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Review on Rare Earth Activated Lithium Alkaline Phosphate Phosphor for Lighting Application

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Abstract

Rare-earth activated phosphate phosphors have attracted significant attention due to their unique optical properties, which make them useful in a variety of applications, including lighting, displays, and lasers. These materials are primarily based on host lattices of phosphate compounds, doped with rare-earth elements like Eu^{2+}, Eu^{3+}, Ce^{3+}, Tb^{3+}, Dy^{3+}, and others, depending on the desired optical properties. Phosphate-based phosphors doped with rare-earth ions generally exhibit strong luminescence. The optical transitions within rare-earth ions (f-f or d-f transitions) are highly efficient, allowing these materials to be used in high-performance lighting technologies, such as white LEDs. The phosphate structure provides a stable host lattice, which improves the chemical and thermal stability of the phosphor. Phosphate hosts often possess high melting points and resistance to chemical degradation, making them suitable for high-temperature applications. This makes them ideal for color tuning in various devices like white LEDs, lasers and displays.

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Introduction

The first commercially available white light-emitting diodes (wLEDs) were developed in 1997 (Nakamura and Fasol, 1997). These wLEDs revolutionized lighting technology, combining energy efficiency with long lifetimes. Their development primarily involved using a blue LED chip coated with a yellow phosphor, typically made from cerium-doped yttrium aluminium garnet (YAG). This combination of blue light from the LED and yellow light from the phosphor creates the perception of white light. Over time, wLED technology has been continuously refined, leading to improvements in color rendering, energy efficiency, and application flexibility (Kishida *et al.,* 2003). Today, wLEDs are widely used in various industries, including general lighting, displays, automotive lighting, and beyond (DXia *et al.,* 2005).

Recently, an alternative approach to generating white light has been proposed that utilizes red, green and blue (RGB) tri-color phosphors excited by ultraviolet (UV) light, particularly near UV (n-UV) light. In this method, instead of relying on a blue LED and yellow phosphor, UV LEDs are used to excite the RGB phosphors, which then emit light in their respective colors (Setlur *et al.,* 2008). The combination of these primary colors produces white light. This approach offers several advantages, such as enhanced color rendering and greater flexibility in adjusting the spectral composition of the emitted light.

By carefully tuning the proportions of red, green, and blue phosphors, manufacturers can create white light with different color temperatures and improved color quality, making it a promising alternative for applications where precise color control is essential, such as in displays and specialized lighting (Radkov *et al.,* 2004).

As a result, there has been significant interest in discovering new, highly efficient RGB phosphors that can be excited by near-UV (n-UV) LEDs to generate white light. In this pursuit, various $ABPO_4$ systems have been extensively studied, where "A" represents a monovalent cation (Li^+, Na^+, K^+, Rb^+, Cs^+) and "B" represents a divalent cation (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}). These materials have attracted attention due to their excellent thermal and hydrolytic stability, which are essential properties for efficient phosphor host materials in wLEDs. The stability of these $ABPO_4$ systems ensures they can withstand the high temperatures and moisture exposure typical in LED operation without degrading, making them ideal candidates for long-lasting, high-performance white light sources. On-going research is focused on optimizing the emission characteristics of these phosphor systems to improve both the efficiency and colour quality of wLEDs (Wu *et al.,* 2006; Yang *et al.,* 2008; Poort *et al.,* 1997).

In this study, we have reported the structural and optical properties of $LiXPO_4$(X = Mg, Ca, Ba, Sr) phosphor doped with different types of rare earth (RE) prepared by different synthesis techniques. The photoluminescence characteristics, including excitation, emission spectra, and CIE chromaticity coordinates, were thoroughly investigated to explore the potential of this new phosphor material for use in near-UV (n-UV) based white LEDs (w-LEDs). The combination of the n-UV excitation and the novel phosphor shows promise for applications in solid-state lighting. This development contributes to the on-going search for innovative phosphor materials suitable for n-UV based w-LEDs.

