

# Design, Solution Synthesis and Luminescence Properties of Rare-Earth Doped Afterglow Phosphor for Glow-in-the Dark Applications

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**Abstract** - Long afterglow (LA) phosphors are a particular type of luminescent materials that store up the photon energy and demonstrate photoluminescence emission even after the source of excitation has been ceased off. The majority of the researchers now agree that the stored energy gets captured at the various trapping levels associated with intrinsic or intentional defects and later released thermally. As the source of excitation is eliminated, trapped charge carriers may acquire sufficient thermal energy from ambient surroundings resulting into recombination of the charge carriers. Since detrapping of charge carriers is associated with the thermal energy, these are also known as thermo luminescent materials. The entire phenomena of afterglow luminescence include the excitation of charged carriers, charge carrier migration, and trapping at defect centers; the thermal release of the trapped charge carriers; and finally the recombination of the charge carriers resulting in delayed afterglow luminescence.

**Keywords**- Afterglow, thermal energy, Luminescence

## 1. Introduction

Afterglow, also known as persistent luminescence, is a fascinating phenomenon where the material is emitting, usually in the visible range, for a long time, typically with a lifetime more than 0.1s according to the resolving limit of the naked eye, after the irradiation or excitation source has been switched off. Long afterglow (LA) phosphors are a particular type of luminescent materials that store up the photon energy and demonstrate photoluminescence emission even after the source of excitation has been ceased off [1]. The majority of the researchers now agree that the stored energy gets captured at the various trapping levels associated with intrinsic or intentional defects and later released thermally. As the source of excitation is eliminated, trapped charge carriers may acquire sufficient thermal energy from ambient surroundings resulting into recombination of the charge carriers. Since detrapping of charge carriers is associated with the thermal energy, these are also known as thermoluminescent materials. The entire phenomena of afterglow luminescence include the excitation of charged carriers, charge carrier migration, and trapping at defect centers; the thermal release of the trapped charge carriers; and finally the recombination of the charge carriers resulting in delayed afterglow luminescence. The current chapter presents a broad review of conventionally and recently developed oxide-based LA phosphors, which show unusual photon energy trapping property. These materials could be easily excited by sunlight and ambient lightings. Until a few years, the emission color of these LA phosphors was restricted to green (~520 nm) and yellow-green (~555 nm) regions, respectively. However, with the advancement in this field, other primary color emitting such as blue (~440 nm) and red (~610 nm)-emitting oxide phosphors are being developed even though their brightness and decay are comparatively less than that of established green-emitting LA phosphor. Exceptional emphasis has been laid in understanding the physics of materials and fundamental mechanism governing the afterglow luminescence property in oxide lattices [2].

These multifunctional materials are impending candidates in the areas of fingerprint detection, marine mound application, sensors for structural damage, a biological marker, etc. Fig.1. represents the Jablonski diagram for fluorescence and phosphorescence process. The singlet spin state  $S_0$  represents the ground state of the electrons,  $S_1$  and  $S_2$  singlet excited states, respectively [3]. In the case of fluorescence, when excited by electromagnetic radiation, the electrons are excited from the ground state  $S_0$  to any one of the energy levels of the second excited state  $S_2$  or  $S_3$ . After the excitation stops, they spontaneously relax back to their ground state. During this transition, there is no change in multiplicity (electron spins remain paired); thus, such type transitions are classically allowed. In the case of phosphorescent materials, the excited electrons from singlet

excited state track their path to a triplet state nonradiatively. During this transition, the spin of the excited electron is reversed [4].

In a triplet state, the spin of the excited electron is no longer paired with the ground state electron; that is, they have parallel spins, which are against the Pauli Exclusion Principle. Being a forbidden transition, the lifetime of the emission from phosphorescent materials can reach several seconds. In literature, innumerable adjectives have been used to explain this phenomenon. Terms include long afterglow, persistence luminescence, phosphorescence, long lasting, long-duration, long persistence phosphorescence, and long decay [5-6]. Phosphorescence is one of the common manifestations of luminescence. Phosphorescence is associated with longer lifetime or decay ( $>108\text{s}$ ) of luminescence process due to the spin-forbidden transitions taking place at the site of the luminescent ion. However, the literature concerning long afterglow phosphors has wrongly considered such materials as phosphorescent materials, as long as afterglow phosphors can emit light for times ranging from a few hours to days. The origin of afterglow luminescence is mainly related to rare-earth ions, which also show parity- and spin-allowed transitions. The entire phenomena of afterglow luminescence include excitation of charged carriers, charge carrier migration, and trapping at defect centers, the thermal release of the trapped charge carriers; and finally recombination of the charge carriers resulting in delayed luminescence or afterglow phenomena.

