, carried out early work on bioluminescence [15]. Before the development of the safety lamp for use in coal mines, dried fish skins were used in Britain and Europe as a weak source of light [16, 17].

Bioluminescence is a form of luminescence, or "cold light" emission by living organisms; less than 20% of the light generates thermal radiation. It should not be confused with iridescence, structural coloration, and phosphorescence. By etymology, bioluminescence is a hybrid word, originating from the Greek *bios* for "living" and the Latin *lumen* "light". Bioluminescence is a form of chemiluminescence where light energy is released by a chemical reaction. Fireflies, anglerfish, and other creatures produce the chemicals luciferin (a pigment) and luciferase (an enzyme)[18]. The luciferin reacts with oxygen to create light. The luciferase acts as a catalyst to speed up the reaction, which is sometimes mediated by cofactors such as calcium ions or ATP. The chemical reaction can occur either inside or outside the cell. In bacteria, the expression of genes related to bioluminescence is controlled by an operon called the *Lux* operon[19].

Bioluminescence occurs widely among some groups of animals, especially in the open sea; in some fungi and bacteria; and in various terrestrial invertebrates including insects. Many, perhaps most deep-sea animals produce light. Most marine light-emission is in the blue and green light spectrum, the wavelengths that pass furthest through seawater. However, some loose-jawed fish emit red and infrared light, and the genus *Tomopteris* emits yellow light. Sometimes thousands of square miles of the ocean shine with the light of bioluminescent bacteria in the "Milky Seas effect" [20]. Non-marine bioluminescence is less widely distributed. The two best-known forms of land bioluminescence are fireflies and glow worms. Other insects, insect larvae, annelids, arachnids and even species of fungi have been noted to possess bioluminescent abilities. Some forms of bioluminescence are brighter (or exist only) at night, following a circadian rhythm.

In many animals of the deep sea, including several squid species, bacterial bioluminescence is used for counter-illumination camouflage, in which the animal matches the overhead environmental light as seen from below [9]. In these animals, photoreceptors control the illumination to match the brightness of the background [21]. These light organs are usually separate from the tissue containing the bioluminescent bacteria. However, in one species, *Euprymna scolopes*, the bacteria are an integral component of the animal's light organ [22].

The attraction of mates is seen actively in fireflies, which use periodic flashing in their abdomens to attract mates in the mating season [23]. In the marine environment, use of luminescence for mate attraction is well documented only in ostracods, small shrimplike crustaceans. Pheromones may be used for long-distance communication, with bioluminescence used at close range to enable mates to "home in". While most marine bioluminescence is green to blue, the Black Dragonfish produces a red glow. This adaptation allows the fish to see red-pigmented prey, which are normally invisible in the deep ocean environment where red light has been filtered out by the water column [9, 24]. Bioluminescent organisms are a target for many areas of research. Luciferase systems are widely used in the field of genetic engineering as reporter genes. Luciferase systems have also been harnessed for biomedical research using bioluminescence imaging.

## 6. Cathodoluminescence

Cathodoluminescence is due to emission of light when bombarded with high energy electron beam irradiation (CRO & TV Screen Phosphors). Cathodoluminescence is the inverse of the photoelectric effect in which electron emission is induced by irradiation with photons. In the beginning of the last century, it was observed that invisible cathode rays, produced by electrical discharges in evacuated tubes, produced light when they struck the glass walls of the tube. The modern name for cathode rays is electrons and this type of luminescence has retained the name cathodoluminescence. This is one of the useful application of luminescence. The electron microscope employs beams of electrons to produce high resolution images of small specimens. In some cases, the beam produces cathodoluminescence from the specimen. This is particularly useful for the study of minerals in rocks where the presence of trace amounts of transition metal elements can cause the mineral to give light of a distinctive colour. Often the presence of the trace element cannot be detected in any other way. Also, the ubiquitous video display tube also employs beam of electrons to selectively excite red, green or blue phosphors to display colour images. This is such an efficient process that despite continuing revolutions in the semiconductor industry, the video display industry remains dominated by the nineteenth century technology of the colour picture tube [9].

Cathodoluminescence occurs because the impingement of a high energy electron beam onto a semiconductor will result in the promotion of electrons from the valence band into the conduction band, leaving behind a hole. When an electron and a hole recombine, it is possible for a photon to be emitted. The energy (color) of the photon, and the probability that a photon and not a phonon will be emitted, depends on the material, its purity, and its defect state. In this case, the "semiconductor" examined can, in fact, be almost any non-metallic material. In terms of band structure, classical semiconductors, insulators, ceramics, gemstones, minerals, and glasses can be treated the same way.

Recently, cathodoluminescence performed in electron microscopes is being used to study Surface Plasmon Resonance in metallic nanoparticles [25, 26]. Indeed, metallic nanoparticles can absorb and emit visible light because of surface Plasmons. Cathodoluminescence has been exploited as a probe to map the local density of states of planar dielectric photonic crystals and nanostructured photonic materials [3]. Although an electron microscope with a cathodoluminescence detector provides high magnification and resolution it is more complicated and expensive compared to an

easy to use optical cathodoluminescence microscope which benefits from its ability to show actual visible color features directly through the eyepiece [9].

In geology, mineralogy and materials science and semiconductor engineering, a scanning electron microscope with specialized optical detectors, or an optical cathodoluminescence microscope, may be used to examine internal structures of semiconductors, rocks, ceramics, glass, etc. in order to get information on the composition, growth and quality of the material [26].

In these instruments, a focused beam of electrons impinges on a sample and induces it to emit light that is collected by an optical system, such as an elliptical mirror. From there, a fiber optic will transfer the light out of the microscope where it is separated into its component wavelengths by a monochromator and is then detected with a photomultiplier tube. By scanning the microscope's beam in an X-Y pattern and measuring the light emitted with the beam at each point, a map of the optical activity of the specimen can be obtained. The primary advantages to the electron microscope based technique is the ability to resolve features down to 1 nanometer [9, 25], the ability to measure an entire spectrum at each point (hyperspectral imaging) if the photomultiplier tube is replaced with a CCD camera, and the ability to perform nanosecond- to picosecond-level time-resolved measurements if the electron beam can be "chopped" into nano- or pico-second pulses. Moreover, the optical properties of an object can be correlated to structural properties observed with the electron microscope [27-29]. These advanced techniques are useful for examining low-dimensional semiconductor structures, such as quantum wells or quantum dots [30].

Although direct bandgap semiconductors such as GaAs or GaN are most easily examined by these techniques, indirect semiconductors such as silicon also emit weak cathodoluminescence, and can be examined as well. In particular, the luminescence of dislocated silicon is different from intrinsic silicon, and can be used to map defects in integrated circuits.

## 7. Chemiluminescence

Chemiluminescence is produced as a result of a chemical reaction usually involving an oxidation-reduction process. The most common mechanism for such an emission is the conversion of chemical energy, released in a highly exothermic reaction, into light energy in the visible region. In some chemical reactions, energy can be transferred to electrons in the chemical bonds. As these electrons decay down to lower excited states, it leads to emit light. Some of these reactions proceed slowly, so the light can be emitted for a considerable time. This is known as Chemiluminescence. This is distinct from more vigorous chemical reactions where so much heat is released that the chemicals actually catch fire or otherwise glow red hot. This is nothing more than incandescence. Chemiluminescence is displayed by a variety of organisms and the chemical reaction usually involves the oxidation. This type of light emitting chemical is called luciferin. This is an organic molecule with two hydrogen atoms attached with the basic symbol as  $\text{LH}_2$ . With the aid of the molecule responsible for the storage of energy in cells, adenosine triphosphate (ATP) and a special catalyst molecule (the enzyme luciferase), the luciferin is oxidized to  $\text{L}=\text{O}$  in an excited state [9]. When it changes into the ground state a visible light photon is emitted. One visible light photon alone is emitted as each molecule of luciferin is oxidised, so this process is really light without heat. The light is typically light blue in colour, although differing chemical environments can modify the colour. It is believed that this light producing process evolved as a small side branch of the main oxidation-reduction reactions that extract energy from nutrients. Some synthetic molecules, such as Luminol (5-aminophthalhydrazide) and Cyalume are the basis of commercially available chemoluminescent products.