Materials and Methods

The phosphor materials, specifically $LiMgPO_4$doped with Eu^{2+}andEu^{3+} ions, are synthesized using the conventional solid-state reaction method**.** The raw materials$LiCO_3$, $MgCO_3Mg(OH)_25H_2O$ (magnesium carbonate basic pentahydrate), $NH_4H_2PO_4$ and Eu_2O_3 (99.9%) were employed. The starting materials with stoichiometric amounts were mixed in a small covered alumina crucible. The Eu_2O_3 was added in an amount to obtain desiredmol% of Eu in the sample. For further spectroscopic analysis, the sample containing optimalmol % of Eu was selected. The mixture was first heated to 300 °C and kept at this temperature for 5 h in air. After the second homogenization with acetone, the mixture was ground again to ensure uniformity, followed by heating to 600°C for10 hours in an air atmosphere. The samples prepared in a reducing atmosphere followed a specific procedure to ensure the right conditions for the reduction of Europium to the Eu^{2+} state. The crucible containing the sample was heated to 800°C and maintained at this temperature for 20 hours under the reducing atmosphere. After the heat treatment, the crucible was allowed to cool naturally to ambient temperature**.** Slow cooling helps prevent thermal shock and ensures the formation of stable crystal structures in the final product (Baran *et al.,* 2014).

$LiCaPO_4$: Eu^{2+} and $LiCaPO_4$:Ce^{3+}samples were synthesized using the solid-state reaction method**.** The appropriate amounts of raw materials $CaCO_3$, Li_2CO_3, $NH_4H_2PO_4$ and Eu_2O_3 (99.99%) were thoroughly mixed by grinding. They were pre-sinter at 600 ºC for 3h in air, and re-sintered at 850 ºC for 6h in a reducing atmosphere (N_2:H_2 = 90:10) (Zhang *et al.,* 2013).

A series of $LiBaPO_4$: RE (RE = Eu^{2+}, Tb^{3+}, Sm^{3+}) phosphors were prepared using a conventional solid-state reaction and the resultant samples can be used as three basal phosphors for w-LEDs. The starting material was a stoichiometric mixture of reagent grade Li_2CO_3, $BaCO_3$, $(NH_4)_2HPO_4$, Eu_2O_3, Tb_4O_7 and Sm_2O_3. First, the mixtures were heated up to 600 ºC and kept at this temperature for 3 h. Second, the obtained powder samples of $LiBaPO_4$: $Eu^{2+}$and $LiBaPO_4$:Tb^{3+} were thoroughly mixed and then heated up to 1050 ºC for3hinan active carbon atmosphere. However, the obtained powders of $LiBaPO_4$:Sm^{3+} were thoroughly mixed and then heated up to 1050 ºC for 3 hinair atmosphere. After calcining, the samples were cooled to room temperature in the furnace, and ground again into powder for further investigation (Sun *et al.,* 2012).

Li_2CO_3, $SrCO_3$, $NH_4H_2PO_4$, and Eu_2O_3 powders were used as the starting materials for $LiSrPO_4$:Eu^{3+} phosphors with different concentrations of Eu^{3+} ions. These materials were mixed using alcohol as a solvent and then ball-milled for 1 h with zirconia balls. After drying, the mixed powders were subjected to microwave-assisted sintering in a microwave furnace to form the sample $LiSrPO_4$:Eu^{3+} phosphors. The microwave furnace featured controllable microwave powers up to 1.3 kW at

2.45 GHz. Silicon carbide (SiC) was used as a susceptor to provide indirect heating for the powders due to the very strong heating response. The material sample was placed on an alumina crucible surrounded by four silicon carbide susceptors and encapsulated by ceramic fiber insulating material in a microwave cavity. The mixed powders were sintered at 1200 ºC for 3 h under air atmosphere (Yang *et al.,* 2013).

Structural Properties

$LiMgPO_4$ Sintered samples were characterized by x-ray powder diffraction (XRD) patterns using a Philips Xpert/MPD diffraction system with Cu Kα (λ = 1.5405 Å). By comparison of the XRD patterns of the samples with Joint Committee on Powder Diffraction Standards (JCPDS no. 32–0574), no impurities were detected and all the reflections could be well indexed to a $LiMgPO_4$ single-phase, olivine-type orthorhombic structure with the space group P_{nma} and lattice parameters of a = 10.147 Å, b = 5.909 Å, c = 4.692 Å and Z = 4 (Hanic *et al.,* 1982). $LiMgPO_4$ crystal tetrahedral PO4 and octahedral LiO_6, and MgO_6 groups constitute the structure forming a 3D network with perpendicular tunnels along the (01 0) and (0 01) directions occupied by Li ions. The average bond distances Li-O and Mg-O are 2.143 and 2.105Å within polyhedra LiO_6 and MgO_6, respectively.