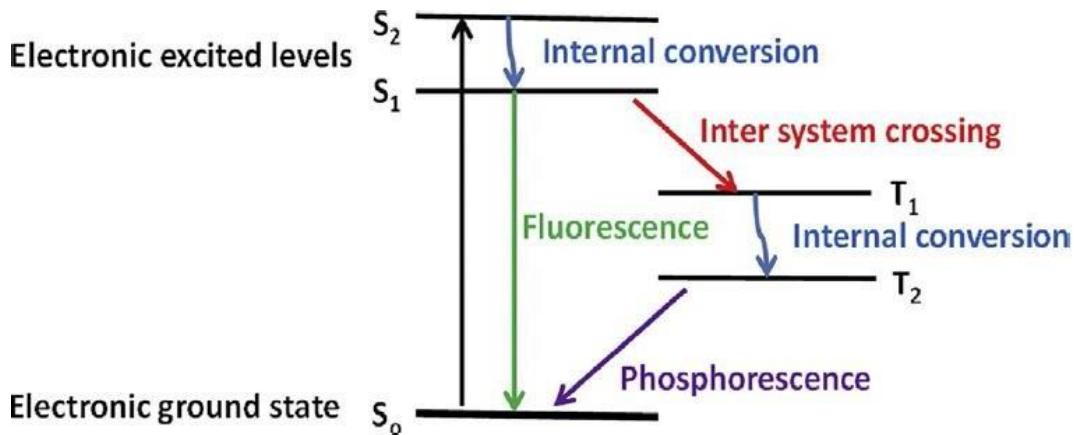


Fig. 1. Energy level diagram representing various electronic transitions involved in fluorescence and phosphorescence.

Most of the concepts governing afterglow luminescence, starting from the nomenclature of the phenomena to elucidation of its mechanism, remain doubtful till date. This is true even after 400 years of discovery of the first naturally occurring afterglow mineral known as Bologna stone [7–8]. The following review article focuses

on the ways of generating afterglow luminescence, recent progress in understanding the mechanism involved, and future of such long afterglow materials concerning advanced applications with specific emphasis on both conventional and futuristic materials.

## 2. First generation

### ➤ Sulfide systems

The sulfide-based long afterglow phosphors are the earliest discovered and investigated luminescent materials. Luminescence in sulfide systems was one of the first genres of luminescence ever discovered and studied in the history of fluorescence. The research, preparation, and application have a history going back to over 100 years. Sulfide-based phosphors are cost-effective with easy color tunability; however, their chemical stability severely limits their applicability. The era of phosphor research began in the late 19th century, with the discovery of ZnS phosphor. ZnS phosphor was first ever discovered by the French chemist Theodore Sidot in 1866. Later, the German scientist Philip E.A. Lenard and his colleagues did revolutionary work in the field of long afterglow phosphor.

Alkaline chalcogenide phosphors were developed by Lenard's group, and these were commonly known as Lenard phosphors (e.g., ZnS:Cu<sup>+</sup>, CaS:Bi<sup>3+</sup>, CaSrS:Bi<sup>3+</sup>, and CaS:Eu<sup>2+</sup>,Tm<sup>3+</sup>) [9–12]. This category of the material system has advantages of the relative ease of preparation, broad excitation characteristics, short excitation time, and tuning of emission colors from blue to red wavelengths in the visible spectrum. Sulfide-based crystal lattice shows an augmented red-shift in emission spectra as compared with their oxide- and silicate-based counterparts, as a consequence of which emission occurs in 500–620 nm range. Strengthened red-shift is primarily explained by an extensive centroid shift for sulfide-based host lattices.