## 8. Electroluminescence

Electro-luminescence is the efficient generation of light in a non-metallic solid or gas by an applied electric field or plasmas [3, 4]. Another type of electro-luminescence is that produced by some crystals when an electric current through them. In this case the current of electrons excites electrons that occupy energy levels involved with chemical bonds inside the crystal. When the excited electrons decay back to their ground state they emit visible light, this phenomenon is known as electroluminescence. There are several different methods of exciting electroluminescence from a crystal. In one method, AC voltages applied to special panels produces light. About 40 years ago, it was thought this sort of light would replace ordinary light bulbs for many domestic applications. This was because electroluminescent coatings could be applied to walls, ceilings, even curtains. There was also virtually no limit to the range of colours that could be produced. Unfortunately, several practical difficulties could not be overcome, such as efficiency, and that high frequency AC was required to excite the luminescent material. However, the light emitting diode (LED), operating on a different principle, has now become a widely used application of electroluminescence including the mobile displays apart from LEDs.

## 9. Ionoluminescence

A more exotic method of producing luminescence is the visible light produced when fast ions collide with organic, and inorganic compounds. This is called ionoluminescence. An early application of ionoluminescence was to luminous clock dials. These relied upon a rather hazardous method of making light that involved radioactive compounds. A radioactive material, such as radium, was mixed with a material that displays luminescence, such as zinc sulphide. As the radium decays, it emits alpha particles and other radiations. This excites electrons in the luminescent material to give off light. This is very handy, since the light persists indefinitely, limited only by the half-life of the radium isotope used,  $^{226}\text{Ra}$ , which is 1600 years. However, the manufacturing process for such watch dials gave radiation exposure, mainly internal exposure to workers involved in this work in 1920s and 1930s. At a luminous dial painting factory, as a result of licking their paint brushes to get a fine brush point, the workers involved got internal radiation exposure [9].

## 10. Lyoluminescence

Lyoluminescence is the phenomenon of light emission during the dissolution of previously irradiated solids in suitable solvents. Lyoluminescence refers to the emission of light while dissolving a solid into a liquid solvent. It is actually a form of chemoluminescence. The most common lyoluminescent effect is seen when solid samples which have been heavily irradiated by ionizing radiation are dissolved in water. The total amount of light emitted by the material increases proportionally with the total radiation dose received by the material up to a certain level called the saturation value. Many gamma-irradiated substances are known to lyoluminesce; these include spices, powdered milk, soups, cotton and paper. While the broad variety of materials which exhibit lyoluminescence confounds explanation by a single common mechanism there is a common feature to the phenomenon, the production of free radicals in solution. Lyoluminescence intensity can be increased by performing the dissolution of the solid in a solution containing conventionally chemoluminescent compounds such as luminol. These compounds are thus called lyoluminescence sensitizers [31].

## 11. Mechanoluminescence (Triboluminescence or Piezoluminescence)

Mechano-luminescence is due to the emission of light on applying an external mechanical energy. It could be excited by cutting, cleaving, grinding, rubbing, and compressing or by impulsive deformation of solids. It is not a fiction, but a scientific fact that light emission takes place during

the elastic deformation, plastic deformation and fracture of solids. Sugar crystal produces a glow of light when it is crushed or fractured in dark, and also the Wintergreen Candy glows when it is bitten in dark. Such phenomenon of light emission induced by fracture of solids is known as fracto-mechanoluminescence (FML). Several materials such as copper-doped ZnS crystals, MgO, etc. emit light when they are plastically deformed where fracture is not required. This phenomenon of light emission induced by plastic deformation of solids is called plastico-mechanoluminescence (PML). A few solids such as X or  $\gamma$ -irradiated alkali halide crystals, ZnS:Mn, SrAl<sub>2</sub>O<sub>4</sub>:Eu, etc. emit light during their elastic deformation where plastic deformation and fracture are not required. Such phenomenon of light emission induced by elastic deformation of solids is known as elastico-mechanoluminescence (EML). In general, the light emission induced by any mechanical action on solids is known as mechanoluminescence (ML), in which elastico ML, plastico ML, and fracto ML are the types of ML induced by elastic deformation, plastic deformation and fracture of solids, respectively [32, 33]. Light emission also takes place during the friction of silky shirt on our body and also during separation of adhesive tape from a substrate. Such phenomenon of light emission induced by rubbing or separation of two solids in contact is known as tribo ML or triboluminescence. The appearance of triboluminescence in modern adhesives and other polymers has brought it to the attention of mothers using diaper tape, photographers unrolling film and the many users of duct tape. Recently, Camara et al. [34] of the University of California, Los Angeles, California, USA, have reported that peeling of common adhesive tape in a moderate vacuum produces radio waves and visible light emission along with nanosecond, 100-mW X-ray pulses that are correlated with stick-slip peeling events. The intensity of X-ray triboluminescence allowed them to use it as a source for X-ray imaging [34].

ML can be excited by any mechanical actions such as grinding, cutting, cleaving, shaking, scratching, stretching, compressing, loading, shaking, crushing, rubbing impulsive deformation of solids, etc.. It can also be excited by thermal shocks caused by drastic cooling or heating of materials or by the shock-waves produced during exposure of samples to laser pulses or ultrasonic waves. ML also appears during the deformation caused by the phase-transition or growth of certain crystals as well as during separation of two solids in contact. Whereas nearly 50% of all inorganic salts and organic molecular solids show ML during their fracture, only a few solids exhibit ML during their elastic and plastic deformation. The ML intensity of SrAl<sub>2</sub>O<sub>4</sub>:Eu, ZrO<sub>2</sub>:Ti, Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>:Ce, europium tetrakis, dibenzoyl methide, triethynyl ammonium, ditriphenylphosphine oxide, manganese bromide, freshly grown impure saccharin, etc. is so intense that it can be seen in day light with naked eye.

The ML was probably first discovered when human lived in caves because many common minerals and rocks produce very bright light emission during their deformation and fracture. The first recorded discovery of ML was made by Francis Bacon in 1605, who reported it in his writings, 'Advancement of Learning', that "hard sugar being nimbly scrapped with a knife would afford a sparkling light". Till now the ML has been tested in thousands of materials and very intense elastico mechanoluminescent, plastico mechanoluminescent and fracto mechanoluminescent materials have been discovered [35].

## 12. Optically Stimulated Luminescence (OSL) or Photo-stimulated Luminescence (PSL)

OSL and PSL offer an alternative technique to conventional X-ray radiography, which consist of a photographic film and an intensifying screen. They are adoptable to digital radiography systems which are based on the conversion of the X-ray image pattern into digital signals utilizing laser beam scanning of an optically stimuable imaging plate [36].

Optically stimulated luminescence (OSL) is a method for measuring doses from ionizing radiation. The method makes use of electrons trapped between the valence and conduction bands in the

crystalline structure of certain types of matter (such as quartz, feldspar, and aluminum oxide). The trapping sites are imperfections of the lattice - impurities or defects. The ionizing radiation produces electron-hole pairs; electrons are in the conduction band and holes in the valence band. The electrons which have been excited to the conduction band may become entrapped in the electron or hole traps. Under stimulation of light, the electrons may free themselves from the trap and get into the conduction band. From the conduction band they may recombine with holes trapped in hole traps. If the centre with the hole is a luminescence centre (radiative recombination centre), emission of light will occur. The photons are detected using a photomultiplier tube. The signal from the tube is then used to calculate the dose that the material had absorbed [9].

The OSL dosimeter provides a new degree of sensitivity by giving an accurate reading as low as 1 milli rem for X-ray and gamma ray photons with energies ranging from 5 keV to greater than 40 MeV. The OSL dosimeter's maximum equivalent dose measurement for X-ray and gamma ray photons is 1000 rem. For beta particles with energies from 150 keV to in excess of 10 MeV, dose measurement ranges from 10 mrem to 1000 rem. Neutron radiation with energies of 40 keV to greater than 35 MeV has a dose measurement range from 20 mrem to 25 rem. In diagnostic imaging the increased sensitivity of the OSL dosimeter makes it ideal for monitoring employees working in low-radiation environments and for pregnant workers [9].

