Chapter - I

• INTRODUCTION
Luminescence

Luminescence is broadly defined as the emission of electromagnetic radiation by various materials in excess of thermal radiation. These types of materials are known as luminescent materials. Luminescent materials are also known as phosphors.

There are hundreds of phosphors, including some natural minerals and some biological compounds and new phosphors are being discovered or synthesized in laboratories throughout the world due to their utilization in many devices of importance [1].

The word 'phosphor' was invented in the early 17th century and its meaning remains unchanged. It is said that an alchemist, V. Casciarlo of Bologna, Italy, found a heavy crystalline stone with a gloss at the foot of a volcano, he fired it in a charcoal oven intending to convert it into a noble metal. Casciarlo obtained no metal but found that the sintered stone emitted red light in the dark after exposure to sunlight. This stone was called as 'Bolognian stone'. From the knowledge now known, the stone found appears to have been Barite (BaSO₄), with the fired product being BaS, which is known to be a host for phosphor materials.

After that, similar findings were reported from many palaces in Europe and these light emitting stones were named as 'phosphors'. This word means 'light bearer' in Greek and appears in Greek myths as the personification of the morning star Venus.

Prior to the discovery of Bolognian stone, the Japanese were reported to have prepared phosphorescent paint from seashells. This fact is described in a 10th century Chinese document. The credit of preparing phosphor for first time should fall to the Japanese [2].
The scientific research on phosphors has a long history going back more than hundred years. Theodore Sidot, a young French chemist, was first one who prepared the ZnS type phosphors accidentally in 1866 [3,4]. It seems that this marked the beginning of scientific research and synthesis of phosphors.

From the 19th century to the early 20th century, Philip, E.A. Lenard and co-workers in Germany made active and extensive research on the phosphor and achieved impressive results [5]. They prepared various kinds of phosphors based upon alkaline earth chalcogenides, ZnS and various phosphors by using rare earth metals as activators also.

Since the end of World War II, research on phosphors has evolved dramatically. Research on these materials have been supported by progress in solid state physics, especially semiconductors and lattice defect physics, advances in the understanding of the optical spectroscopy of solids, especially that of transition metals ions and rare-earth ions.

**Origin of luminescence [6]**

Luminescence is originated by the radiative transitions between two states of atomic, molecules, or extended molecular systems. A radiative transition is one in which the energy released in the form of photon. The nature of photon, the emission, depends on the nature of the initial and final state and the route to the excited state. The radiative luminescence takes places when the electronic transitions from the lowest excited state of singlet or triplet to the ground state as represented in Fig 1. The radiative transition from singlet to ground state is a spin allowed transition and
Fig. 1: Various radiative and non-radiative process in solid.

<table>
<thead>
<tr>
<th>Electronic states</th>
<th>Transitions</th>
<th>Lifetime, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_0 ) = ground singlet state</td>
<td>( A ) = absorption to excited states</td>
<td>( 10^{-15} )</td>
</tr>
<tr>
<td>( S_1 ) = first excited singlet state</td>
<td>( VD ) = vibrational deactivation</td>
<td>( 10^{-13} ) to ( 10^{-11} )</td>
</tr>
<tr>
<td>( S_2 ) = second excited singlet state</td>
<td>( IC ) = internal conversion</td>
<td>( 10^{-12} ) to ( 10^{-11} )</td>
</tr>
<tr>
<td>( T_1 ) = first excited triplet state</td>
<td>( F ) = fluorescence</td>
<td>( 10^{-8} )</td>
</tr>
<tr>
<td>( T_2 ) = second excited triplet state</td>
<td>( IX ) = intersystem crossing</td>
<td>( 10^{-8} ) to ( 10^{-7} )</td>
</tr>
<tr>
<td>EVS = excited vibrational states</td>
<td>( P ) = phosphorescence</td>
<td>( 10^{-4} ) to several ( \xi \times )</td>
</tr>
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</table>
therefore the time scale of the transition is of order of a few nanoseconds. This type of radiative transition is known as fluorescence.

But the emission due to transition triplet to ground state is much larger, ranging from micro to several seconds because the process is spin forbidden. In this transition form excited to ground state passes via triplet state or singlet to triplets to ground state. This type of luminescence is called phosphorescence. The radiation emitted by phosphor materials may fall in UV, visible and in infrared region [7] shown in Fig [1].

Luminescence may be divided into two kinds on the basis of emission[8]:

1. Fluorescence
2. Phosphorescence

**Fluorescence**

Emission of light by the materials halts abruptly on removal of exciting source. There is no after glow. All the varieties of fluorescence are due to the regeneration of electron-hole pairs in a semiconductor under excitation. The average life time of electron-hole pairs is a small fraction of millisecond (10^{-8} to 10^{-3} sec) and this explain why the process does no longer emission after stimulation ceases. This process is known as antistock phenomena.

Fluorescence is of three types:

(i) Photofluorescence
(ii) Electrofluorescence
(iii) Cathodofluorescence
Phosphorescence

The emission of light by the materials which continues for a considerable time after the excitation source has been withdrawn, up to several seconds or even minutes. The wavelength of the luminescent radiation is always longer than that of the exciting radiation. This phenomena is continued for long time because electron hole pairs exist for longer, due to a mechanism called trapping, in which a atom can be held in a metastable state.

Phosphorescence can be produced by some methods:

(i) Materials that emit light upon stimulation by other light. This type of phenomena is called photoluminescence. The stimulating light usually has higher energy than the emitted light. This phenomenon is used in plasma display devices and common fluorescent lamps.

(ii) Phenomena during which some materials emit light upon stimulation by an electric field are called electrophosphorescence. These phenomena are used for thin film and thick film electroluminescent displays, back light for liquid crystal displays and electroluminescent lamps used in the wristwatch and in many other display devices.

(iii) Materials that emit light by the stimulation of electron bombardment. This type of phenomena is known as cathodophosphorescence. This phenomenon is used in cathode ray tubes and field emission displays.
Luminescence is also categorized by the method of initiation [6]

(a) Photoluminescence: When the excited state is generated by the absorption of the photons emits radiation then the process is known as photoluminescence. Excitation can be either a single or multiphoton process. Many nonluminescent materials can be made luminescent by suitable and highly selective chemical reactions. This phenomenon is used in fluoro-immuno assay, radio-immuno assay and in quantitative analysis.

(b) Chemiluminescence: Process in which the radiation emitted from an excited state, which is generated from the energy released in a chemical reaction (excluding flame) is known as the chemiluminescence. It is first discovered by Brand in 1669, on the air–oxidation of phosphorus.

Applications of chemiluminescence are diverse. They are commercial emergency lights that require only the breaking of a seal to permit the mixing of solution. Long-lived chemiluminescence is bright enough to read.

(c) Bioluminescence: Bioluminescence is a type of chemiluminescence process arising from a living matter. Although grouped separately, these are actually chemiluminesences in which the reactants are produced by and organized in living organisms.

Fireflies and ship's wake are best examples. Fireflies glow due to the enzymatic oxidation of the protein luciferin. Bioluminescence has had a crucial role in direct studies of cellular and biochemical processes.
(d) Electroluminescence: Electroluminescence occurs on electron flow in a solid state device or electrochemical cell. This phenomena is used in various industrials uses like, light emitting diodes, film type semiconductor devices and many more.