However, the drawbacks of sulfide-based long afterglow phosphors are indoor products only because of their high sensitivity toward moisture/water. These are chemically unstable materials resulting in the disruption of the phosphor lattice and thereby degrading the afterglow properties [13] as they come into contact with moisture. Apart from that, these have low luminous intensity and afterglow time (>1 h). To overcome such serious drawbacks, radioisotopes such as promethium (Pm-147) and tritium (H-3) were also added to the sulfide phosphors [14]. Although radioactive ions enhanced the afterglow time, their usage was still limited due to safety and environmental concerns. These disadvantages considerably limit the applications of sulfide-based phosphorescent materials.

The first modern phosphor developed for commercial application was ZnS:Cu to be used in many marketable entities including markings in watch dials, afterglow paints, glow-in-the-dark switches, and items for aesthetic beauty. Various critical parameters such as the influence of crystalline phase, synthesis procedure

adapted, and the role of co-activators governing afterglow properties of sulfide-based materials have been studied so far. Later on, a series of persistent luminescent materials such as ZnS, ZnS–CdS, ZnS–ZnSe, and alkaline earth sulfides were developed [15–21]. A list of the reported sulfide- based long afterglow phosphors has been listed in Table 1.

Table 1 List of sulfide-based long afterglow phosphors

S . N . .	Host lattice	Activator	Co-activator	Emissio n(nm)	Afterglo wtime	Synthesis	Ref
1 .	CaS	Eu <sup>2+</sup>	Ce <sup>3+</sup> , Tm <sup>3+</sup>	648	1h	Solid state	[22]
2 .	SrS	Eu <sup>2+</sup>	Pr <sup>3+</sup>	611	1000 min	Liquid-phase reaction	[23]
3 .	BaS	Cu <sup>+</sup>	-----	610	30 min	Solid state	[8]
4 .	Y <sub>2</sub> O <sub>2</sub> S	Eu <sup>3+</sup>	Ti <sup>4+</sup> /Mg <sup>2+</sup>	612	30 min	Cold isostatic pressing	[24]
5 .	ZnS	Au <sup>+</sup>	In <sup>3+</sup>	530	>0.5h	Solid state	[25]
6 .	Gd <sub>2</sub> O <sub>2</sub> S	Er <sup>3+</sup>	Yb <sup>3+</sup>	526, 550, 660,	15 min	Solid state	[26]
7 .	La <sub>2</sub> O <sub>2</sub> S	Sm <sup>3+</sup>	-----	605, 645	3 min	Solid state	[27]

### 3. Second generation: Aluminate and silicate systems

#### ➤ Aluminum oxide-based systems

Aluminates are the most studied and applied persistent luminescent material matrices in recent times. The aluminate systems usually use the rare-earth and transition metal ions as dopants. The host material encompasses alkaline earth aluminate-based lattice. Aluminate-based phosphor system has been known since the 1960s. In the late 1960s, Palilla et al. suggested the use of SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup> phosphor systems for cathode-ray tube (CRT) applications with emission maxima at 520 nm. Later, Abbruscato et al. prepared non-stoichiometric SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup> phosphor that exhibits rapid luminescence decay followed by gradual loss of emission intensity. Even so, the afterglow time ranges only from a few seconds to a few minutes. A

breakthrough in the field of long afterglow phosphors came in 1996 when Matsuzawa et al. [28] from Osaka University, Japan, discovered alkaline earth aluminate materials codoped with trivalent rare-earth ions. The aluminate systems represent the second generation of persistent luminescent materials. Their luminescence efficiency, intensity, persistent lifetime, and stability of the material exceed the sulfide system to a large extent. Matsuzawa et al. have explained the phenomena of afterglow regarding thermoluminescence, and photoconductivity studies on the phosphor that describe Dy<sup>3+</sup> ions act as a hole-trapping center in trivalent rare earth–codoped alkaline earth aluminates. Dy<sup>3+</sup> and Nd<sup>3+</sup> ions were used as auxiliary ions to promote the afterglow properties. Furthermore, the estimated trap depth was found to be more in the case of codoped SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor than that of the SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>. Photoconductivity studies were done by illuminating the only half portion of sample close to the negative and positive electrode one after another.