Lightfoot *et al.,* (1991) pointed out that the XRD pattern of $LiCaPO_4$ indexed as JCPDS 14-0403 is not correct because of the presence of second phase $Ca_3(PO_4)_2$ due to the loss of Li at high temperature. They reported a single phase $LiCaPO_4$ and the corresponding pattern are indexed as JCPDS 79-1936 (Lightfoot *et al.,* 1991). However, present reports on $LiCaPO_4:Eu^{2+}$ by Zhang *et al.,* (2011) show that their XRD patterns agree with JCPDS 14-0403, which means those observed luminescent properties might be a combination of $LiCaPO_4:Eu^{2+}$ and $Ca_3(PO_4)_2:Eu^{2+}$. All the peaks can be indexed to $LiCaPO_4$ phase as JCPDS 79-1936, which indicates that phase pure phosphor was obtained, and the doped Eu^{2+} did not change the host crystal lattice. $LiCaPO_4$ has the hexagonal structure with P31c(159) space group. The unit cell volume and lattice parameters of the matrix are V=488.67Å3, a=7.5247Å, b=7.5247Å, c =9.9657Å (Lightfoot *et al.,* 1991).

The $LiBaPO_4$ compounds have a stuffed tridymite structure with a hexagonal unit cell and space group P63 (Elamman *et al.,* 1988). All the diffraction peaks can be indexed to the phases of LiBaPO4 (Joint Committee On Powder Diffraction Standards (JCPDS) 14-0270). However, as an exceptional case, one additional weak diffraction peak near 23.0 for the samples should be ascribed to the residual starting material BaO. The other three additional weak diffraction peaks of the samples near 36.8, 37.1, and 53.9 should be assigned to the material Li_3PO_4.

$LiSrPO_4:Eu^{3+}$ phosphors with different concentrations of Eu^{3+} ions prepared by microwave assisted sintering. The results indicate that all peaks of the Eu^{3+}-ion-doped $LiSrPO_4$ phosphors can be indexed to pure $LiSrPO_4$ according to the Joint Committee on Powder Diffraction Standards (JCPDS #14-0202) and match the reference data well (Sun *et al.,* 2011). As a large (1.12 Å) divalent cation, Sr^{2+} can be replaced by a rare earth (RE = Eu^{2+}, Sm^{3+}, Tb^{3+}etc.) to achieve full-color luminescence. The Eu^{3+}cations (1.09 Å) are expected to prefer to occupy Sr^{2+} sites, without distorting the crystallinity of the host. However, when the Eu^{3+} ion concentration was further increased, the impurity phase of Eu_2O_3 appeared implying that the amount of Eu^{3+} ions incorporated into $LiSrPO_4$ rose even further given the low availability of Sr.

Optical Properties

The description of photoluminescence excitation (PLE) spectra of the $LiMgPO_4:Eu^{3+}$ and $LiMgPO_4:Eu^{2+}$ are presented in this section. It has been observed that, depending on the excitation wavelength, $LiMgPO_4$:Eu yields emission related to Eu^{2+} and/or Eu^{3+}. Under the excitation wavelength at 260 nm, the luminescence spectrum showed two distinct bands peaking at 380 nm and 490 nm, attributed to the $4f^6\ 5d^1 \rightarrow 4f^7$ transitions in Eu^{2+} ion and recombination of europium-trapped exciton (ETE) (Seo and Ceram, 2013), respectively and several sharp lines, observed in the spectral region between 580 and 710 nm, ascribed to the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3, 4) transitions of Eu^{3+}. Under excitation with 325 nm, only luminescence related to the $4f^6\ 5d^1 \rightarrow 4f^7$ transition in the Eu^{2+} and ETE emission is observed, whereas for excitation with 394 nm only emission from Eu^{3+} is obtained. The excitation spectra of the emission monitored at 378 nm and 490 nm, corresponding to the $4f^6\ 5d^1 \rightarrow 4f^7$ transition in the Eu^{2+} and ETE emission, respectively.

The PLE and PL spectra of $LiCaPO_4$: Eu^{2+} phosphor can be realized that the excitation band monitored at 470 nm is intense and consists of several broad band around 261, 315 and 410 nm, which are mainly ascribed to the transition of Eu^{2+} from 4f-ground state to 5d-excited state

and the first band may also partly contributed to the valence-to-conduction band of $LiCaPO_4$ host lattice. The difference between PLE spectrum and More *et al.,* (2011) is due to the difference of several experimental details. More's luminescence spectrum is obtained from $LiCaPO_4$ doped with Eu^{2+} makes the intensity of lowest energy absorption band stronger in PLE spectrum. Besides, different raw materials and synthesis conditions will affect the crystallinity and the specific coordination environment, and eventually the scope of luminescent spectrum may change. Excited at 395 nm, the phosphor exhibits a wide and strong blue emission band centering at 470 nm, and the full-width half maximum (FWHM) is about 37 nm, which is due to the $4f^6\ 5d^1 \rightarrow 4f^7$ allowed electric dipole transition of Eu^{2+}.