(e) Cathodoluminescence: The luminescence arising in gas or low-pressure electrical discharges, due to either in electrical discharge itself or on the electrode or targets is known as cathodoluminescence. It forms the basis of innumerable devices used in TV's, Atomic Absorption Spectrophotometer, advertising signs and discharge lighting etc.

(f) Radioluminescence: The luminescence which arise from interactions between ionizing radiation and matter is called radioluminescence. The radiation may be particles such as $\alpha$, $\beta$, $\gamma$ or cosmic rays, photon or X-rays. Materials exhibiting radioluminescence are also called scintillators. Scintillators are used in many devices which are used in medical diagnosis.

(g) Thermoluminescene: Luminescence that arises on gentle warming of a material and usually occurs below incandescence is known as thermoluminescence. These materials can, however be reactivated and used separately.

(h) Others type of luminescence

(i) Triboluminescence:

The phenomena of emission of radiation by crystals when they are broken or grouped up are called the triboluminescence. The observed luminescence is then a mechanically induced cathodoluminescence.
(ii) **Crystalloluminscence**:  
The luminescence developed during the growth of crystal and may arises from cleavage is known as the crystalloluminscence.

(iii) **Sonoluminescence**:  
Process in which emission of radiation takes place when liquids subjected to intake ultra sounds is called sonoluminescence.

**Theory of luminescence**

**Absorption, Relaxation and Radiative decay:**  
The process of absorption, relaxation and emission occurring in a phosphor is often schematically illustrated in a configuration coordinate diagram, such as shown in Fig. 2. The ordinate is the energy of the system consisting of the activator impurity ion and its surrounding ions, whereas the abscissa is an interaction coordinate that defines the configuration of the surrounding ions. In the process of absorption, activator center is raised to an excited electronic state. Because electronic transition is fast as compared to the time required for lattice relaxation in the Frank-Condon principle the transition is vertical.

The difference between the minimum in the parabola of the ground state and the minimum in the parabola of the excited state is measured by $\Delta Q$. If $\Delta Q$ is large as in the Fig. 2a, the size and shape of the defect or impurity differ significantly from the ground state. Absorption occurs to many vibrational levels $v$ of the excited state and the probability per unit time for absorption from ground state vibrational level $g_v$ to a given vibrational level of the excited state $e_v$ is given by the time dependent perturbation theory (Fermi Golden Rule) [9].
\[ P(g_v \rightarrow e_v) = \frac{(2\pi)^2}{h^2} \left| \int \psi_g R \psi_e dr \right|^2 \int x_v x_v dr \right|^2 \delta(\Delta E - \hbar \nu) \]  

(1)

Where \( \Delta E \) is the energy difference, \( \nu \) the radiation frequency and \( h \) the Planck constant. The first factor is the square of the radiation matrix element connecting the ground and excited state electronic wave functions. Assuming parabola ground and excited state configuration-coordinate curves and adiabatic approximation, the absorption and emission band shapes illustrated in Fig. 2 have been calculated. In the case of certain defect centers at low temperature, the vibronic progression indicated in the figure can be seen and the vibrational frequencies associated with the defect center or host lattice can be identified. In other centers, the no phonon line and a broad band are observed at low temperatures. However in most cases, \( \Delta Q \) is too large to observe the no-phonon line even at low temperatures. In addition, vibronic coupling occurs to many vibrational modes, with the result that only the envelope of the vibronic transitions indicated by dashed line is observed. A smooth Gaussian-shaped band is observed in absorption and emission.

Examples of broad band absorbing and emitting phosphor are those that undergo interconfigurational electronic transitions in absorption or emission. Important broad band activators include Sb(III), Pb(II), Bi(III), and Sn(II) which undergo \((ss) \rightarrow (sp)\) transitions; Eu(II) and Ce(III) which have \(f \rightarrow d\) transitions; and Cu (II) which undergoes \(s \rightarrow d\) transitions. The anions \( \text{VO}_4^{3-} \), \( \text{WO}_6^{2-} \), and \( \text{UO}_6^{2-} \), undergo charge transfer transitions in both absorption and emission. Transition metal ions, such as Mn(II), Mn(IV), Fe(III), and Cr(II) give also broad band emission when they undergo \((t \rightarrow e)\) transitions.
Because the positions of the absorption and emission bands are a sensitive function of $\Delta Q$, they can vary greatly, depending on the choice of the host matrix. The emission bands of Eu(II) and Ce(III), for example vary from the near ultraviolet to the yellow region of the spectrum with different host matrices.

After absorbing a photon, the impurity center undergoes severe enharmonic vibrational motion. The weak electromagnetic radiation that occurs during this relaxation is called hot luminescence. Relaxation generally occurs within less than one hundred lattice vibrations or tens of picoseconds with the result that hot luminescence can be detected only by measuring the radiation emitted within picoseconds after excitation. Ordinary luminescence takes place after the exited state has relaxed and established thermal equilibrium, emission occurring from the lowest vibrational levels of the excited state. The ordinary luminescent emission band occurs at energy less than the absorption band so-called Stokes shift. The energy differences are converted to lattice vibrational energy or heat.

In sharp contrast to the broad band emitters and absorbers, are the intraconfiguration $f-f$ transitions among the rare earth and actinide activators and certain spin flip intraconfiguration transitions in transition metals activators. For these transitions $\Delta Q \approx 0$ that is, there is little difference in the size or shape of the defect in its ground and excited state (Fig. 2b). The absorption and emission occur mainly to and from the no-phonon line. The width of the narrow band or line is determined mainly by inhomogeneous broadening, i.e, different activator-ion environments. Weak vibrational structure may accompany a narrow band absorption or emission.
Fig. 2: General configuration co-ordinate diagrams.

(a) For band absorbers and emitters
(b) Represents narrow-band or line emitters
In a real phosphor, absorption may occur to many excited state parabolas and is followed by relaxation and intersystem crossing until the excitation is trapped at an excited state minimum. Configuration coordinate diagrams can be constructed from careful measurements of the optical properties of phosphors. Approximate configuration coordinate diagrams can be calculated using molecular orbital theory, assuming a molecular cluster consisting of the activator and its surrounding atoms.

**Non-radiative decay:**

To have any technical importance, a luminescent material should have a high quantum efficiency which is the ratio of the number of quanta emitted to the number of quanta absorbed. Phosphors used in fluorescent lamps usually have quantum efficiencies of at least 0.75.

All the quanta absorbed would be remitted if there were no nonradiative losses. Nonradiative processes are illustrated in Fig. 3. Classically, the occurrence of nonradiative losses is explained by assuming that at sufficiently high temperatures the emitted state could relax to the ground state via the crossover at B of the two parabolas [10]. In fact, for many broad band emitting phosphors the temperature dependence of the nonradiative decay rate \( P_{(nr)} \) can be fitted with an activation energy,

\[
P_{(nr)} = A \exp(-E^*/kT)
\]  

(2)

However, the occurrence of nonradiative processes is better explained using the time dependent perturbation theory by substituting a nonradiative interaction operator in place of the radiation interaction in an equation 1. Direct energy transfer can occur to high vibrational levels of the ground state via any of the dashed arrows.
C shown in Fig. 3 or over the activation barrier marked by the solid arrow A. The important terms in equation 1 is the squared vibrational overlap integral weighted by thermal populations. The nonradiative decay rate by a path C can be orders of magnitude greater than the radiative decay rate, even at moderate temperatures, when only the lowest vibrational levels of the excited state are significantly populated [11].