**Table 2 List of aluminate-based long afterglow phosphors**

S . N . .	Host lattice	Activator	Co-activator	Emissio n(nm)	Afterglo wtime	Synthesis	Ref
1 . .	SrAl <sub>2</sub> O <sub>4</sub>	Eu <sup>2+</sup>	Dy <sup>3+</sup> ,	530	30h	Calcinatio n	[29]
2 . .	Sr <sub>4</sub> Al <sub>14</sub> O <sub>25</sub>	Eu <sup>2+</sup>	Dy <sup>3+</sup>	467	>30 h	Solid state	[30]
3 . .	CaAl <sub>2</sub> O <sub>4</sub>	Eu <sup>2+</sup>	Nd <sup>3+</sup>	440	10h	Solid state	[31]
4 . .	BaAl <sub>2</sub> O <sub>4</sub>	Eu <sup>2+</sup>	Dy <sup>3+</sup>	500	1h	Solid state	[32]
5 . .	CaAl <sub>2</sub> O <sub>4</sub>	Tb <sup>3+</sup>		493, 590	1h	Solid state	[33]
6 . .	CaYAl <sub>3</sub> O <sub>7</sub>	Ce <sup>3+</sup>		417	1h	Solid state	[34]
7 . .	Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub>	Sm <sup>3+</sup>	Nd <sup>3+</sup>	440	3 min	Solid state	[35]
8 . .	SrMgA l <sub>10</sub> O <sub>1</sub> 7	Eu <sup>2+</sup>	Dy <sup>3+</sup>	460,516	5 min	Urea Combustio n	[36]
9 . .	SrAl <sub>4</sub> O 7	Eu <sup>2+</sup>	Dy <sup>3+</sup> , Gd <sup>3+</sup>	495	10 min	Gel Combustio n	[37]
10 . .	MgAl <sub>2</sub> O <sub>4</sub>	Tb <sup>3+</sup>		520	50 min	Floating zone melting	[38]

On comparing the photocurrent at both the terminals, it was found that photocurrent at the negative terminal was three times more than that at the positive terminal. This indicates that the charged species are holes, and the photoconductivity of  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$  is due to the motion of holes in the valence band of the host matrix.

Besides the  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ , the researchers, further developed a series of persistent aluminate–phosphor systems activated by rare-earth materials, such as  $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$  and  $\text{CaYAl}_3\text{O}_7:\text{Ce}^{3+}$ , exhibiting blue afterglow luminescence. Aluminate-based afterglow host lattices have been listed in Table 2. However, the alkaline earth aluminates show deprived resistance toward water and moisture, making their applications limited [39]. It is also difficult to tune emission colors of alkaline earth aluminate systems toward the red side of the visible spectrum, making it difficult to realize red color-emitting long afterglow phosphors.

#### ➤ Silicon dioxide-based systems -

The silicate systems are yet another intriguing category of persistent luminescent materials. Luminescence properties of silicate systems are comparable with that of aluminate systems but are more efficient and stable. Silicate-based systems are chemically stable materials, unlike the traditional sulfide-based systems, thus making these potential candidates for outdoor applications. These possess water stability properties, unlike the existing aluminate and sulfide-based systems, which require protective coatings to tolerate the impact of water. Since lattice energy of Si—O bond is strong enough, these do not show degradation under the influence of water/moisture. Silicate-based phosphors can be directly used to formulate water-based paints. Owing to superior properties afterglow phosphors are currently a hot topic of study across the globe. Silicate-based afterglow host lattices reported so far have been summarized in Table 3.

On a broader perspective, most of the studies in silicate-based afterglow phosphors can be classified as binary- and ternary-based silicate systems. The binary system includes orthosilicates ( $\text{SiO}_4^{4-}$ ) and metasilicates ( $\text{SiO}_3^{2-}$ ), whereas ternary silicate systems mainly include the disilicates and metasilicates. The very first report in the field of silicate-based materials was reported in 1949 by Arthur L. Smith [40]. Complex silicate of  $\text{CaBeSiO}_4:\text{Mn}^{2+}$  (trimerite structure) shows cathodoluminescence. The afterglow caused by cathode-ray excitation is of high level and long duration (decays to 1% of original value in 500 ms). In 1975, afterglow luminescence of  $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}, \text{As}^{3+}$  was reported by researchers at Chiba Institute of Technology in Japan.

