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Luminescence Properties of Eu Doped Phosphate Phosphors: A Review

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Abstract: Several Researchers have tried hard to get a most effective Luminescent Material but first of all Matsuzawa et al. reported in 1996 on the $SrAl_2O_4$: Eu^{2+} co-doped with Dy^{3+} ions' extremely long-lasting afterglow, which was more than 10-times brighter than the previously extensively used ZnS: Cu. Since then, the search for stable and efficient phosphors has grown in popularity. However, the number of luminous materials is still relatively modest over 15 years after the creation of $SrAl_2O_4$: Eu^{2+}. Furthermore, the mechanism underlying this occurrence is unknown. Although the majority of the authors agree on some broad characteristics, such as the existence of long-lasting trap levels, many aspects remain unknown. We offer an overview of the major phosphate-based phosphors of known luminous materials based on Eu^{2+} doping and how they were made in this study, as well as a closer look at the mechanisms and applications proposed to explain strong afterglow in diverse compounds.
***Key Word:** Rare -Earths, Europium oxide, Luminescence; phosphorescent;*

I. INTRODUCTION

Luminescence is "cold light," or light emitted by other sources of energy, that can occur at both normal and low temperatures. In luminescence, an energy source excites an atom's electron, which then gives back the energy in the form of light, allowing it to return to its ground state [1-2].

Phosphors are another name for luminescent materials. The term 'phosphor' is derived from the Greek language and refers to light-emitting or luminescent materials; barium sulfide is one of the first naturally occurring phosphors. A phosphor is luminous, which means it emits light as energy from an excited electron. The absorption of energy from an external source, such as another electron, a photon, or an electric field, excites the electron. An excited electron is in a quantum state with a higher energy than the ground state. The electrical ground state in semiconductors and insulators refers to electrons in the valence band, which is totally filled with these electrons.

The excited quantum state is frequently found in the conduction band, which is unoccupied and separated from the valence band by an energy gap known as the band gap, as shown in Eg. Phosphors are solid luminous materials that produce photons when an external energy source, such as an electron beam or ultraviolet light, is used to stimulate them. Phosphors have a host lattice and a luminous core, which is referred to as a "Activator." The activator takes the stimulating radiations and becomes stimulated. By emitting radiation, the excited state returns to the ground state. The activator may not take the excitation radiation in some materials, but another ion may absorb the excitation energy and then transfer it to the activator. The absorbing ion is referred to as a sensitizer in this circumstance. In many circumstances, the host lattice acts as a "Sensitizer" by transferring excitation energy to the activator [3]. At least one type of oxide is present in the host lattice, such as sulphide, aluminate, alumino silicate, silicate, tantalite, niobate, phosphate, halophosphate, Borate, tungstate, and so on.

Because phosphate-based phosphors are key luminescence hosts and have substantial absorption in the VUV range (100– 200 nm), as well as a high chemical stability and low cost, phosphate compounds have attracted a lot of attention as plasma display panels (PDPs) materials in recent years. Because of their great physical and thermal stability, long afterglow and high brightness, as well as lower temperature synthesis, phosphor phosphors are one of the most essential luminescent materials. Eu2+-activated $ABPO_4$ phosphors (A and B are monovalent and divalent cations, respectively) have been described as blue-emitting phosphors triggered by near UV-LEDs among them. The luminous properties of $KSrPO_4$:Eu^{2+}, $KBaPO_4$:Eu^{2+}, and $LiCaPO_4$:Eu^{2+}, for example, are good, including quantum efficiency and thermal quenching behavior. As a result, they are thought to have potential as phosphors for white light emitting diodes [4]. We offered a review of Eu2+ doped phosphate compounds in this work.

II.MATERIAL AND METHODS

We have explored a variety of methodologies and materials that have already been synthesized in this study. Table 1 is a list of some of them.