For narrow band emitters, such as the rare earth activators, equation 1 can be shown to give a nonradiative decay rate that depends exponentially on the energy gap between two levels.

\[ P_{(nr)} = A \exp(-\Delta E) \]  

(3)

If the magnitude of E is less than a few phonon frequencies, raditionless relaxation always occurs. The exponential energy gap law holds well for some rare earth f-f transition [12].

However, although the temperature dependence of the nonradiative decay rate and it's dependence on the energy separation of the two parabolas is in good agreement with theory, a quantitative understanding of the important phenomenon of raditionless decay appears useless [13]. Even the nature of the nonadiabatic interaction between an emitting state and the ground state vibranic is unknown. Energy transfer to the ground state parabola may occur at a very high vibrational level and anharmonicity in the ground state has a large influence on the vibrational overlap integral. A simple Morse curve gives non-radiative decay rate orders of magnitude greater that the harmonic values [10].
Fig. 3: A configuration-coordinate diagram showing the mechanisms of radiation less decay to the ground state. Non-radiative decay to the ground state vibrational manifold can occur via the path A→B or A→C. The dashed line represents a Morse curve ground state potential.
Energy transfer:

In addition to either emitting a photon or decaying nonradiatively to the ground state, an excited defect center may also transfer energy to another center either radiatively or nonradiatively, as in Fig. 4. The ion that transfers energy is called a sensitizer.

Radiationless energy transfer is induced by an interaction between the state of the system in which the sensitizer S is in its excited state and the activator A in the ground state, and the state in which the activator is excited and the sensitizer is in the ground state. The probability per unit time for energy transfer is:

\[ P(S \rightarrow A) = \frac{(2\pi)^2}{\hbar^2} \int \psi_s^* \psi_A^* V |\psi_A^g \psi_s^g| dr \int f_s^{em} f_A^{abs} dv \]  

(4)

The frequency integral represents the overlap of the emission band of the sensitizer and the absorption band of the activator.

In the presence of energy transfer, the emission decay \( I(t) \) of a sensitizer ion is shortened:

\[ I(t) = I(0) \exp[-P_{(rad)}t - P(S \rightarrow A)t] \]  

(5)

where \( P_{(rad)} \) is the probability for decay in the absence of energy transfer. The measured luminescence decay is a statistical average of equation 5 over different sensitizer ions. The interaction \( V \) is usually expanded in terms of the distance between the sensitizer and activator ions giving rise to dipole-dipole (1/R^6), dipole-quadrupole (1/R^8) and quadrupole-quadrupole (1/R^10) contributions. The luminescence yield and decay of sensitizer emission in the presence of energy by each of the above mechanisms has been derived [14,15]. An exchange interaction
Fig. 4: A systematic diagram showing energy transfer from S to a activator A, followed by the emission from the activators.
caused by the overlap of the wave functions on the sensitizer and activator ions that varies approximately as exp (-cR ) can be lattice energy transfer [16]. Because of the importance of radiationless energy transfer in many commonly used phosphors, energy transfer mechanisms have been studied extensively in the past.

For example, in halophosphate phosphors, energy transfer occurs from Sb(III) centers, which absorb most of the UV radiation from the mercury discharge, to manganese ions. The intensity of the manganese emission is determined by the concentration and is adjusted to give a suitable white light. Fig 5 shows the quantum yield of the antimony emission versus manganese concentration. Fig. 6 shows the decay curve for antimony emission. A careful measurement of the decay curve shows that energy transfer occurs via an exchange mechanism rather than the longer range dipole-dipole or dipole-quadrupole mechanisms [17]. On the other hand, rare earth centers generally transfer energy by dipole and quadrupole mechanisms.

In some phosphors, energy transfer occurs within the sensitizer system which can be the host lattice. Energy transport by migration through the lattice occurs, for example, in the important red emitting phosphor YVO₄:Eu(III), short and long range of uv radiation is absorbed near the surface of the phosphor particle and then undergoes a random walk from one vanadate group to an adjacent group until transfer occurs to near by Eu(III); that this is the correct model can be shown by adding phosphate to give Y(VO₄)PO₄:Eu(III). Increasing the phosphate concentration increases the amount of energy emitted by the vanadate group relative to that transferred to Eu(III).

If significant energy transfer occurs within the activators system, the excitation migrates through the lattice until it reaches sites in the lattice where the
Fig. 5: The relative numbers of quanta emitted by antimony in calcium fluorescent phosphors as a function of manganese concentration. Also shown are theoretical curves assuming dipole-dipole, dipole-quadrupole and exchange mechanisms of energy transfer.

Fig. 6: The decay of antimony emission is shown in a phosphor containing 1.84 atom % manganese.
energy can be lost nonradiatively. This occurs in many phosphors once the activator concentration is increased above a critical concentration and is known as concentration quenching.

Finally, energy transfer through an excitation has been studied, at least theoretically. The exciting photon excites not a single defect center but a wave function that is a linear combination of the defect center wave functions.

**Representation of phosphors:**

Generally the phosphor have two parts, one is the host lattice and another part is impurity which also known as luminescent center or dopant. Dopants are present in very low concentration levels varying from few ppm upto one or two percent of the host lattice. These are main localized centers for luminescence of the phosphor materials. The phosphor is represented in a formula as given below:

\[ \text{Ab:D,C(0.02)} \]

Phosphors consisting host lattice represented as Ab and active center or dopant represented as D, in bracket its concentration in moles is mentioned and C is the co-activator. In a formula represented as for example-

\[ \text{ZnS:Cu,Cl(0.02), here ZnS is host lattice, Cu is activator whose concentration is 0.02 moles, Cl is a co-activator.} \]

**Mechanism for phosphorescence**

Phosphor consists essentially of highly purified inorganic materials doped with small quantities of suitable additives called dopant or activator. The activator is usually present in concentration levels varying from few ppm upto one to five moles of the host lattice. Some of the phosphor have more than one activators. In these cases, the
term co-activator may be used in such cases. In addition, the phosphor particles can be lightly milled to remove agglomerates and can be further annealed to increase crystallinity of the particles, possibly in the presence of fluxing agent.

Light of different colours can be produced from the same phosphor by introducing different dopant or activators. This enables the production of colour TV cathode ray tubes, where three separate electron beams are aimed at a pattern of especially doped phosphor dots coated on the inside of the screen.

Most of the phosphors are the inorganic materials. More recently, phosphor powders have been utilized in many advanced display devices that provide illumination. But there are a number of requirements for phosphor powders, which can vary depending upon the specific application of the powder. Generally the phosphor powders should have one or more of the following properties; high purity; high crystallinity; small particle size distribution; spherical morphology; homogenous distribution of the activator ion; good dispersibility and low porosity.

The proper combination of the foregoing properties result in a phosphor powder with high luminescent intensity and long life that can be used in various applications. It is also advantageous for many applications to provide phosphor powders that are surface coated, such as with a thin uniform dielectric or semiconducting coating.

Almost all the phosphors are synthesized by the solid state reaction between raw materials at high temperature. In this process the high purity phosphor precursor materials mixed in the solid state (host, activators, flux) and blended all the component regularly and heated in furnace so that the precursors react and form a powder of the phosphor materials.
The resulting phosphor is broken up or crushed into smaller particles. Solid state route and many other production methods, utilize such as grinding step to reduce the particle size of the powder. Excess mechanical grinding damage the surface of the phosphor, which inhibit the brightness of the phosphor powder [18].