The afterglow time reported was 30 min. A breakthrough was reported in 2001 by Lin et al. on alkaline earth silicate-based compound ( $\text{SrMgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ ) having afterglow time of 10 h in the blue region (465 nm) of the visible spectrum [41].

Table 3 List of Silicate-based long afterglow phosphors

S . N .	Host lattice	Activat or	Co- activator	Emission (nm)	Afterglo wtime	Synthesis	Ref
1 . 7	Sr <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub>	Eu <sup>2+</sup>	Dy <sup>3+</sup> ,	465	20h	Solid state	[42]
2 .	Ca <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub>	Eu <sup>2+</sup>	Dy <sup>3+</sup>	533	12 h	Solid state	[43]
3 .	Ba <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub>	Eu <sup>2+</sup>	Tm <sup>3+</sup>	405	15 min	Solid state	[44]
4 . 7	Ba <sub>2</sub> ZnSi <sub>2</sub> O <sub>7</sub>	Eu <sup>2+</sup>		496	30 min	Combustion	[45]
5 .	Ca <sub>3</sub> MgSi <sub>2</sub> O <sub>8</sub>	Eu <sup>3+</sup>	Dy <sup>3+</sup>	475	5h	Solid state	[46]
6 . 7	BaMgSi <sub>2</sub> O <sub>7</sub>	Ce <sup>3+</sup>	Mn <sup>2+</sup> , Dy <sup>3+</sup>	630	2h	Solid state	[47]
7 .	Sr <sub>3</sub> MgAl <sub>10</sub> O <sub>17</sub>	Eu <sup>2+</sup>	Dy <sup>3+</sup>	458	>1 min	Solid state	[48]
8 .	Ca <sub>4</sub> A <sub>6</sub> Si <sub>3</sub> O <sub>19</sub>	T <sub>b<sup>3+</sup></sub>		350-600	1 h	Melt Growth	[49]
9 . 0	Sr <sub>3</sub> Al <sub>10</sub> SiO <sub>2</sub> <sub>0</sub>	E <sub>b<sup>3+</sup></sub>	Ho <sup>3+</sup>	466	6 h	Solid state	[50]
10 .	Ba <sub>13</sub> A <sub>22</sub> Si <sub>10</sub> O <sub>6</sub>	T <sub>b<sup>3+</sup></sub>		370-700	43 min	Solid state	[51]

#### 4. General methods to design long afterglow phosphors

For the practical applications of long persistent phosphors, the persistence time of their afterglow emission has always been of most interest. Many methods have been used to increase the persistence time by producing more traps in the host and with increasing trapping efficiency. In addition to the long persistence time, the emission color of the phosphor is also very important. The perceived color of the phosphor, for example, should remain stable throughout the decay time.

**4.1. Selection of Host Materials:** Host materials are of critical importance for long persistent phosphors. Early host materials for long persistence were of the ZnS type. ZnS has low band gap energy of 2.16 eV.

The persistence time for ZnS-type of phosphors is usually less than an hour. It is difficult to have long persistent emission in these materials because the deep traps are hard to create in narrow band gaps. The sulfides have the longest recorded history of all persistent luminescent compounds. During the 1970s, CaS and other alkaline earth sulfides were developed as long persistent phosphor host materials because Eu<sup>2+</sup> and Bi<sup>3+</sup>doped CaS exhibit strong afterglow emission under visible excitation. Host mixing of alkaline earth sulfides has been used to adjust emission color and has been found effective because of their simple cubic structure. Unfortunately, these materials are chemically unstable, for example, CaS + 2H<sub>2</sub>O → Ca(OH)<sub>2</sub> + H<sub>2</sub>S. Encapsulation is usually required in such applications [52]. After sulfide materials, alkaline earth aluminate hosts became important and a large number of long persistent phosphors were developed using the aluminates. Aluminates are more chemically stable than CaS, but they are also sensitive to moisture. Many ions exhibit long persistence in elements, even without co-doped trapping centers; this is because it is easy to create defects in aluminates due to charge compensation and cation disorder. The alkaline earth aluminates MAl<sub>2</sub>O<sub>4</sub> (M = Ca, Sr, Ba) are by far the most studied families of persistent luminescent materials. The bright green luminescence of the monoclinic SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>, was discovered in 1966 [53] and described by Blasse and Bril two years later, together with that of CaAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup> and BaAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup> [54]. The band gap energies of aluminates are usually above 6 eV, where deep traps can be created. On the other hand, because of the wide band gap, excitation energies for the long persistent phosphors using aluminates are usually in the UV or VUV regions, which is a disadvantage in some applications.