Table 1. *the europium ions Eu2+ based phosphate luminescent materials*

Synthesized Phosphors	Starting Precursors	Synthesis Method	References
$LiCaPO_4$: Eu^{2+}	$LiNO_3$, $Ca(NO_3)_2{\cdot}4H_2O$ $Eu(NO_3)_3$,	Polymerizable complex (PC) method	4
KLa1-xEuxP4O12	K2CO3, La2O3 , $NH_4H_2PO_4$, Eu_2O_3	Co-precipitation method	5
$Mg_{21}Ca4Na4(PO4)_{18}$	$Mg(NO_3)$, $Ca(NO_3)_2$ $NaNO_3$, $NH_4H_2PO_4$	Combustion-assisted synthesis technique	6
$Ca_4(PO_4)_2O$	$CaCO_3$, $NH_4H_2PO_4$, Eu_2O_3 and CeO_2	solid-state method	7
$Na_2CaP_2O_7$: RE^{3+}	Na_2CO_3, $CaCO_3$, $NH_4H_2PO_4$, $(NH_4)_2Ce(NO_3)_6$, Tb_4O_7, Sm_2O_3 and Eu_2O_3	Solid state reaction method	8
$Sr_5(PO_4)_3F$: Eu^{3+}	$Sr(NO_3)_2$, $NH_4H_2PO_4$, NH_4F, Eu_2O_3	Combustion synthesis	9
$KSrY(PO_4)_2$: Eu^{2+}	K_2CO_3, $SrCO_3$, $Y2O_3$, $NH_4H_2PO_4$, and Eu_2O_3	Amorphous metal complex method and solid state reaction method	10
$LaPO_4$	La_2O_3, $[(NH_4)_2H\ PO_4)]$, Ce_2O_3 and Tb_4O_7	Solid state synthesis method.	11
$Li_2Zr(PO_4)_2$	Li_2CO_3, ZrO_2, $NH_4H_2PO_4$ and Eu_2O_3	Solid-state reactions	12

III.IDENTIFIED AND STUDIED COMPOUNDS

Although a wide range of host materials are utilized as luminous compounds, the number of known hosts for sustained luminescence is rather small. The phosphate is the focus of the majority of studies on this phenomena, with $Na_2CaP_2O_7$: RE^{3+} and $Mg_{21}Ca_4Na_4(PO_4)_{18}$ being the most well-known examples. Only a few host crystals have been reported to display luminescent behavior with Eu^{2+} activators, in addition to these two primary types of materials. In this paragraph, we will present an overview of the compounds where Eu^{2+}-based luminescence has been reported. These materials are often labeled as "phosphorescent," but the term's definition is murky, because it's also applied to luminescence in which a quasi-stable state is complex, resulting in a longer fluorescence decay lifespan. Even the decline from such a quasi-stable state, however, usually takes less than a second [13].

Marciniak et al. [5] studied the spectroscopic properties of $KLa1\text{-}xEuxP_4O_{12}$ nano-crystals. In contrast to the CT emission intensity, the intensity of the ligand-to-metal CT band in the excitation spectra diminishes with increasing Eu^{3+} concentration, suggesting severe concentration quenching. With increasing dopant concentration, the CT emission decay periods are significantly shortened. Due to the overlap between CT emission and 4fn absorption bands of Eu^{3+}, these phenomena were interpreted in terms of energy transfer from CT to 4fn states with increasing Eu3+ concentration. CT band intensity was found to be proportional to 1/N2, where N is the concentration. The tight relationship between CT intensity and Eu^{3+} concentration is crucial for the development of novel light sources based on Eu^{3+} doped systems.

Zhang et al. [6] created tri active $Mg_{21}Ca_4Na_4(PO_4)_{18}$ (MCNP) phosphors using Eu2+, Tb^{3+}, and Mn^{2+} ions. Three crystallographic positions of Ca^{2+} ions exist in the structure of MCNP in the trigonal space group R3, which might be substituted with Eu2+ ions. When exposed to UV light, MCNP: Eu^{2+} emits a blue light with a broad asymmetric band that may be divided into three Gaussian profiles that correspond to the three types of Ca^{2+} ions. In the MCNP host, the ET processes from Eu^{2+} to Tb^{3+} ions and Eu^{2+} to Mn^{2+} ions have been validated as dipole–dipole interaction and quadrupole–quadrupole interaction, respectively. The concentration quenching method was also used to calculate their critical distances. Tb^{3+} and Mn^{2+}, which are both sensitive to Eu^{2+} ions, can release bright green and red light at 550 and 645 nm, respectively. Color-tunable emission can be achieved by coupling emission bands centered at 425, 550, and 645 nm, respectively, due to contributions from Eu^{2+}, Tb^{3+}, and Mn^{2+}. These findings suggest that UV-converted white LEDs could benefit from MCNP: Eu^{2+}, Tb^{3+}, Mn^{2+} phosphors with tunable white emission as produced.