**Luminescent properties of a phosphor**

Generally the phosphor have two parts, one is host lattice whose concentration maximum may be 99.98% and another part is impurity which also known as active center or activator or luminescent center or dopant. Dopants are present in a very low concentration level varying from few ppm upto one or two percent of the host lattice. These are main localized center for luminescence of the phosphor materials.

Most phosphor have localized luminescent centers and contain a far longer variety of ions than delocalized centers. The localized centers of different types can be classified by their electronic transitions as follows [19]:

(Below, an arrow to the right indicates optical absorption and to the left indicates, emission)

1. $2s \rightarrow 2p$; an example is an F center.
2. $ns^2 \rightarrow nsnp$; this group includes Ti$^+$-type ions, Ga$^+$, In$^+$, Ti$^+$, Ge$^{2+}$, Sn$^{2+}$, Pb$^{2+}$, Sb$^{3+}$, Bi$^{3+}$, Cu$^+$, Ag$^+$, Au$^+$, etc.
3. $3d^{10} \rightarrow 3d^0 4s$; Ag$^+$, Cu$^+$, Au. Acceptors in IIb-VIb compounds are not including in this group.
4. $3d^n \rightarrow 3d^n$, $4d^n \rightarrow 4d^n$ $1^{st}$ and $2^{nd}$ row transition metals ions from this group.
5. $4f^n \rightarrow 4f^n$, $5f^n \rightarrow 5f^n$ rare earth and actinides ions.
6. \(4f^n \leftrightarrow 4f^{n-1}5d\) Ce\(^{3+}\), Sm\(^{2+}\), Eu\(^{2+}\), Tm\(^{2+}\), Yb\(^{2+}\), only absorption transition observed for Pr\(^{3+}\) and Tb\(^{3+}\).

7. A charge transfer transition or transition between an anion p electron and an empty cation orbital. Examples are intramolecular transitions in complexes such as VO\(_4^{3-}\), WO\(_4^{3-}\), and MoO\(_4^{3-}\).

8. \(\pi \rightarrow \pi^*\) and \(n \rightarrow \pi^*\) organic molecules having \(\pi\) electrons make up this group. The notation \(n\) indicates a nonbonding electron of a heteroatom in an organic molecule.

**Rare earth's as activator**

The largest area of advancement in phosphor materials has been the use of rare earths as activators. In the last decades, a large number of phosphors based on rare earth as activators in different host lattices had been invented. Rare earth activators have permitted the use of highly specific spectral distribution with the efficacy required for commercial use. However, they are costly but have provided benefits for phosphors that justify their uses. Because of their huge demand in industrial and commercial use, the chemical technology for preparation and purification of these compounds has been improved greatly, providing consistent and reliable materials in purity levels required for efficient phosphor absorption and emission.

The rare earth are 15 elements from lanthanum to lutetium. The electronic configuration of trivalent rare earth ions in the ground state shown in the table 1.

The lanthanides from Ce to Lu have one to fourteen 4f electrons added to their inner shell configuration. Ions with no 4f electrons, i.e Sc, Y, La and Lu have
TABLE 1: Electronic configuration of different trivalent lanthanides in ground state.

<table>
<thead>
<tr>
<th>Atomic number</th>
<th>Ions</th>
<th>Corresponding element</th>
<th>4f electrons</th>
<th>S</th>
<th>L</th>
<th>J</th>
<th>ΣS</th>
<th>ΣL</th>
<th>Σ(L+S)</th>
</tr>
</thead>
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<tr>
<td>21</td>
<td>Sc³⁺</td>
<td>Ar</td>
<td>↑</td>
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<td>0</td>
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<tr>
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<td>Y³⁺</td>
<td>Kr</td>
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<td>4</td>
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<td>3</td>
<td>5/2</td>
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<tr>
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<td>Xe</td>
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<td>9/2</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
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<td>Ce³⁺</td>
<td>Xe</td>
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<td>0</td>
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<td>6</td>
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<td>Nd³⁺</td>
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<td>Pm³⁺</td>
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<tr>
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</tr>
<tr>
<td>66</td>
<td>Dy³⁺</td>
<td>Xe</td>
<td>↑↑↑↑↑↑↑↑↑↑↑↑↑↑</td>
<td>5/2</td>
<td>5</td>
<td>5/2</td>
<td>3</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>67</td>
<td>Ho³⁺</td>
<td>Xe</td>
<td>↑↑↑↑↑↑↑↑↑↑↑↑↑↑</td>
<td>5/2</td>
<td>5</td>
<td>5/2</td>
<td>3</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>68</td>
<td>Er³⁺</td>
<td>Xe</td>
<td>↑↑↑↑↑↑↑↑↑↑↑↑↑↑</td>
<td>5/2</td>
<td>5</td>
<td>5/2</td>
<td>3</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>69</td>
<td>Tm³⁺</td>
<td>Xe</td>
<td>↑↑↑↑↑↑↑↑↑↑↑↑↑↑</td>
<td>5/2</td>
<td>5</td>
<td>5/2</td>
<td>3</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>70</td>
<td>Yb³⁺</td>
<td>Xe</td>
<td>↑↑↑↑↑↑↑↑↑↑↑↑↑↑</td>
<td>5/2</td>
<td>5</td>
<td>5/2</td>
<td>3</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>71</td>
<td>Lu³⁺</td>
<td>Xe</td>
<td>↑↑↑↑↑↑↑↑↑↑↑↑↑↑</td>
<td>5/2</td>
<td>5</td>
<td>5/2</td>
<td>3</td>
<td>3</td>
<td>6</td>
</tr>
</tbody>
</table>
no electronic levels that can induce excitation and luminescence processes in or near the visible region.[20-22]

In contrast, the ions from Ce to Yb, which have partially filled 4f orbitals, have energy levels characteristic of each ion and show a variety of luminescence properties around the visible region. Many of these ions can be used as activators in phosphors for using different lattices.

The characteristic energy levels of 4f electrons of trivalent lanthanides ions have been precisely investigated by Dieke and co-workers, which is known as Dieke diagram [23] as given in Fig. 7.

The levels were determined experimentally by considering the optical spectra of individual ions in host crystal. This diagram is applicable to ions in almost any environment because the maximum variation of the energy levels is, at most, of the order of several hundred cm$^{-1}$.

The rare-earth ions show 4f$^{n-1}$5d$^1$ states and charge transfer states [24]. Both of these show allowed strong optical absorptions. The energy of the 4f$^{n-1}$5d$^1$ and charge transfer states are more dependent on their environments [22, 24-33] than the energy of 4f states, but the relative order of the energies of these states are found to be the same for the whole series of rare-earth ions in any host materials [22, 24-33].

The 4f$^{n-1}$5d transition in Ce$^{3+}$, Pr$^{3+}$, Tb$^{3+}$ and the charge transfer state absorptions in Eu$^{3+}$ and Yb$^{3+}$ have energies less than ca 40×10$^{-13}$ cm$^{-1}$. Therefore, they interact with 4f levels, leading to f-f emissions. In case the energy level of these states are lower than those of 4f levels, direct luminescence from these levels are found, such as 5d-4f transition in Ce$^{3+}$, Pr$^{3+}$ and Eu$^{2+}$. Spectra of this luminescence vary as a result of crystal field splitting in host crystals [34-90].
Fig. 7: Different energy levels of trivalent lanthanides ions.
The tetravalent ions such as Ce$^{4+}$, Pr$^{3+}$ and Tb$^{4+}$ show the same luminescence as in the La$^{3+}$, Ce$^{3+}$, Gd$^{3+}$.