#### ➤ **Electron and hole traps via codoping**

Codoped ions into the host lattice either act as self-trapping centers or produce defect related trapping centers. Codopant ions introduce electron and hole traps. Electron and hole traps are responsible for capturing electrons and holes that are present just below the conduction band (CB) and above the valence band (VB), respectively. Codopant ions not only alter trap distribution but also enhance trap density in the host lattice. As reported by Claubua et al. [55], peaks in the TL glow curves of sample SRA with and without

codoped elements ( $Dy^{3+}$ ) differ only in width and position of the peak; however, the peakshape is found to be similar.

Results undoubtedly indicate that the chemical nature of the trap states is not affected by codoping the phosphor crystal system. Point defects such as oxygen vacancies and metal cation vacancies perform as trapping centre in the phosphor system.

#### ➤ Defect-related trapping centers

Defect-related trapping levels are ascribed to the intrinsic defects, and the defects generated as a consequence of doping. Doping-related defects include strain and stress dislocation, color center vacancy, and interstitial defects. The difference in ionic size of the dopant ion and substituting host anion can also introduce additional defect related energy levels. Dopant ion replacing host ion with different coordination can also result in a non-homogeneous broadening of afterglow emission spectra. In some of the reports available, the incorporation of chemical fluxes was also found to create additional trapping energy, which prolongs the afterglow luminescence time. It was observed that the stoichiometrically grown  $CaS:Eu^{2+}$  (without chemical additives such as  $NH_4Cl$ ) does not evince any afterglow. However, the afterglow is observed in a sample prepared with  $NH_4Cl$  as a flux. This likely occurs due to partial substitution of  $Eu^{2+}$  at leftover  $Cl^-$  ions substituted at  $S^{2-}$  sites due to incomplete removal of flux from the lattice [55]. Another example of defect-related trapping centers is the formation of vacancies and interstitial defects due to charge compensation effect [56]. It has been observed that the defect-related trapping levels are simpler to create in large bandgap materials with intricate crystal structure.

#### ➤ Co-Doped Trapping Centers:

The afterglow is triggered by trapping electrons or holes produced during the excitation process of phosphor materials. A meta-stable ionic state such as  $Tm^{2+}$  in  $CaS:Eu^{2+}$ ;  $Tm^{3+}$  and  $Dy^{4+}$  in  $SrAl_2O_4:Eu^{2+};Dy^{3+}$  can also be used as traps. When these meta-stable ionic states act as traps in the host they are very different from the stable ionic states with the same valence in the same host. These processes are illustrated in Figs. 1 and 2. The excited electrons or holes do not modify the bonding situation of the dopants, they are just represented by  $(Dy^{4+})^*$  or  $(Tm^{2+})^*$  where  $(Dy^{4+})^* = Dy^{3+} + h^+$  and  $(Tm^{2+})^* = Tm^{3+} +$

e<sup>-</sup>. The electrons and holes created in such a way are loosely bound and can be easily detached thermally. Even though the exact nature of meta-stable ionic states of the co-dopants is not well understood, these states are not simply altered ionic states but are considered more complex ionic entities.

The formation of an electron or a hole trap by a defect depends on the energy level position of these ions within the host band gap and these positions may be determined experimentally. Traps induced due to incorporation of co-dopants, the nature of the traps is not clearly understood, and hence it is difficult to determine the exact energy position of the traps.

## 5. Mechanisms Responsible for Long Afterglow

Trapping and detrapping of electrons or holes are understood to be the principal mechanisms responsible for long persistent phosphorescence, which have been discussed by many researchers. For electrons, trapping can take place through electron tunneling or through the promotion of the conduction band.