**12.1 OSL Applications.** Optical dating of ancient materials: mainly geological sediments, but also sometimes fired pottery, bricks, etc., although in the latter case thermoluminescence dating is used more often than radiation dosimetry, which is the measurement of accumulated radiation dose in the tissues of health care, nuclear research and other workers, as well as in building materials in regions of nuclear disaster. In order to carry out OSL dating, mineral grains have to be extracted from the sample. Most commonly these are so-called coarse grains - 100-200  $\mu\text{m}$ , or fine grains - 4-11  $\mu\text{m}$ . Occasionally, other grain sizes are also used [36, 37]. The difference between radiocarbon dating and OSL is that the former is used to date organic materials, while the latter is used to date minerals. Events that can be dated using OSL are, for example, the mineral's last exposure to sunlight; Mungo Man, Australia's oldest human find, was dated in this manner [38, 39]. It is also used for dating the deposition of geological sediments after they have been transported by air (eolian sediments) or rivers (fluvial sediments). In archaeology, OSL dating is applied to the dating of ceramics: the dated event is the time of their last heating to a high temperature (in excess of 400  $^{\circ}\text{C}$ ) [9, 40-42].

### 13. Radioluminescence (or Scintillation)

Radioluminescence occurs when an incoming radiation particle collides with an atom or molecule, exciting an orbital electron to a higher energy level. The electron then returns to its ground energy level by emitting the extra energy as a photon of light. Radioluminescence is produced by ionizing radiations. Some polymers contain organic molecules which emit visible light when exposed to such radiations as X-rays, gamma rays or cosmic rays, and thus act as detectors for high energy radiations.

Radioactive elements can emit alpha particles (helium nuclei), electrons, and gamma rays (high-energy electromagnetic radiation). The term radioluminescence, therefore, means that an appropriate material is excited to luminescence by a radioactive substance. When alpha particles bombard a crystal or phosphor, tiny scintillations or light are visible to microscopic observation.

**13.1 Radioluminescence Applications.** Radioluminescence is used as a low level light source for night illumination of instruments or signage or other applications where light must be produced for long periods without external energy sources. Formerly, radioluminescent paint was used for clock

hands and instrument dials allowing them to be read in the dark. Radioluminescence is also sometimes seen around high power radiation sources, such as nuclear reactors and radioisotopes [9].

Currently, tritium ( $^3\text{H}_1$ ) is virtually the only radioisotope permitted to be used commercially as a radioluminescent light source. It is used on wrist watch faces, gun sights and emergency exit signs. The tritium gas is contained in a small glass tube, coated with a phosphor on the inside. Beta particles emitted by the tritium strike the phosphor molecules and cause them to fluoresce, emitting light, usually yellow-green. Tritium is used because it is believed to pose a negligible threat to human health, in contrast to the previous radioluminescent source, radium, which proved to be a significant radiological hazard. The low-energy 5.7 keV beta particles emitted by tritium cannot pass through the enclosing glass tube. Even if they could, they are not able to penetrate human skin. Since tritium is a gas, if a tritium tube breaks, the gas dissipates in the air and is diluted to safe concentrations within no time. Tritium has a half life of 12.3 years, so the brightness of a tritium light source will decline to half its initial value in that time. Historically, a mixture of radium and copper-doped zinc sulfide was used to paint instrument dials giving a greenish glow. Phosphors containing copper doped zinc sulfide ( $\text{ZnS}:\text{Cu}$ ) yield blue-green light; copper and manganese doped zinc sulfide ( $\text{ZnS}:\text{Cu},\text{Mn}$ ), yielding yellow-orange light, are also used. Radium based luminescent paint is no longer used due to the radiation hazard posed to those manufacturing the dials. These phosphors are not suitable for use in layers thicker than 25 mg/cm<sup>2</sup>, as the self-absorption of the light then becomes a problem.

#### 14. Sonoluminescence

Sonoluminescence is the emission of light due to the excitation by Sound waves including ultrasonic waves. The Royal Navy employed the services of physicist Lord Rayleigh in the early 20th century to understand the degradation of ship propellers. Lord Rayleigh concluded that collapsing air bubbles were the cause [43]. The sonoluminescence effect was first discovered at the University of Cologne in 1934 as a result of work on sonar. H. Frenzel and H. Schultes put an ultrasound transducer in a tank of photographic developer fluid. They hoped to speed up the development process. Instead, they noticed tiny dots on the film after developing and realized that the bubbles in the fluid were emitting light with the ultrasound turned on. It was too difficult to analyze the effect in early experiments because of the complex environment of a large number of short-lived bubbles. This phenomenon is now referred to as multi-bubble sonoluminescence (MBSL).

Sonoluminescence can occur when a sound wave of sufficient intensity induces a gaseous cavity within a liquid to collapse quickly. This cavity may take the form of a pre-existing bubble, or may be generated through a process known as cavitation. Sonoluminescence in the laboratory can be made to be stable, so that a single bubble will expand and collapse over and over again in a periodic fashion, emitting a burst of light each time it collapses. For this to occur, a standing acoustic wave is set up within a liquid, and the bubble will sit at a pressure anti-node of the standing wave. The frequencies of resonance depend on the shape and size of the container in which the bubble is contained [9, 44].

The light flashes from the bubbles are extremely short—between 35 and a few hundred picoseconds long—with peak intensities of the order of 1–10 mW. The bubbles are very small when they emit the light—about 1 micrometre in diameter—depending on the ambient fluid (e.g., water) and the gas content of the bubble (e.g., atmospheric air) [43].

Single-bubble sonoluminescence pulses can have very stable periods and positions. In fact, the frequency of light flashes can be more stable than the rated frequency stability of the oscillator making the sound waves driving them. However, the stability analysis of the bubble shows that the

bubble itself undergoes significant geometric instabilities, due to, for example, the Bjerknes forces and Rayleigh–Taylor instabilities.

The addition of a small amount of noble gas (such as helium, argon, or xenon) to the gas in the bubble increases the intensity of the emitted light. Spectral measurements have given bubble temperatures in the range from 2,300 K to 5,100 K, the exact temperatures depending on experimental conditions including the composition of the liquid and gas [44]. Detection of very high bubble temperatures by spectral methods is limited due to the opacity of liquids to short wavelength light characteristic of very high temperatures [45].

## 15. Thermally Stimulated Luminescence (TSL)

Thermoluminescence (TL) or more specifically Thermally Stimulated Luminescence (TSL) is stimulated thermally after initial irradiation given to a phosphor by some other means ( $\alpha$ - rays,  $\beta$  - rays,  $\gamma$  - rays, UV rays and X-rays). Thermally stimulated luminescence (TSL) is the phenomenon of emission of light from a solid which has been previously exposed to ionizing radiation under conditions of increasing temperature. Unlike other luminescence process such as Chemiluminescence, here heat is not an exciting agent, but it acts only as a stimulant. Hence it is better known as thermally stimulated luminescence (TSL). Excitation is achieved by any conventional sources like ionizing radiation,  $\alpha$ -rays,  $\beta$ -rays,  $\gamma$ -rays, cosmic rays, UV rays and X-rays. TSL is exhibited by a host of materials, glasses, ceramics, plastics and some organic solids. By far insulating solids doped with suitable chemical impurities, termed as activator, are the most sensitive TL materials [3, 46]. The band theory of solids is normally used to explain this phenomenon. When a solid is irradiated, electrons and holes are produced. The defects in the solid result in the presence of localized energy levels within the forbidden gap. On irradiation, electron and holes can be trapped at these defect sites. When the solid is heated, these trapped electrons/holes get enough thermal energy to escape from the trap to the conduction band (or valence band). From there they may get re-trapped again or may recombine with trapped holes/electrons. The site of recombination is called recombination center. If this recombination is radiative, then center is called luminescence center. It is not required that all charge recombination should result in luminescence, they may be non-radiative too. The plot of intensity of emitted light (Y-axis) versus the temperature (X-axis) is known as a TL glow curve. A glow curve may exhibit one or many peaks depending upon the number of electron/hole traps with different trap depths, present in the lattice. These peaks may or may not be well separated. The position, shape and intensity of the glow peaks therefore are characteristic of the specific material and the impurities and defects present. Each TSL peak corresponds to the release for an electron (or hole) from a particular trap level within the band gap of the material. The nature of the TL glow peaks gives information about the luminescent centers present in the material. It may be mentioned that TSL is highly sensitive to structural imperfections in crystals. Defects densities as low as  $10^7/\text{cm}^3$  also can give measurable TSL if radiative recombinations are dominant, whereas techniques such as Electron Paramagnetic Spectroscopy (EPR) and Optical Absorption Spectroscopy (OAS) are sensitive only for relatively higher defect concentrations of  $10^{12}/\text{cm}^3$  or more. The first step towards understanding the mechanism for TSL glow peaks is the identification of the trapping centers and the recombination centers for the observed light emission [46, 47]. Apart from being a tool for the study of defects in solids, TSL has also found widespread use in radiation dosimetry, archeological dating of pottery, ceramics, minerals, etc., and in meteorite research.