**LUMINESCENCE OF RARE-EARTH’S**

1. **Ce$^{3+}$**

Among all the lanthanide ions, the 4f – 5d transition energy is lowest in Ce$^{3+}$, but the energy gap between the 5d states to the nearest level $^{2}\text{F}_{7/2}$ is so large that the 5d level serves as an efficient light emitting state. Luminescence photon energy depends strongly on the structure of the host crystal through the crystal-field splitting of 5d state. The Ce$^{3+}$ activated phosphors show generally two emission peaks are due to two terminating, levels $^{2}\text{F}_{5/2}$ and $^{2}\text{F}_{7/2}$ [91]. The decay time of Ce$^{3+}$ emission in $10^{-7}$ to $10^{-8}$ sec [92].

For example in a phosphor with structural formula Y$_2$SiO$_5$: Ce$^{3+}$, Tb$^{3+}$ is Ce$^{3+}$ activated which is used in flying spot scanners.[93-95]

2. **Pr$^{3+}$**

Luminescence of Pr$^{3+}$ consists of many multiplets, as follows:

515 nm ($^{3}\text{P}_0 \rightarrow ^{3}\text{H}_4$),~670nm ($^{3}\text{P}_0 \rightarrow ^{3}\text{F}_2$), ~770m, ($^{3}\text{P}_0 \rightarrow ^{3}\text{F}_4$), ~ 630 nm ($^{1}\text{D}_2 \rightarrow ^{3}\text{H}_4$), ~ 410 nm ($^{1}\text{S}_0 \rightarrow ^{1}\text{I}_6$), and ultraviolet (5d→4f) transitions. The relative intensities of peaks depend upon the host crystals. An example of this type is Y$_2$O$_2$ S: Pr$^{3+}$ [96] and it emits light at 670 nm which is due to emission from $^{3}\text{P}_0$ to $^{3}\text{F}_2$. 
3. **Nd$^{3+}$**

The Nd$^{3+}$ ions give the following transitions in the infrared region when used as activator. These peaks are reported when Nd$^{3+}$ is used in Y$_3$N$_5$O$_{12}$ : Nd$^{3+}$ [97]. Peaks between 870 – 950 nm due to $^4F_{\frac{5}{2}} \rightarrow ^4I_{\frac{11}{2}}$; between 1050-1120 nm due to $^4F_{\frac{5}{2}} \rightarrow ^4I_{\frac{3}{2}}$ and between 1340 nm due to the transition $^4F_{\frac{5}{2}} \rightarrow ^4I_{\frac{13}{2}}$.

4. **Sm$^{3+}$**

When Sm$^{3+}$ is used as activators, it gives the following transition at $\sim$ 610 nm ($^4G_{\frac{5}{2}} \rightarrow ^4H_{\frac{5}{2}}$) and $\sim$ 650 nm ($^4G_{\frac{5}{2}} \rightarrow ^4H_{\frac{7}{2}}$), however Sm$^{3+}$ acts as auxiliary activator in photo-stimulable SrS:Sm$^{3+}$ phosphor.

5. **Sm$^{2+}$**

Sm$^{2+}$ ions give transition at 550 to 850 nm due to $^4D_{o} \rightarrow ^7F_{o-1}$. Example of this type is BaFCl : Sm$^{2+}$ phosphor [98] where Sm$^{2+}$ acts as an activator.

6. **Eu$^{3+}$**

A number of luminescence lines due to $^4D_{o} \rightarrow ^7F_{o}$, are shown by Eu$^{3+}$ when it is used as activator. The emission around 610-630 nm is due to the electric dipole transition of $^5D_{o} \rightarrow ^7F_{2}$ induced by the lack of inversion symmetry of the Eu$^{3+}$ site, and is much stronger than that of the transition to the $^7F_{1}$ state. Luminescence Eu$^{3+}$ ions in commercial red phosphors such as YVO$_4$, Y$_2$O$_3$, and Y$_2$O$_3$S, occupy the site that have no inversion symmetry. The strong
emission due to the electric dipole transition is utilized for practical applications. The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor in which $\text{Eu}^{3+}$ has been used as activator gives the red emitting component at $\sim 612\text{nm}$.

7. **Eu$^{2+}$**

Eu$^{2+}$ usually gives broad band emission due to f-d transition. The wavelength positions of the emission band depend very much on host, changing from the near UV to the red region of visible range. This dependence is interpreted as due to the crystals field splitting of 5d levels [99]. With increasing crystal field strength, the emission bands shift to longer wavelength.

Sharp line luminescence at $\sim 360\text{nm}$ due to $f-f$ transition and having a life time of milliseconds is observed when the crystal field is very weak so that the lowest excited state of $4f^8(6P_j)$ is lower than the $4f^65d^1$ state.

One of the best example is the blue luminescence in $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$, observed and this phosphor is used for three band fluorescent lamps.

8. **Gd$^{3+}$**

The longest excited it level of Gd$^{3+}$ ($^4\text{I}_{9/2}$) give rise to sharp line luminescence at $\sim 315\text{ nm}$ [100] and sensitize the luminescence of other rare-earth ions [101]. The energy level of the charge transfer spectra and the $4f^65d^1$ states are the highest among rare-earth ions, so that Gd$^{3+}$ causes no quenching in other rare-earth ions.
9. Tb$^{3+}$

Luminescence spectra consisting of lines due to $^5D_4 \rightarrow ^7F_x$, are observed for Tb$^{3+}$, but among all these, the $^5D_4 \rightarrow ^7F_5$ emission line at approximate 550 nm is strongest in nearly all host crystals\[102\]. An example of Tb$^{3+}$ activator phosphor is Ln$_2$O$_2$S : Tb$^{3+}$

10. Dy$^{3+}$

Luminescence lines of Dy$^{3+}$ \[103, 104\] are in the 470 to 500 nm range due to the $^4F_{\frac{3}{2}} \rightarrow ^4H_{\frac{5}{2}}$ transition and in 570 to 600 nm range due to $^6F_{\frac{5}{2}} \rightarrow ^4H_{\frac{5}{2}}$ transition. The colour of luminescence Dy$^{3+}$ of is very close to white.

11. Dy$^{4+}$

Luminescence lines at 525nm due to $^1D_4 \rightarrow ^7F_4$ transition and at 630 nm due to $^3D_4 \rightarrow ^7F_3$ transition have been reported for example Cs$_3$Dy F$_7$ : Dy$^{4+}$ \[105\].

12. Er$^{3+}$

The green luminescence due to $^4S_{\frac{3}{2}} \rightarrow ^4I_{\frac{15}{2}}$ transition of Er$^{3+}$ has been reported in infrared to visible up-conversion phosphors.

Good examples of Er$^{3+}$ as activator are Y$_2$O$_3$ : Er$^{3+}$ \[106\] and Y$_2$O$_3$ S : Er$^{3+}$ \[107\].
13. Tm$^{3+}$

The blue luminescence of Tm$^{3+}$ due to the ($^2G_{4} \rightarrow ^3H_{6}$) transition has been reported in infra-red to visible up-conversion phosphors.

ZnS:Tm$^{3+}$ [108] is best example of the Tm$^{3+}$ when it is used as activator.