### 5.1. Trapping Mechanism:

The electron trapping mechanisms are usually associated with electron excitation and delocalization. Following the excitation of an electron from the ground state to an excited state, the electron is delivered to a trap by some mechanism associated with an electron. Under normal circumstances, in both the ground and excited states, electrons are localized around their parent ion. If sufficient photo-energy is provided to allow the electron to reach the conduction band of the host, it becomes mobile and delocalization of an electron can occur. This process is called photoionization. Phonon-assisted delocalization can also occur when the excited state to which an electron is promoted lies just below the host conduction band. At finite temperatures, electrons can be thermally excited to the conduction band where delocalization can occur. This mechanism is called thermal ionization and is much weaker than photoionization.

Two-photon ionization process or excited state absorption (ESA) [57] is also observed at times. This process will not be strong enough to trap a large number of electrons to produce persistence. It has been recently reported that the delocalization rate is in the same order of magnitude as the electron–phonon relaxation rate (of the order of  $10^{13} \text{ s}^{-1}$ ) for a *d* electron in Ce<sup>3+</sup> [58].

Delocalization of electrons generally happens in the *p* and *d* orbitals. Because of better shielding, the delocalization of electrons in the *f* orbital does not generally occur even when the *f* orbital energies are larger than the *d* state energies. As a result of this, long persistence phosphorescence from rare-earth ions can be found only when the electrons are excited to the high lying 5*d* excited states. UV or VUV photons are needed for the ionization and delocalization. Long persistent phosphors that can be charged by natural light are rare

as a consequence.

## 5.2 Detrapping Mechanism:

The traps that give rise to persistence usually have depths ranging from a few tenths to several eV. In the case of thermal activation, the detrapping rate  $A$  is associated with temperature and is given by:

$$A = S e^{\Delta E / kT}$$

Where  $S$  is the frequency factor for electron detrapping,  $\Delta E$  is the trap depth, and  $T$  the temperature [59]. Trap depths are measured from the bottom of the conduction band and the  $S$  factor is related to the electron–phonon interaction. Excited electrons at times may return to the trap and the process is called *retrapping*. Detrapping mechanisms become complicated if retrapping processes are included and taking this into account, the higher order model of the processes has been developed. If the retrapping rate is very low or negligible, the decay of the afterglow intensity is exponential and the decay is given by:

$$I = \sum_{i=1}^n I_i e^{-\Delta E_i / kT}$$

Where  $I$  is the intensity of the afterglow and  $i$  refers to the  $i$ th trap with trap depth  $\Delta E$ , and  $n$  is the number of different types of traps in the material [30]. This model is called the first order or monomolecular reaction mechanism. If the retrapping rate is very high, then a second-order mechanism applies. The decay of afterglow intensity is given by:

$$I = I_0 / (1 + \gamma t)^n$$

Where  $I_0$  is the initial afterglow intensity and  $n$  is generally less than 2 and depends on the material.  $\gamma = N/A n t_0$ , where  $N$  is the density of traps,  $n t_0$  the population of trapped electrons at  $t = 0$ , and  $A$  the detrapping rate as defined. This model is also a bimolecular reaction type.

## 6. Research Gap

Phosphorescence lifetimes are usually longer than the lifetime of the excited state and depend on the trap depth and trapping/de-trapping rates. Fluorescence lifetimes, on the other hand, depend on the transition strength between the two states involved, which includes a ground state and an excited state only. Phosphorescence can be categorized by its lifetime as: Very Short Persistent Phosphorescence (VSPP) that has lifetime of the same order of magnitude as the lifetime of excited state, i.e. in the order of milliseconds, and it is associated with very shallow traps. Some examples are scintillators and display phosphors. Short Persistent

Phosphorescence (SPP) that lasts for seconds and generally becomes noticeable to the human eyes. Most phosphors show short persistent phosphorescence after they are exposed to the UV, visible light, plasma beam, electron beam or X-rays. Persistent Phosphorescence (PP) lasts for minutes and is due to the deep traps in the materials. These traps hold electrons or holes for some time and afterwards release thermally. Long Persistent Phosphorescence (LPP) shows lifetimes of the order oftens of minutes or hours.