Thus three essential requirements are necessary for the production of TL: (a) The material must be an insulator or a semiconductor (metals do not exhibit luminescent properties). (b) The materials must have at some stage absorbed energy during exposure to radiation. (c) The luminescence emission is triggered by heating the materials. One particular characteristic of thermoluminescence is that, once heated to excite the light emission, the materials cannot be made to emit

thermoluminescence again by simply cooling the specimen and again reheating. In order to exhibit the luminescence, the material has to be re-exposed to radiation and then raising the temperature will once again produce light emission [48, 49].

## 16. Phase Change Thermoluminescence (PCTL)

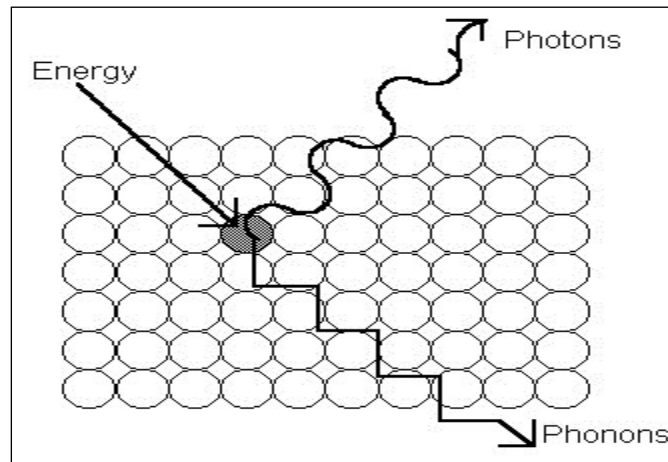
Some of the organic molecules, agricultural products and few minerals (zeolites) containing water molecules in their structure do exhibit the thermoluminescence without prior irradiation. This phenomenon is known as Phase Change Thermoluminescence (PCTL). Using this phenomenon one can find the phase transitions of materials and minerals [50].

## 17. Phosphor

All the materials either synthesized or in natural form if they exhibit luminescence of any type are called phosphors.

**17.1 Phosphor Configuration.** Phosphor, 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 applications 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 [51, 52].



**Fig. 5** An illustration of how a phosphor emits light. The dark circle denotes an activator ion which is surrounded by a host lattice [51, 52].

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/anti-site defects– in which a cation and an anion interchange.

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

**17.2 Doping.** It is known fact that the band gap energies of few materials have emission in band width that corresponds to the visible spectrum. However, materials with a relatively wide band gap can be made to emit luminescence in the visible. This is possible by the addition of different atoms or imperfections into the crystal. The additional atoms, called dopants, have a different electron orbital structure compared to the host crystal lattice. Therefore, in regions of the crystal around the dopant atom, additional energy levels become available. That is, within the forbidden band gap of the material, energy levels can co-exist that can accommodate electrons or holes. These levels can be close to the conduction band, in which case the dopant is called a donor, or close to the valence band, in such a case it is called an acceptor. Transitions between these levels can give rise to visible luminescence and, in such cases, the dopant is known as an activator. In most cases, the activator is present in extremely small concentrations, ranging from as much as one dopant atom in 5000 host atoms down to as little as one dopant atom in 1 million host atoms [53].

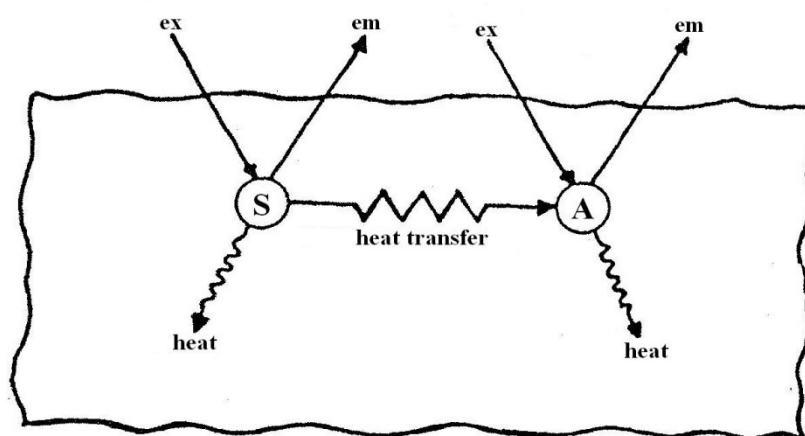
Sometimes the excited electron can find other ways to dissipate its energy. Several non-radiative recombination mechanisms are also possible. These are usually associated with defects in the crystal, or levels in the middle of the band gap, called deep levels, introduced by impurities called inhibitors. Still other defects in the crystal can result in shallow levels which are close to the edge of either the valence or conduction bands. Shallow levels in the band gap can trap the excited electrons. Certain characteristics of these shallow levels prevent the electron from decaying immediately back into the valence band. Instead, the decay may only occur after a very long time [54, 55]. However, a small amount of heat may dislodge the electron back into the conduction band from where it can readily decay back to the valence band. This is the mechanism behind the technique of thermoluminescence.

**17.3 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.

The rare earths as dopants have found very important place in the development of thermoluminescent dosimeters. The most famous and globally used thermoluminescent dosimeter,  $\text{CaSO}_4:\text{Dy}$ , gives us an idea of the importance of lanthanides in this field. The other examples of rare earth based TLDs are  $\text{CaSO}_4:\text{Tm}$ ;  $\text{MgB}_4\text{O}_7:\text{Dy,Tm}$ ;  $\text{Mg}_2\text{SiO}_4:\text{Tb}$ ;  $\text{CaF}_2:\text{Dy}$ , etc..

**17.4 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 ( $\text{Eu}^{2+}$ ) and transition metal ions ( $\text{Cu}^+$ ) in crystal lattice of alkaline earth aluminates and sulfides, respectively, act as activators.

**17.5 Sensitizer.** In case of two dopants in a crystal lattice, one is known as sensitizer (S) and another is activator (A). The 'S' absorbs most of the energy and transfers it to the 'A' for the process of emission as seen in Fig. 6. The metal ions, for example, forming sensitizer  $\rightarrow$  activator pairs are  $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$  and  $\text{Eu}^{2+} \rightarrow \text{Mn}^{2+}$ .



**Fig. 6** Schematic representation of luminescence process

**17.6 Co-activator.** The dopant ion that does not luminesce 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:  $\text{Al}^{3+}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$  in  $\text{ZnS}$  lattice act as co-activators [51, 52].

**17.7 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  $\text{ZnS}$  act as nonradiative centers, and thus called quenchers [2, 55].

## 18. Summary

The intrinsic luminescence refers to a situation in which the luminescence comes from within a pure material or crystal. The substances emitting the luminescence are called phosphors. Some phosphors are basically semiconductor describable in terms of energy band model. They may be in micro or macro forms. Professionals have examined the PL of different materials and developed many macro and microscopic luminescence based devices. A brief account of various fluorescence applications are discussed.