14. Yb$^{3+}$

The Yb$^{3+}$ gives infra-red absorption at 1000 nm due to the $^5F_{7/2} \rightarrow ^5F_{5/2}$ transition. The example of Yb$^{3+}$ as activator is La$_2$O$_2$S:Yb$^{3+}$ [109].

15. Yb$^{2+}$

The emission and absorption of Yb$^{2+}$ due to the $4f^{14} \rightarrow 4f^{13} 5d^1$ transition have been reported [110]. Sr$_3$(PO$_4$)$_2$:Yb$^{2+}$ is an example which emits light at 432 nm.

There are different classes of phosphors, which may be classified according to the host lattice [91, 111-117]:

<table>
<thead>
<tr>
<th>Types</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Aluminates</td>
<td>Sr$<em>4$Al$</em>{14}$O$_{25}$:Eu$^{2+}$</td>
</tr>
<tr>
<td>2. Silicates</td>
<td>(Sr,Ba)Al$_2$Si$_2$O$_8$:Eu$^{2+}$</td>
</tr>
<tr>
<td>3. Phosphates</td>
<td>(Sr,Mg)$_2$P$_2$O$_7$:Eu$^{2+}$</td>
</tr>
<tr>
<td>4. Sulphides</td>
<td>ZnS:Cu</td>
</tr>
<tr>
<td>5. Others</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>germinate</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>ii</td>
<td>yttrate</td>
</tr>
<tr>
<td>iii</td>
<td>vanadate</td>
</tr>
<tr>
<td>iv</td>
<td>tungstate</td>
</tr>
<tr>
<td>v</td>
<td>oxides</td>
</tr>
<tr>
<td>vi</td>
<td>sulphate</td>
</tr>
<tr>
<td>vii</td>
<td>titanate</td>
</tr>
<tr>
<td>viii</td>
<td>oxysulphide</td>
</tr>
<tr>
<td>ix</td>
<td>borate</td>
</tr>
<tr>
<td>x</td>
<td>halosilicate</td>
</tr>
<tr>
<td>xi</td>
<td>halophosphate</td>
</tr>
</tbody>
</table>

1. Sulphide lattice based phosphors (ZnS):

Sulphide lattice based phosphors are widely used commercially. However, ZnS lattice type phosphor are synthesized all around in the world. Research on these is still continued. These phosphors are required in many fields of science and technology. Important applications of these types of phosphor are that these are used in light sources, display devices and detector system.

Various ZnS lattice based phosphor have been developed by changing the activators. Some of important are given below [118-120]:

- ZnS:Cu,Cl
- ZnS:Ag
- ZnS:Ag,Cu,Al
- ZnS:Ag,In
(Zn,Cd)S:Ag

(Zn,Cd)S:Ag,Au,Al

(Zn,Cd)S:Ag,Ni

(Zn,Cd)S:Cu etc.

2. Aluminate lattice based phosphors:

Aluminate lattice based phosphors were introduced to three band fluorescent lamps by Verstegen et al [97] in 1974. Popularization of these lamps for general lighting purposes has made the aluminates as important lamp phosphors. Most of the aluminate phosphors are activated by rare-earth ions and require high temperature firing for synthesis. Accordingly, their emission efficiency and stability are excellent and various aluminate phosphors being extensively used, not withstanding their high price.

The excellent stability of these phosphors makes them possible to develop very high-loading fluorescent lamps such as compact fluorescent and high-loading photocopying lamps etc. Some of important aluminate phosphors are given below [94, 99, 111, 123-130];

BaMg$_2$Al$_{16}$O$_{27}$:Eu$^{2+}$

BaMg$_2$Al$_{16}$O$_{27}$:Eu$^{3+}$,Mn$^{2+}$

CeMg$_2$Al$_{11}$O$_{19}$:Ce$^{3+}$,Tb$^{3+}$

SrAl$_{14}$O$_{25}$:Eu$^{2+}$

LiAlO$_2$:Fe$^{3+}$

Y$_3$Al$_5$O$_{12}$:Tb$^{3+}$
3. **Silicate lattice based phosphor:**

Silicate lattice based phosphors were the most important fluorescent lamp phosphors until 1949. But from 1957 to 1970, Pb\(^{2+}\) activated alkaline earth silicate phosphors were successively developed; these materials have efficient UV emissions. After that barium zinc silicate, barium silicate, strontium magnesium silicate developed have been used in insect catching and for photocopy lamps and for diazo-sensitive paper system. These phosphor, however, have mostly been replaced by rare-earth activated phosphate phosphors.

Recently, Eu\(^{2+}\) activated silicate phosphors have attracted much attention. Very complex silicates, halosilicates and aluminosilicates phosphors have been developed. Depending on the host materials, blue to blue/green emitting phosphors can be obtained. Some important silicate lattice based phosphor are listed below [93, 95, 131, 136]:

\[
\begin{align*}
\text{Zn}_2\text{SiO}_4: \text{Mn}^{2+} \\
\text{CaSiO}_3: \text{Pb}^{2+}, \text{Mn}^{2+} \\
\text{BaSi}_2\text{O}_5: \text{Pb}^{2+} \\
\text{Ba}_3\text{MgSi}_2\text{O}_8: \text{Eu}^{2+} \\
\text{Y}_2\text{SiO}_5: \text{Ce}^{3+}, \text{Tb}^{3+} \\
(\text{Sr}, \text{Ba}, \text{Mg})_3\text{Si}_2\text{O}_7: \text{Pb}^{2+}
\end{align*}
\]

4. **Phosphate lattice based phosphors:**

Numerous types of phosphate compounds have been utilized as host materials in many phosphors for many years, due to their low material cost, easy synthesis and reasonable stability made these types of phosphors more important to be used in industrial sectors. The development of the first synthesized alkaline earth phosphate
phosphor can be traced back to 1938. In the 1960's rare-earth activated alkaline earth phosphate phosphors were practically used in photocopying fluorescent lamps. These phosphors represented a landmark in the history of fluorescent lamp development. Recently, rare-earth activated, green emitting phosphate phosphors have successively been developed for three band lamps as competitive materials to aluminate phosphors.

Phosphates are still being explored as one of the promising matrix crystals for new lamp phosphor development. Some of the important phosphate lattice based phosphors are listed below [91, 115, 137-144];

\[
\begin{align*}
\text{Sr}_2\text{P}_2\text{O}_7:\text{Sn}^{2+} \\
\text{Sr}_2\text{P}_2\text{O}_7:\text{Eu}^{2+} \\
(Ca,Zn)_3(\text{PO}_4)_2:\text{Tl}^+ \\
\text{Sr}_3(\text{PO}_4)_2:\text{Eu}^{2+} \\
\text{LaPO}_4:Ce^{3+},\text{Tb}^{3+} \\
\text{SrO.0.084 P}_2\text{O}_5.0.16 \text{B}_2\text{O}_5:\text{Eu}^{2+}
\end{align*}
\]

### 5. Other lattice based phosphors:

Many types of host lattices have also been used for making good quality phosphors for numerous purposes. Their huge demands in industrial and commercial use require more research on them. Depending upon host lattice these are many, some examples are given below [145-157]:

<table>
<thead>
<tr>
<th>Types</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Borate</td>
<td>( \text{Cd}_2\text{B}_2\text{O}_5:\text{Mn}^{2+} ), ( \text{SrB}_4\text{O}_7\text{F:Eu}^{2+} )</td>
</tr>
<tr>
<td>(ii) Yttrate</td>
<td>( \text{Y}_2\text{O}_3:\text{Eu}^{3+} )</td>
</tr>
</tbody>
</table>
Applications of phosphors in various fields

Phosphors are widely applied today for commercial and industrial uses. These have been utilized in many advanced display devices that provide illuminated text, graphics or video output, including flat panel display devices such as liquid crystal displays, plasma displays, thick and thin film electro-luminescent displays and field emission displays. Large number of their applications in various fields can be listed as below:

1. Lamps industries
2. Cathode-ray tubes
3. X-ray and ionizing radiation
4. Vacuum fluorescent displays
5. Field emission displays
6. Plasma displays
7 Electroluminescent
8 Luminous paints
9 Ceramics and glasses
10 For marking and stamp printed ink
11 X-ray screen and storage plate for medical imaging and radiographing
12 Taggants to authentic documents, currency, fibers, packing and product
13 Tagging of organic molecules for immunological assays
14 Materials for toys and safety.