Although many new phosphors have been developed recently, only a few can be excited under natural light like sunlight. The issue of convenient excitation source is very important and actually limits the applications of long persistent phosphors. Many novel methods in the synthesis have been developed to produce persistent materials. These methods have mainly included, selective codoping with various ions to generate electronor hole traps and defect related electron traps.

## 7. Motivation

Fundamental and applied research on various aspects of luminescence phenomenon is advancing with a tremendous pace, involving conventional and advanced experimental methods. Many blue, green, yellow, orange, and red color long persistent phosphors have been developed so far. Long persistent phosphors have potential applications in some special areas. In particular, long persistent phosphors emitting electromagnetic radiations in the visible region; have found ever-increasing commercial interest in this decade, especially, because of their usage in illumination engineering, dark vision display devices, multiple domestic and industrial applications. Considerably bright, long-decay blue, blue-green and yellow-green emitting phosphors have been developed. However, developing uniform red emitting long persistent phosphor is still an open challenge for the researchers. It will be worthwhile to explore novel host lattices such as titanate, silicates, oxysulphides etc. to achieve the long afterglow phosphors. Apart from the incorporation of rare-earth ions as dopants, other metal ions such as transition ions may be used. If one succeeds in achieving the LP phosphors with transition ions, it may reduce the production cost and produce phosphors with multiple emission colors due to  $d \rightarrow d$  electronic transition. Such phosphors may open up new areas in phosphor chemistry. Thermo luminescence glow curves need to be studied with other rare-earth ions as well to understand the role of cation and anion defects to enhance the process of delayed emission in detail. There is a requirement of commercial production of long persistent phosphors using indigenous chemicals and technology.

## 8. Expected outcome of the proposed research work:-

Major advances have been made by many research groups around the world recently in demonstrating

Afterglow phosphor, fabricating new luminescent materials, developing high efficiency afterglow phosphors for several applications, such as safety signages, luminescent paints, interior decorations, and as tracer particle for photodynamic therapy and the mechanism involved. There are still many areas that need additional work, including:-

- (1) Development of new Afterglow phosphor. This will require a better understanding of Energy Transfer mechanism, and also a better understanding of materials properties and new materials fabrication process.
- (2) We will discuss the possible mechanisms, which involve the variation of trap distribution during the trapping and de-trapping process, complicated photo-ionization reaction of trap site levels and impurity centers together with their corresponding migration kinetics of carriers.
- (3) Meanwhile, we emphasize the characterization techniques of defects, used to qualitatively or quantitatively describe the types, concentrations and depths of the traps.
- (4) The structure information of the samples was studied in X-Ray Diffraction (XRD) and FESEM.
- (5) Photoluminescence and phosphorescence properties of the phosphor were investigated systematically. The reason why the photoluminescence and phosphorescence color can be tuned has been discussed.
- (4) Clear and direct demonstrations of ET between ions. It is necessary to develop new methods for the measurements of Afterglow materials properties including QE.

## **9. Proposed Methodology/ Plan of work during the tenure of the research work**

Afterglow phosphors can be synthesized by various routes as described in the literature such as Solid-state reaction, Sol-gel, Pechini, Auto combustion, Hydrothermal, Microwave sintering and Floating zone methods. In the present study, we have adopted a “Complex Based Precursor solution Method using TEA as complexing Agent” for synthesis of up-conversion Phosphor. The preparation procedure involved the evaporation of aqueous precursor solutions, which were composed of stoichiometric amounts of the desired metal ions, complexed with TEA. TEA is an efficient chelating agent that has good coordination properties with the metal ions. One to two moles of TEA per mole of the total metal ions is stoichiometrically required for formation of stable complexes with metal ions. However, TEA in the precursor solution has always been maintained to be in excess of the required stoichiometry. During evaporation of the precursor solution, the TEA present in the

system may have probably led to the formation of vinyl functional groups, which causes the polymerization. The reason for using complexing agent i.e. TEA, in our synthesis procedure, is its ability of bond formation with the metal cations by its hydroxyl groups and the nitrogen atom. The amount of TEA should be maintained properly to control the particle size.

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