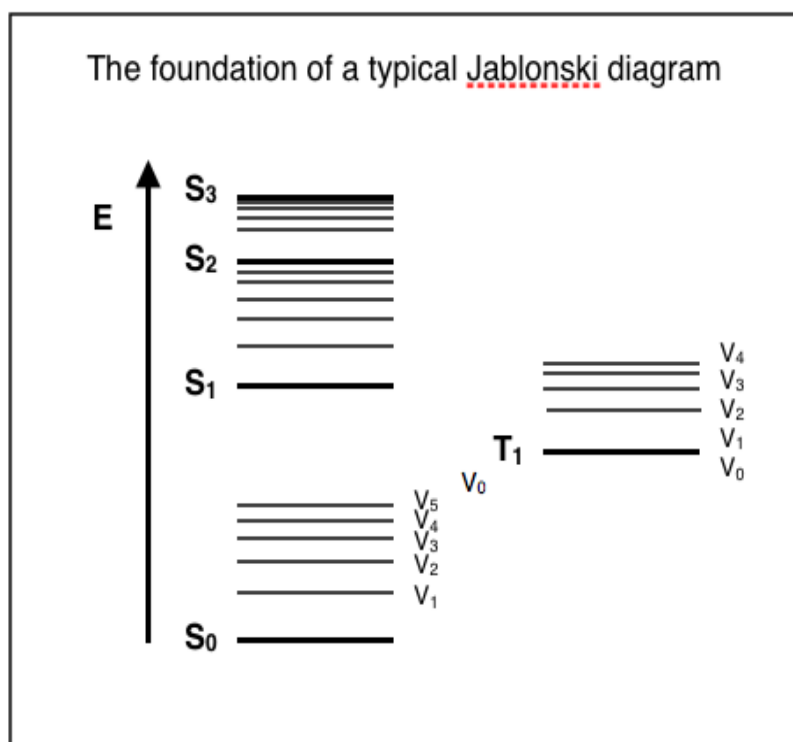


Light emitting diode (LED) is one of the most efficient solid state lighting sources. For lighting applications, white light LEDs are very comparable to sunlight spectrum. Currently, white light LEDs can be achieved by combining blue, green, and red LEDs, or by coating the three colour phosphors to a UV LED, or green and red phosphors to a blue LED.

All the materials either synthesized or in natural form, if they exhibit luminescence of any type, are called phosphors. It is known fact that the band gap energies of few materials have emission in band width that corresponds to the visible spectrum. However, materials with a relatively wide band gap can be made to emit luminescence in the visible. 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. The dopant ion that is responsible for decrease or complete disappearance of luminescence is known as quencher.

### 19. Appendix: Jablonski Diagram

Aleksander Jablonski was a Polish academic who devoted his life to the study of molecular absorbance and emission of light. A Jablonski diagram [56] is basically an energy diagram, arranged with energy on a vertical axis. The energy levels can be quantitatively denoted, but most of these diagrams use energy levels schematically (Fig. 1). Within each electronic energy state are multiple vibronic energy states that may be coupled with the electronic state. Usually only a portion of these vibrational eigenstates are represented due to the massive number of possible vibrations in a molecule. Each of these vibrational energy states can be subdivided even further into rotational energy levels; however, typical Jablonski diagrams omit such intense levels of detail. As electronic energy states increase, the difference in energy becomes continually less, eventually becoming a continuum that can be approached with classical mechanics. Additionally, as the electronic energy levels get closer together, the overlap of vibronic energy levels increases.



**Fig. 1** S and T represent singlet and triplet states, respectively

Through the use of straight and curved lines, these figures show transitions between eigenstates that occur from the exposure of a molecule to a particular wavelength of light. Straight lines show the conversion between a photon of light and the energy of an electron. Curved lines show transitions of electrons without any interaction with light. Within a Jablonski diagram several different pathways show how an electron may accept and then dissipate the energy from a photon of a particular wavelength. Thus, most diagrams start with arrows going from the ground electronic state and finish with arrows going to the ground electronic state.

### Absorbance

The first transition in most Jablonski diagrams is the absorbance of a photon of a particular energy by the molecule of interest. This is indicated by a straight arrow pointing up (Fig. 2). Absorbance is the method by which an electron is excited from a lower energy level to a higher energy level. The energy of the photon is transferred to the particular electron. That electron then transitions to a different eigenstate corresponding to the amount of energy transferred. Only certain wavelengths of light are possible for absorbance, that is, wavelengths that have energies that correspond to the energy difference between two different eigenstates of the particular molecule. Absorbance is a very fast transition, on the order of  $10^{-15}$  seconds. Most Jablonski diagrams, however, do not indicate a time scale for the phenomenon being indicated. This transition will usually occur from the lowest (ground) electronic state due to the statistical mechanical issue of most electrons occupying a low lying state at reasonable temperatures. There is a Boltzmann distribution of electrons within these low lying levels, based on the energy available to the molecules. This energy available is a function of the Boltzmann's constant and the temperature of the system. These low lying electrons will transition to an excited electronic state as well as some excited vibrational state.

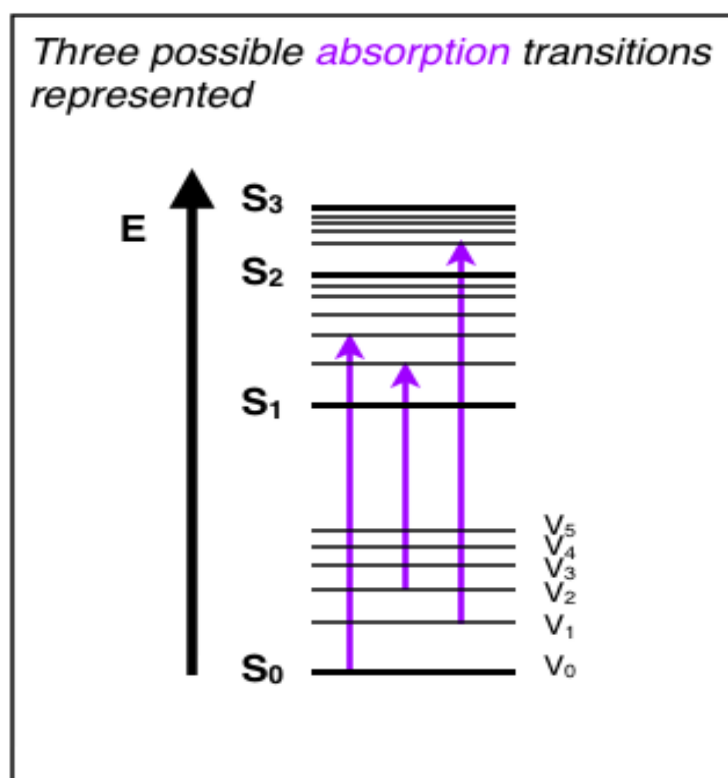


Fig. 2 Absorbance transitions

### Vibrational Relaxation and Internal Conversion

Once an electron is excited, there is a multitude of ways that energy may be dissipated. The first is through vibrational relaxation, a non-radiative process. This is indicated on the Jablonski diagram

as a curved arrow between vibrational levels (Fig. 3). Vibrational relaxation is where the energy deposited by the photon into the electron is given away to other vibrational modes as kinetic energy. This kinetic energy may stay within the same molecule, or it may be transferred to other molecules around the excited molecule, largely depending on the phase of the probed sample. This process is also very fast, between 10-14 and 10-11 seconds. Since this is a very fast transition, it is extremely likely to occur immediately following absorbance. This relaxation occurs between vibrational levels, so generally electrons will not change from one electronic level to another through this method.

However, if vibrational energy levels strongly overlap electronic energy levels, a possibility exists that the excited electron can transition from a vibration level in one electronic state to another vibration level in a lower electronic state. This process is called internal conversion and mechanistically is identical to vibrational relaxation. It is also indicated as a curved line on a Jablonski diagram, between two vibrational levels in different electronic states. Internal Conversion occurs because of the overlap of vibrational and electronic energy states. As energies increase, the manifold of vibrational and electronic eigenstates becomes ever closer distributed. At energy levels greater than the first excited state, the manifold of vibrational energy levels strongly overlaps with the electronic levels. This overlap gives a higher degree of probability that the electron can transition between vibrational levels that will lower the electronic state. Internal conversion occurs in the same time frame as vibrational relaxation, therefore, is a very likely way for molecules to dissipate energy from light perturbation. However, due to a lack of vibrational and electronic energy state overlap and a large energy difference between the ground state and first excited state, internal conversion is very slow for an electron to return to the ground state. This slow return to the ground state lets other transitive processes compete with internal conversion at the first electronically excited state. Both vibrational relaxation and internal conversion occur in most perturbations, yet are seldom the final transition.