Under the stimulation of UV light, Yinqun et al. [7] published experimental results that the $Ca_4(PO_4)_2O$:$_{0.1}Ce^{3+}/Li^+$, 0.06 Eu^{2+} phosphor had two emission bands positioned in the blue and yellow regions. Under varied excitation wavelengths, $Ca_4(PO_4)_2O$: 0.1 Ce3+/Li^+, 0.06 Eu^{2+}could be systematically tweaked to generate white light. The $Ca_4(PO_4)2O$:0.1$Ce3^+/Li^+$,0.06Eu^{2+} phosphor was discovered to have prospective applications as a single-phase white-emitting phosphor for UV white LEDs in this study.

The luminous characteristics of Eu^{3+} doped and Li^{+} co-doped Sr5(PO4)3F phosphate phosphors were studied. [9] by Shinde et al. The ability of the combustion process to do atomic level doping of impurity ions in host lattices is demonstrated by the generation of homogenous single phase lamp phosphors, which also validates combustion's highly exothermic character. The combustion process has several advantages, including reduced processing time, energy savings, and the fine particle nature of the combustion products. The $Sr5(PO_4)_3F$: Eu^{3+} phosphors exhibit red/orange emission from Eu^{3+} when excited at 395 nm. Because of the charge compensation, the luminescence intensity of $Sr_5(PO_4)_3F$: Eu^{3+} was greatly increased when co-doped with Li^{+}. This fundamental research could be useful in the development of new luminescent technologies for tricolor lamps, light emitting diodes, and other applications.

Kim et al. [4] used a polymerizable complex (PC) technique with a water-soluble polyethylene glycol-conjugated phosphate ester to make $LiCaPO_4$: Eu^{2+} phosphor with strong photoluminescence (PEG-P). A process involving polyethylene glycol 300, phosphorus pentoxide, and pyrophosphoric acid yielded PEG-P. In an aqueous environment, the PEG-P was stable. When PEG-P was utilized as a source of P during the PC procedure, a translucent solution and gel were formed, however H_3PO_4 created an unwanted precipitate. The $LiCaPO_4$: Eu^{2+} synthesized using the PC technique with the PEG-P had a higher emission intensity than the $LiCaPO_4$: Eu^{2+} synthesized using the solid state reaction approach and the PC method with H_3PO_4. The remarkable homogeneity of elements in the sample produced with PEG-P could be attributed to its strong luminescent characteristics.

Saito et al. [10] examined the luminescence properties of phosphates of various compositions by synthesizing Eu^{2+} doped samples. A green light emitting $KSrY(PO_4)_2$:Eu^{2+} was discovered as a result of the research, which is unusual for a phosphate phosphor. The excitation band for $KSrY(PO_4)_2$:Eu^{2+} was between 250 and 450 nm, and it emitted green light with a maximal emission at 520 nm. This shows that $KSrY(PO_4)_2$:Eu^{2+} could be used as a phosphor for white LEDs when excited by a near-ultraviolet LED.

Patil et al [11] effectively synthesized $LaPO_4$ phosphor doped with Eu and Tb rare-earth ions, maintaining Eu concentration constant and altering Tb concentration as 0.1, 0.5, and 1.5 percent utilizing solid state synthesis. The dominant peak in the XRD pattern, which corresponds to a d-value of around 3.11A0 and is followed by several less powerful peaks, belongs to the monoclinic system of Lanthanum Phosphate crystal structure. The strength of the PL increases as the Tb concentration rises. As a result of the high PL intensity, the $LaPO_4$ Eu,Tb phosphors can be used in a wide range of lamps and displays.

IV. CONCLUSION

We discussed Eu activated several phosphate phosphors in this review study. Based on advancements in LED conversion phosphors, the hunt for novel and improved materials containing Eu^{2+} ions as activators has lately shifted to alternative host materials. In addition, the search for the mechanism underpinning luminescence has taken a new turn. Various models have been developed in recent decades with little experimental support, but only recently have researchers begun to apply new and promising approaches that could confirm or refute these theories. For the development of practical applications such as emergency lights, traffic signals, dials and displays, textile printing, medical diagnostics, and so on, a better understanding of the exact mechanism is essential. Long-lasting phosphors activated by Eu^{2+} will play a critical part in the bright future of luminescence technology.

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