Uses of phosphors in some important fields are as follows:

1. Use in lamps industries:

Various systems in which phosphors in combination with suitable excitation sources, have been developed and widely used. Among these the optical radiation source for lighting (lamps) is one of the most representative application of phosphors. The light source using phosphors, fluorescent lamps are most widely used and are produced in the largest quantity.

Different kinds of lamps are used to describe the degree of improvement in colour rendering of their lamps; deluxe type, super deluxe type, natural colour. Japanese Institute of Science first introduced a standard designation system according to the colour rendering indices and characteristic of Spectral Power Distribution by selecting phosphor, it is possible to obtain emission anywhere between 285 and 720 nm. The phosphors used in various lamps [158-167] like three band lamps, high pressure mercury discharge lamps [168-170], high intensity
discharge lamps [167,170], fluorescent glow lamps [171-172], fluorescent sign tube [173-175], cold cathode fluorescent lamps, electrodeless fluorescent lamp etc. Various important phosphors used in different kinds of lamps are listed below:

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Luminescence colour</th>
<th>Peak wavelength</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca₃(PO₄)₂Ca(F,Cl)₂:Sb³⁺,Mn²⁺</td>
<td>Daylight</td>
<td>480, 575</td>
<td>Standard lamp</td>
</tr>
<tr>
<td>Sr₁₀(PO₄)₆Cl₂:Eu²⁺</td>
<td>Blue</td>
<td>447</td>
<td>Three band lamp</td>
</tr>
<tr>
<td>SrMgP₂O₇:Eu²⁺</td>
<td>Blue</td>
<td>394</td>
<td>Photocopy lamp</td>
</tr>
<tr>
<td>Sr₂P₂O₇:Sn²⁺</td>
<td>Blue green</td>
<td>464</td>
<td>High colour rend.</td>
</tr>
<tr>
<td>BaSi₂O₅:Pb⁺²⁺</td>
<td>Ultraviolet</td>
<td>350</td>
<td>Black light</td>
</tr>
<tr>
<td>LiAlO₂:Fe³⁺</td>
<td>Infrared</td>
<td>735</td>
<td>Plant growth</td>
</tr>
<tr>
<td>CeMgAl₁₁O₁₉:Ce³⁺,Tb³⁺</td>
<td>Green</td>
<td>543</td>
<td>Tricolour lamp</td>
</tr>
<tr>
<td>CaWO₄</td>
<td>Blue</td>
<td>415</td>
<td>Colour correction</td>
</tr>
<tr>
<td>Y₂O₃:Eu²⁺</td>
<td>Red</td>
<td>611</td>
<td>Three band lamp</td>
</tr>
<tr>
<td>6MgO·As₂O₅: Mn²⁺</td>
<td>Deep red</td>
<td>655</td>
<td>High colour rend.</td>
</tr>
</tbody>
</table>

2. Use in Cathode ray tubes:

Cathode ray tube (CRT) more popularly called Braun tube in Japan, is the most widely used in display devices. It has application ranging from colour TV sets to giants screens of computers.

Numerous phosphors are used in different types of CRT’s, like colour CRT [176], storage tube [177-178], CRT for radar [179], printing CRT [180], flying spot scanner CRT [181], display tubes projection CRT [182], flat CRT [183], CRT for giant screens [184-186] etc.

Some of the important phosphors which are used in different type of CRT’s are:
<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Emission</th>
<th>Peak wave Length (nm)</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$_2$MgSi$_2$O$_7$:Ce$^{3+}$</td>
<td>Ultraviolet</td>
<td>385</td>
<td>Flying spot equipment, photographic application</td>
</tr>
<tr>
<td>Zn(S,Se):Ag</td>
<td>Yellowish blue</td>
<td>400</td>
<td>Oscilloscopes</td>
</tr>
<tr>
<td>Y$_2$O$_2$S:Eu$^{3+}$</td>
<td>Red</td>
<td></td>
<td>Character display</td>
</tr>
<tr>
<td>ZnS:Cu$_x$Al + Y$_2$O$_2$S:Eu$^{3+}$</td>
<td>Green</td>
<td></td>
<td>Graphic display</td>
</tr>
<tr>
<td>Zn$_2$SiO$_4$:Mn$^{2+}$</td>
<td>Yellowish green</td>
<td>525</td>
<td>Oscilloscopes radar</td>
</tr>
<tr>
<td>ZnS:Cu + Zn$_2$SiO$_4$:Mn$^{2+}$</td>
<td>Yellowish green</td>
<td>520</td>
<td>Radar, display</td>
</tr>
<tr>
<td>Gd$_2$O$_3$:Tb$^{3+}$</td>
<td>Yellowish green</td>
<td>544</td>
<td>Displays</td>
</tr>
<tr>
<td>Y$_2$O$_2$S:Tb$^{3+}$</td>
<td>Yellowish green</td>
<td>544</td>
<td>Projection tube</td>
</tr>
<tr>
<td>(KF,MgF$_2$):Mn$^{2+}$</td>
<td>Orange</td>
<td>585</td>
<td>Radar</td>
</tr>
<tr>
<td>Zn$_3$(PO$_4$)$_2$:Mn$^{2+}$</td>
<td>Reddish orange</td>
<td>635</td>
<td>Colour monitor TV's</td>
</tr>
</tbody>
</table>

3. Use in X-ray and ionizing radiation:

Many phosphors are used in X-ray intensifying screens, which are used in radiological diagnosis, and in industrial non-destructive testing [187-188]. These are utilized in X-ray intensifying screens which enhance the photographic image formed on photographic film.