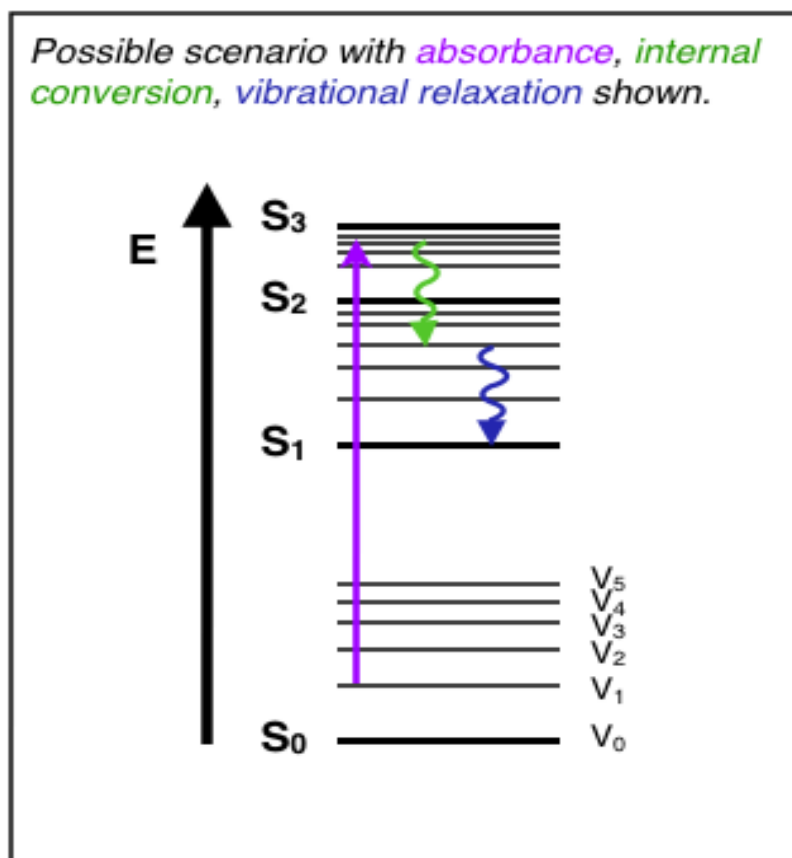


Fig. 3 Internal conversion and Vibrational relaxation

### Fluorescence

Another pathway for molecules to deal with energy received from photons is to emit a photon. This is termed fluorescence. It is indicated on a Jablonski diagram as a straight line going down on the energy axis between electronic states (Fig. 4). Fluorescence is a slow process on the order of  $10^{-9}$  to  $10^{-7}$  seconds; therefore, it is not a very likely path for an electron to dissipate energy especially at electronic energy states higher than the first excited state. While this transition is slow, it is an allowed transition with the electron staying in the same multiplicity manifold. Fluorescence is most often observed between the first excited electron state and the ground state for any particular molecule because at higher energies it is more likely that energy will be dissipated through internal conversion and vibrational relaxation. At the first excited state, fluorescence can compete in regard to timescales with other non-radiative processes. The energy of the photon emitted in fluorescence is the same energy as the difference between the eigenstates of the transition; however, the energy of fluorescent photons is always less than that of the exciting photons. This difference is because energy is lost in internal conversion and vibrational relaxation, where it is transferred away from the electron. Due to the large number of vibrational levels that can be coupled into the transition between electronic states, measured emission is usually distributed over a range of wavelengths.

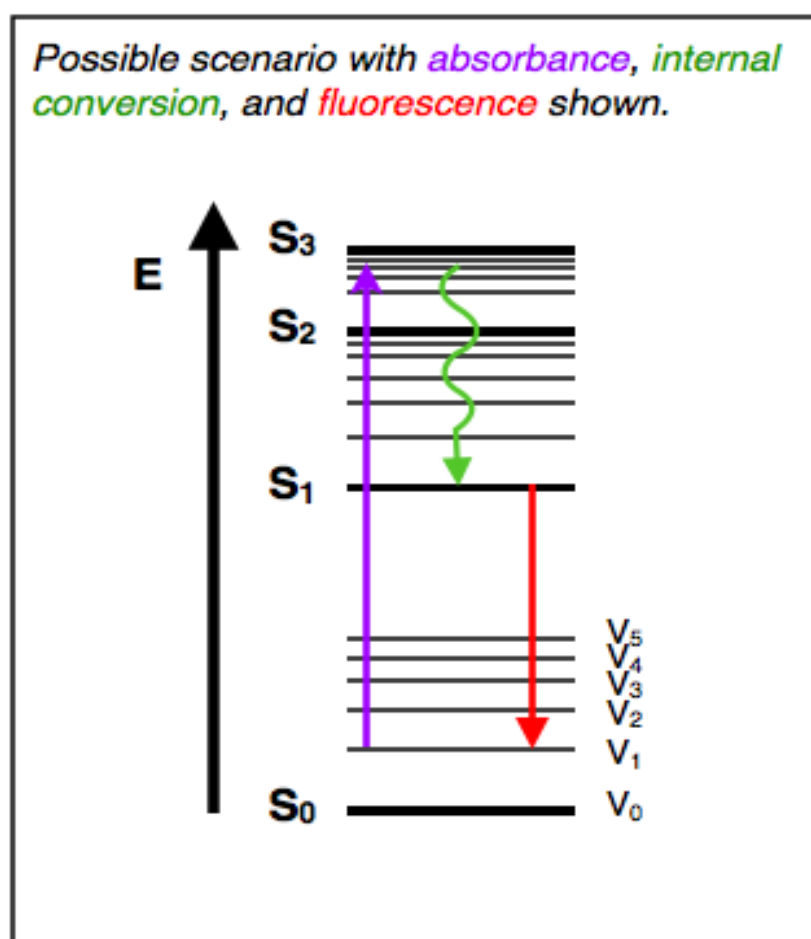
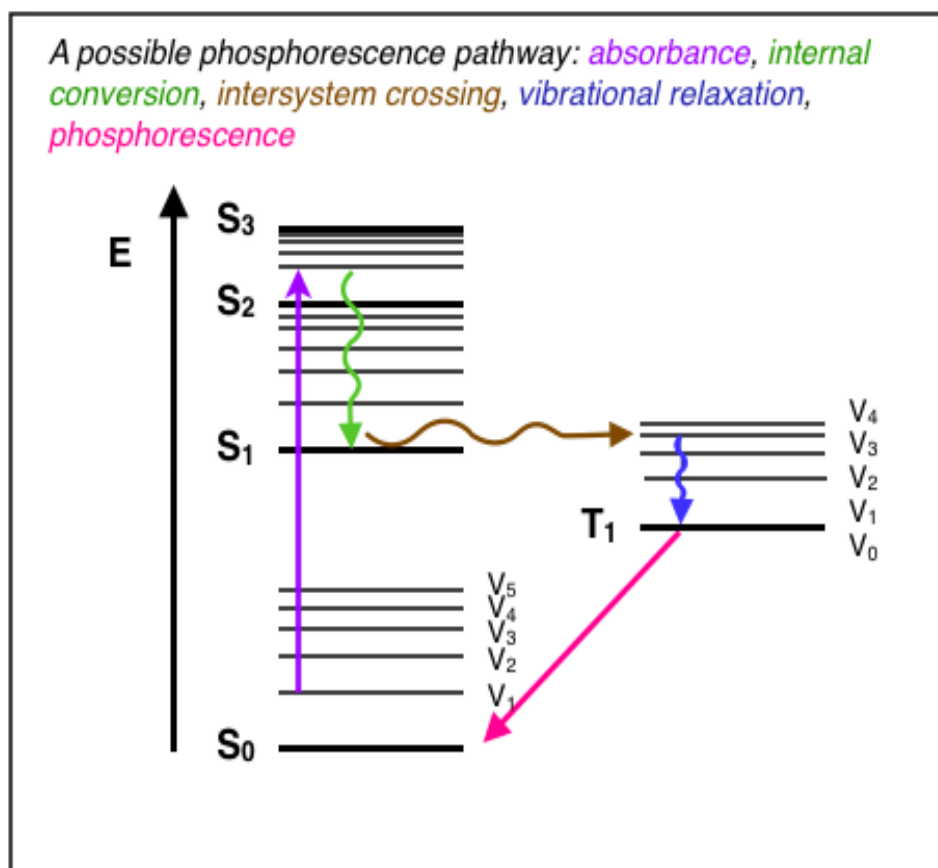


Fig. 4 Schematic of Fluorescence emission

### Intersystem Crossing

Yet another path a molecule may take in the dissipation of energy is called intersystem crossing. This is where the electron changes spin multiplicity from an excited singlet state to an excited triplet state. It is indicated by a horizontal, curved arrow from one column to another (Fig. 5). This is the slowest process in the Jablonski diagram, several orders of magnitude slower than fluorescence. This slow transition is a forbidden transition, that is, a transition that based strictly on electronic

selection rules should not happen. However, by coupling vibrational factors into the selection rules, the transition becomes weakly allowed and able to compete with the time scale of fluorescence. Intersystem crossing leads to several interesting routes back to the ground electronic state. One direct transition is phosphorescence, where a radiative transition from an excited triplet state to a singlet ground state occurs. This is also a very slow, forbidden transition. Another possibility is delayed fluorescence, the transition back to the first excited singlet level, leading to the emitting transition to the ground electronic state.



**Fig. 5** Schematic of intersystem crossing leading to Phosphorescence emission

Other non-emitting transitions from excited state to ground state exist and account for the majority of molecules not exhibiting fluorescence or phosphorescent behavior. One process is the energy transfer between molecules through molecular collisions. Another path is through quenching, energy transfer between molecules through overlap in absorption and fluorescence spectrums. These are non-emitting processes that will compete with fluorescence as the molecule relaxes back down to the ground electronic state. In a Jablonski diagram, each of these processes is indicated with a curved line going down to on the energy scale.

### Time Scale

It is important to note that a Jablonski diagram shows what sorts of transitions that can possibly happen in a particular molecule. Each of these possibilities is dependent on the time scales of each transition. The faster the transition, the more likely it is to happen as determined by selection rules. Therefore, understanding the time scales each process can happen is imperative to understanding if the process may happen. Below is a table of time scales for basic radiative and non-radiative processes (Table 1).

**Table 1** Time scales for various processes

Transition	Time Scale	Radiative Process?
Absorption	$10^{-15}$ s	yes
Internal Conversion	$10^{-14}$ - $10^{-11}$ s	no
Vibrational Relaxation	$10^{-14}$ - $10^{-11}$ s	no
Fluorescence	$10^{-9}$ - $10^{-7}$ s	yes
Intersystem Crossing	$10^{-8}$ - $10^{-3}$ s	no
Phosphorescence	$10^{-4}$ - $10^{-1}$ s	yes

Each process outlined above can be combined into a single Jablonski diagram for a particular molecule to give an overall picture of possible results of perturbation of a molecule by light energy. Jablonski diagrams are used to easily visualize the complex inner workings of how electrons change eigenstates in different conditions. Through this simple model, specific quantum mechanical phenomena are easily communicated.

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### References

- [1] E. Wiedemann, "Über Fluoreszenz und Phosphoreszenz, I. Abhandlung" (On fluorescence and phosphorescence), *Annalen der Physik* 34 (1888) 446-463.
- [2] A.S. Shionoya, W.M. Yen (Eds.), *Phosphor Handbook*, CRC Press, Boca Raton, FL., USA, 1999.
- [3] S.W.S. Mckeever, *Thermoluminescence of Solids*, Cambridge University, Cambridge, 1985.
- [4] *Luminescence of Solids*, D.R. Vij (Ed.), Plenum Press, New York, 1998.
- [5] G.F.J. Garlick, *Luminescence Materials*, Clarendon Press, Oxford, 1949, p. 4.
- [6] G. Blasse, B.C. Grabmaier, *Luminescent Materials*, Springer Verlag, Berlin, 1994.
- [7] A.H. Kitai, *Solid State Luminescence*, Chapman & Hall, London, 1993.
- [8] T. Tsutsui, *Fundamentals of Luminescence*, in: A.S. Shionoya, W.M. Yen (Eds.), *Phosphor Handbook*, CRC Press, Boca Raton, FL., USA, 1999, pp. 63-64.

- 
- [9] Information available in the free encyclopedia, [www.wikipedia.com](http://www.wikipedia.com)
- [10] A. De Sio, J. Achard, A. Tallaire, R.S. Sussman, A.T. Collins, F. Silva, E. Pace, Electro-optical response of a single-crystal diamond ultraviolet photoconductor in transverse configuration, *App. Phys. Lett.* 86 (21)(2005)1-3.
- [11] A.T. Collins and Cheng-Han Ly, Misidentification of nitrogen–vacancy absorption in diamond, *J. Phys.: Condens. Matter* 14 (2002) L467-L471.
- [12] A.T. Collins, Spectroscopy of defects and transition metals in diamond: Diamond and related materials, 9 (3-6) (2000) 417 – 423.
- [13] M.D. Sastry, M. Gaonkar, S. Mane, S. Athavale, K.V.R. Murthy, S. Desai, H. Bagla, J. Panjekar, K.T. Ramchandran, Non-linear Optical Properties of Coloured Diamonds: Observation of frequency up-conversion, *Diamonds and Related materials*, 17 (2008) 1288-1291.
- [14] Ch.K. Babu, K.V.R. Murthy, B. Subba Rao, P. Sujitha, Synthesis and characterization of SrS:Eu,Ga Phosphor, *Int. J. on Science Innovations and Discoveries*, 2(3) (2012) 231-235.
- [15] Poisson, Jacques "Raphaël Dubois, from pharmacy to bioluminescence". *Rev. Hist. Pharm. (Paris)* (in French) (France) 58 (365) (2010) 51–56. ISSN 0035-2349. PMID 20533808.
- [16] E. Thomas & Williams Ltd., Original Types of Miners' Flame Safety Lamps, [Welshminerslamps.com](http://Welshminerslamps.com). 2013.
- [17] Samuel Smiles, *Lives of the Engineers. Volume III (George and Robert Stephenson)*. London: John Murray, 1862, 107. ISBN 0-7153-4281-9. (ISBN refers to the David & Charles reprint of 1968 with an introduction by L.T.C. Rolt).
- [18] Scott Kirkwood, "Park Mysteries: Deep Blue". *National Parks Magazine* (National Parks Conservation Association), Spring 2005, pp. 20–21, ISSN 0276-8186.
- [19] J.W. Hastings, Biological diversity, chemical mechanisms, and the evolutionary origins of bioluminescent systems, *J. Mol. Evol.* 19 (5) (1983) 309–321.
- [20] D. Tong, N.S. Rozas, T.H. Oakley, J. Mitchell, N.J. Colley, M.J. McFall-Ngai, Evidence for light perception in a bioluminescent organ, *Proceedings of the National Academy of Sciences of the USA*, 106 (24) (2009) 9836–9841.
- [21] R.E. Young, C.F. Roper, Bioluminescent countershading in midwater animals: evidence from living squid, *Science* 191 (4231) (1976) 1046–1048.
- [22] R.E. Young, Oceanic Bioluminescence: an Overview of General Functions, *Bulletin of Marine Science* 33 (4) (1983) 829–845.
- [23] S. Milius, Glow-in-the-dark shark has killer smudge, *Science News*, 1 Aug. 1998.
- [24] P. Vršanský, D. Chorvát, I. Fritzsche, M. Hain and R. Ševčík, Light-mimicking cockroaches indicate Tertiary origin of recent terrestrial luminescence, *Naturwissenschaften* 99 (9) (2012) 739–749.