Many phosphors are used in ionizing radiation. They are used in XCT [189] (x-ray computed tomography), PET [190] (positron emission tomography), X-ray camera [191], nuclear and high energy physics detectors etc. Some important phosphor used in ionizing radiation are given below:
4. Use in vacuum fluorescent displays:

Vacuum fluorescent display was invented in Japan in 1965 and is now a practical display device [196]. Its operation is like same as cathode ray tubes. Electrons emitted from a cathode are accelerated and controlled so as to bombard on anode that is coated with a phosphor; excited by the electrons, the phosphor emits light [197]. Most recent technological trend, however, is represented by the front luminous vacuum fluorescent displays (FLVFD). Various important phosphors used in vacuum fluorescent display are the following [198-200]:

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Emission colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO:Zn</td>
<td>Green</td>
</tr>
<tr>
<td>ZnS:Cl + In$_2$O$_3$</td>
<td>Blue</td>
</tr>
<tr>
<td>ZnS:Au,Al + In$_2$O$_3$</td>
<td>Yellow green</td>
</tr>
<tr>
<td>Zn$<em>{0.3}$Cd$</em>{0.7}$S:Au,Al, + In$_2$O$_3$</td>
<td>Orange</td>
</tr>
<tr>
<td>Zn$<em>{0.2}$Cd$</em>{0.8}$S:Au,Al, + In$_2$O$_3$</td>
<td>Reddish orange</td>
</tr>
</tbody>
</table>

5. Use in field emission displays:

These devices are vacuum fluorescent display that employ field emission cathodes. Many phosphors are used in them, some of which are listed below [198-199]:

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Peak wavelength</th>
<th>Application [192-195]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaI:Tl$^+$</td>
<td>415</td>
<td>XCT, PET, nuclear detectors</td>
</tr>
<tr>
<td>CsI</td>
<td>305/&gt;400</td>
<td>Nuclear detectors</td>
</tr>
<tr>
<td>CdWO$_4$</td>
<td>470/540</td>
<td>XCT</td>
</tr>
<tr>
<td>Bi$_4$Ge$_3$O$_12$</td>
<td>480</td>
<td>XCT, PET, nuclear detectors</td>
</tr>
<tr>
<td>Lu$_2$SiO$_5$:Ce$^{3+}$</td>
<td>420</td>
<td>PET</td>
</tr>
<tr>
<td>CaF$_2$:Eu$^{2+}$</td>
<td>435</td>
<td>β-ray, detection</td>
</tr>
<tr>
<td>Gd$_2$O$_3$:Pr$^{3+}$,Ce$^{3+}$</td>
<td>510</td>
<td>XCT, Ceramic</td>
</tr>
<tr>
<td>HFG:Ce$^{3+}$</td>
<td>310</td>
<td>Nuclear detectors</td>
</tr>
</tbody>
</table>
### Chemical composition | Emission colour
---|---
SnO$_2$:Eu$^{3+}$ | Orange
(Zn$_{0.9}$Cd$_{0.1}$)S:Au,Al, + In$_2$O$_3$ | Greenish yellow
ZnS:Cu,Al + In$_2$O$_3$ | Yellow green
ZnO:Zn | Green
ZnS:Cl + In$_2$O$_3$ | Blue

6. Use in infrared up-conversion:

Up converter phosphors are useful in immuno-assay applications. In them the phosphor is delivered to the biological substrate and the interaction between substrate and the underlying phosphor result in a detector colour shift which can be correlated with the concentration of the initial bioactive molecules present in the sample. Recently new type of up conversion luminescence developed is known as analanche up-conversion. Various important phosphors used in infrared converters are the following [200-202]:

### Chemical composition | Emission colour
---|---
Y$_{0.78}$Yb$_{0.02}$Er$_{0.02}$F$_3$ | Green
BaY$_{1.34}$Yb$_{0.60}$F$_8$ | Green
25ErCl$_3$.75BaCl$_2$ | Green
Y$_{0.65}$Yb$_{0.35}$Tm$_{0.001}$F$_3$ | Blue

7. Use in Plasma Display’s:

Plasma display panel can be defined as flat panel information display devices in which the pixels consist of small gas-discharge cells that radiate visible light directly or emit luminescence produced by the phosphors. A discharge cell is used [205], which stimulate a type of display cell in practical PDP’s [206]. A large number of phosphors are used in PDP’s, some of them are the following:
<table>
<thead>
<tr>
<th>Blue colour emitters</th>
<th>Green colour emitters</th>
<th>Red colour emitters</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaWO₄: Pb⁺⁺⁺⁺</td>
<td>ZnSiO₄: Mn²⁺⁺⁺⁺</td>
<td>Y₂O₃: Eu³⁺⁺⁺⁺</td>
</tr>
<tr>
<td>Y₂SiO₅: Ce³⁺⁺⁺⁺</td>
<td>ZnSiO₄: Mn²⁺⁺⁺⁺</td>
<td>Y₂O₃: Eu³⁺⁺⁺⁺</td>
</tr>
<tr>
<td>YP₀.85V₀.15O₄</td>
<td>ZnSiO₄: Mn²⁺⁺⁺⁺</td>
<td>Y₀.65V₀.35O₄: Eu³⁺⁺⁺⁺</td>
</tr>
<tr>
<td>BaMgAl₁₂O₂₃: Eu²⁺⁺⁺⁺</td>
<td>ZnSiO₄: Mn²⁺⁺⁺⁺</td>
<td>YBO₃: Eu</td>
</tr>
<tr>
<td>BaMgAl₁₂O₂₃: Eu²⁺⁺⁺⁺</td>
<td>ZnSiO₄: Mn²⁺⁺⁺⁺</td>
<td>Y₀.65Gd₀.₃₅BO₃: Eu³⁺⁺⁺⁺</td>
</tr>
<tr>
<td>BaMgAl₁₂O₂₃: Eu²⁺⁺⁺⁺</td>
<td>BaMgAl₁₉O₁₉: Mn²⁺⁺⁺⁺</td>
<td>Y₀.65Gd₀.₃₅BO₃: Eu³⁺⁺⁺⁺</td>
</tr>
</tbody>
</table>

A brief-chart in Fig. 8, gives the diverse applications of phosphors in making devices.
<table>
<thead>
<tr>
<th>Exitation Devices</th>
<th>Color</th>
<th>Black &amp; White</th>
<th>Projection</th>
<th>View Finder</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRT for TV</td>
<td>Color</td>
<td>Monochrome</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRT for display</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRT for measurements</td>
<td></td>
<td>Oscilloscope</td>
<td>Storage tube</td>
<td></td>
</tr>
<tr>
<td>Other CRT</td>
<td>Flying spot scanner</td>
<td>Radar</td>
<td>Image intensifier(output screen)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vacuum fluorescent display</td>
<td>Field emission display</td>
<td>Large sized outdoor display</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fluorescent lamp</td>
<td>General illumination</td>
<td>Wide band type</td>
<td>Narrow 3-band type</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High color rendering</td>
<td>Special uses</td>
<td>LCD back light</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LCD back light</td>
<td>Outdoor display</td>
<td>Copying machine</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Black light Viewer</td>
<td>Medical use</td>
<td>Agricultural use</td>
</tr>
<tr>
<td></td>
<td>High pressure mercury lamp</td>
<td>Plasma display</td>
<td>Neon sign</td>
<td>Neon tubing</td>
</tr>
<tr>
<td></td>
<td>UV-Vis-IR</td>
<td>Luminous paint, Fluorescent pigment.</td>
<td>Fluorescent marking, IR-Vis up-conversion</td>
<td>Solid state laser material, Laser dye</td>
</tr>
<tr>
<td></td>
<td>High energy radiation</td>
<td>Fluoroscopic screen</td>
<td>Intensifying screen</td>
<td>Sintillator</td>
</tr>
<tr>
<td></td>
<td>(X-ray and others)</td>
<td></td>
<td>Image intensifier(input screen)</td>
<td>Radiographic imaging plate</td>
</tr>
<tr>
<td></td>
<td>Electric field</td>
<td>High field EL</td>
<td>Thin film type</td>
<td>Powder phosphor type</td>
</tr>
<tr>
<td></td>
<td>(Electroluminescence)</td>
<td>Injection EL</td>
<td>Light emitting diode</td>
<td>Semiconductor laser</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Organic EL</td>
<td>EL panel</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 8: Different application of phosphors in various devices.
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