- [25] Luiz Fernando Zagonel, Stefano Mazzucco, Marcel Tencé, Katia March, Romain Bernard, Benoît Laslier, Gwénolé Jacopin, Maria Tchernycheva, Lorenzo Rigutti, Francois H. Julien, Rudeesun Songmuang and Mathieu Kociak, Nanometer Scale Spectral Imaging of Quantum Emitters in Nanowires and Its Correlation to Their Atomically Resolved Structure, *Nano Letters*, 11 (2) (2011) 568–573.
- [26] F. J. García de Abajo, Optical excitations in electron microscopy, *Reviews of Modern Physics* 82 (2010) 209-275.
- [27] R. Sapienza, T. Coenen, J. Renger, M. Kuttge, N. F. van Hulst and A. Polman, Deep-subwavelength imaging of the modal dispersion of light, *Nature Materials* 11 (2012) 781–787.
- [28] B.G. Yacobi and D.B. Holt, *Cathodoluminescence Microscopy of Inorganic Solids*, Plenum, New York, 1990.
- [29] C. E. Norman, Reaching the Spatial Resolution Limits of SEM- based CL and EBIC, *Microscopy and Analysis*, Cambridge, UK, 16(2) (2002) 9-12.
- [30] C. M. Parish and P. E. Russell, Scanning Cathodoluminescence Microscopy, in: *Advances in Imaging and Electron Physics*, P. W. Hawkes (Ed.), 147 (2007) 1.
- [31] G.T. Reynolds, Lyoluminescence, *Journal of Luminescence*, 54(1) (1992) 43–69.
- [32] B.P. Chandra, Mechanoluminescence, in: *Luminescence of Solids*, D. R. Vij (Ed.), Plenum Press, New York, 1998, pp. 361-389.
- [33] B.P. Chandra, Mechanoluminescent Smart Materials and their Applications, in: *Electronic and Catalytic Properties of Advanced Materials*, A. Stashans, S. Gonzalez and H. P. Pinto (Eds.), Transworld Research Network, Trivandrum, Kerala, India, 2011, pp.1-37.
- [34] C. G. Camara, J. V. Escobar, J. R. Hird and S.J. Putterman, Correlation between nanosecond X-ray flashes and stick-slip friction in peeling tape, *Nature*, 455 (7216) (2008) 1089-1092.
- [35] B.P.Chandra, Mechanoluminescence and its applications, *Int. J. Luminescence and Applications* 2(3) (2012) 44-72.
- [36] E.G. Yukihiro and S.W.S. McKeever, *Optically Stimulated Luminescence: Fundamentals and Applications*, John Wiley & Sons Ltd., London, 2011.
- [37] G. Kocurek, M. Carr, R. Ewing, K.G. Havholm, Y.C. Nagar, A.K. Singhvi, White Sands Dune Field, New Mexico: Age, dune dynamics and recent accumulations. *Sedimentary Geology* 197 (2007) 313-331.
- [38] Y.S. Mayya, P. Morthekai, M.K. Murariand A.K. Singhvi, Modelling of the dose-rate variations with depth in the Martian regolith using EANT4, *Radiation Measurements* 41 (2006) 1032-1039.
- [39] P. Morthekai, J. Thomas, M.S. Pandian, V. Balaram, A.K. Singhvi, Variable range hopping mechanism in band-tail states of feldspars: A time-resolved IRSL study, *Radiation Measurements* 47 (2012) 857-863.



- 
- [40] Y.C. Nagar, M.D. Sastry, B. Bhushan, A. Kumar, K.P. Mishra, A. Shastri, M.N. Deo, G. Kocurek, J.W. Magee, S.K. Wadhawan, N. Juyal, M.S. Pandian, A.D. Shukla, A.K. Singhvi, Chronometry and formation pathways of gypsum using Electron Spin Resonance and Fourier Transform Infrared Spectroscopy, *Quaternary Geochronology* 5(6) (2010) 691-704.
- [41] V. Pagonis, M. Jain, A.S. Murray, C. Ankjaergaard, R. Chen, Modeling of the shape of infrared stimulated luminescence signals in feldspars, *Radiation Measurements* 47 (2012) 870-876.
- [42] A.K. Singhvi, S. Stokes, N. Chauhan, Y. Nagar, M.K. Jaiswal, Changes in natural OSL sensitivity during single aliquot regeneration procedure and their implications for equivalent dose determination, *Geochronometria* 38 (2011) 231-241.
- [43] S.J. Puttermann, Sonoluminescence: Sound into Light, *Scientific American*, 1995, pp. 32-37.
- [44] Y.T. Didenko, W.B. McNamara, K.S. Suslick, Effect of Noble Gases on Sonoluminescence Temperatures during Multibubble Cavitation, *Physical Review Letters* 84 (4) (2000) 777-780.
- [45] David J. Flannigan and Kenneth S. Suslick, Plasma formation and temperature measurement during single-bubble cavitation, *Nature* 434 (7029) (2005) 52-55.
- [46] R. Chen and Y. Krish, Analysis of thermally stimulated processes, Pergamon Press, London, 1981.
- [47] R. Chen and S.W.S. McKeever, Theory of Thermoluminescence and Related Phenomena, World Scientific, Singapore, 1997.
- [48] M. J. Atkin, Archaeological Dating, Academic Press, New York, USA, 1985.
- [49] K.V.R. Murthy and T.R. Joshi, Natural Thermoluminescence of zeolites mineral (Scolecite), Thermoluminescence and its Applications, TaTa McGraw Hill Co. Ltd., 1992, pp. 22-24.
- [50] K.V. R. Murthy, Phase Change Thermoluminescence, Luminescence and its Applications, in: K.V.R. Murthy, T.R. Joshi and L.H. Prasad (Eds.), Proceedings of International Conference on Luminescence and its Applications (ICLA-2000), Luminescence Society of India, Vol. I (2000) 212-214.
- [51] Rahul Ghildyal, Ph.D. Thesis submitted to Faculty of Applied Science & Technology, M. S. University of Baroda, 2008.
- [52] Pallavi S. Page, Ph.D. Thesis submitted to Faculty of Applied Science & Technology, M. S. University of Baroda, 2009.
- [53] K.V.R. Murthy and J.N. Reddy, Thermoluminescence basic theory application and experiment, Publ. Nucleonix, Hyderabad, India, Feb. 2008, pp. 1-72, [www.nucleonix.com/manuals/tld%20exp%20man.pdf](http://www.nucleonix.com/manuals/tld%20exp%20man.pdf)

- [54] D. Curie, Luminescence in Crystals, 3rd ed., John Wiley & Sons Inc., New York, 1963.
- [55] A. Lakshmanan, Luminescence and display Phosphors: Phenomena and Applications, Nova Science Publ. New York, USA, 2008.
- [56] Aleksander Jablonski, Jablonski diagram write up available on <http://chemwiki.ucdavis.edu>

## **Luminescence Related Phenomena and their Applications**

10.4028/www.scientific.net/DDF.347

## **Luminescence Phenomena: An Introduction**

10.4028/www.scientific.net/DDF.347.1

### **DOI References**

- [1] E. Wiedemann, Über Fluorescenz und Phosphorescenz, I. Abhandlung, (On fluorescence and phosphorescence), *Annalen der Physik* 34 (1888) 446-463.  
<http://dx.doi.org/10.1002/andp.18882700703>
- [11] A.T. Collins and Cheng-Han Ly, Misidentification of nitrogen-vacancy absorption in diamond, *J. Phys.: Condens. Matter* 14 (2002) L467-L471.  
<http://dx.doi.org/10.1088/0953-8984/14/25/105>
- [30] C. M. Parish and P. E. Russell, Scanning Cathodoluminescence Microscopy, in: *Advances in Imaging and Electron Physics*, P. W. Hawkes (Ed. ), 147 (2007) 1.  
[http://dx.doi.org/10.1016/S1076-5670\(07\)47001-X](http://dx.doi.org/10.1016/S1076-5670(07)47001-X)
- [37] G. Kocurek, M. Carr, R. Ewing, K.G. Havholm, Y.C. Nagar, A.K. Singhvi, White Sands Dune Field, New Mexico: Age, dune dynamics and recent accumulations. *Sedimentary Geology* 197 (2007) 313-331.  
<http://dx.doi.org/10.1016/j.sedgeo.2006.10.006>
- [38] Y.S. Mayya, P. Morthekai, M.K. Murariand A.K. Singhvi, Modelling of the dose-rate variations with depth in the Martian regolith using EANT4, *Radiation Measurements* 41 (2006) 1032-1039.  
<http://dx.doi.org/10.1016/j.radmeas.2006.08.004>
- [39] P. Morthekai, J. Thomas, M.S. Pandian, V. Balaram, A.K. Singhvi, Variable range hopping mechanism in band-tail states of feldspars: A time-resolved IRSL study, *Radiation Measurements* 47 (2012) 857-863.  
<http://dx.doi.org/10.1016/j.radmeas.2012.03.007>
- [41] V. Pagonis, M. Jain, A.S. Murray, C. Ankjaergaard, R. Chen, Modeling of the shape of infrared stimulated luminescence signals in feldspars, *Radiation Measurements* 47 (2012) 870-876.  
<http://dx.doi.org/10.1016/j.radmeas.2012.02.012>
- [42] A.K. Singhvi, S. Stokes, N. Chauhan, Y. Nagar, M.K. Jaiswal, Changes in natural OSL sensitivity during single aliquot regeneration procedure and their implications for equivalent dose determination, *Geochronometria* 38 (2011) 231-241.  
<http://dx.doi.org/10.2478/s13386-011-0028-3>