The PLE spectrum of the $LiBaPO_4:Eu^{2+}$ phosphor measured by monitoring the emission of 470 nm, exhibits a broad band from 230 to 430 nm, which is assigned to the 4f→5d transition of the Eu^{2+} ion (Du *et al.,* 2009). This indicates that the phosphor can be effectively excited by near-UV LED chips (350–420 nm), which is necessary for potential applications in w-LEDs fabricated with near-UV chips. Under the excitation of 350 nm, the PL spectra of $LiBaPO_4$: Eu^{2+} consist of a broad band from 400 to 600 nm with a maximum wavelength at about 470 nm, which can be attributed to the $4f^6\ 5d^1 \rightarrow 4f^7$ transition of the Eu^{2+} ion. On the other hand the $LiBaPO_4$: Tb^{3+} phosphors emit a green luminescence under the excitation of near-UV light.

The PLE spectrum of $LiBaPO_4$: Tb^{3+} phosphor includes two parts, one strong absorption band centered at 228 nm in the short UV region within the range of 210–300 nm corresponding to the $4f^8 \rightarrow 4f^7\ 5d^1$ transition. Furthermore, the PLE spectrum of Sm^{3+} doped $LiBaPO_4$ phosphor monitored by 599 nm has several peaks, which are located at 221, 306, 317, 332, 345, 362, 375, 402, 417, 440, 475 and 529 nm, respectively.

The excitation spectra in the region from 200 nm to 450 nm for the $LiSrPO_4:Eu^{3+}$ phosphors with different concentrations of Eu^{3+} ions prepared by microwave-assisted sintering. The spectra of the $LiSrPO_4:Eu^{3+}$ phosphors exhibit a broad band in the UV region centered at about 248 nm to 252 nm, and several sharp lines between 300 nm and 450 nm. The broad absorption band is named the charge-transfer state (CTS) band due to europium–oxygen interactions. All the $LiSrPO_4:Eu^{3+}$ phosphors were excited by a xenon lamp at wavelength of 395 nm, indicating that the $LiSrPO_4:Eu^{3+}$ phosphors can be effectively excited by commercial UV LED chips (300 nm to 410 nm). The emission spectra of the $LiSrPO_4:Eu^{3+}$ phosphors show four emission bands at 581 nm, 595 nm, 617 nm, 656 nm and 700 nm, respectively. In this study, the $LiSrPO_4:Eu^{3+}$ phosphors exhibit red light due to the strongest 617 nm emission, corresponding to the emission of the forced electric dipole transition of the highly sensitive $^5D_0 \rightarrow {}^7F_2$ transition (Zhang *et al.,* 2011).

Features and Advantages

The rare earth activated phosphate based phosphors have many features and advantages. Some of them are as follows.

- **High Luminescence Efficiency**: Phosphate-based phosphors doped with rare-earth ions generally exhibit strong luminescence. The optical transitions within rare-earth ions (f-f or d-f transitions) are highly efficient, allowing these materials to be used in high-performance lighting technologies, such as white LEDs.
- **Stable Host Matrix**: The phosphate structure provides a stable host lattice, which improves the chemical and thermal stability of the phosphor. Phosphate hosts often possess high melting points and resistance to chemical degradation, making them suitable for high temperature applications.
- **Wide Range Emission Wavelengths**: Depending on the dopant, rare-earth activated phosphates can emit across a wide range of the visible spectrum, as well as in the UV and near-IR regions. For example, Eu^{3+}-doped phosphors typically emit red light, while Ce^{3+}-doped materials emit blue light. This makes them ideal for color tuning in various devices.
- **Energy Transfer Mechanisms**: Rare-earth ions exhibit efficient energy transfer processes, enabling the fine control of emission characteristics. This energy transfer can occur between different ions in the lattice, optimizing the phosphor's performance. For example, Ce^{3+} can transfer energy to Tb^{3+} in Ce^{3+}/Tb^{3+} co-doped phosphates, enhancing green emission.

Challenges and Limitations

There are many challenges of phosphate phosphors during the synthesis of samples and some limitations also.

- **Cost and Availability of Rare-Earth Elements**: The production of rare-earth doped materials depends

heavily on the availability of these elements, some of which are scarce and expensive. This poses a potential economic challenge for large-scale commercial applications.

- **Complex Synthesis**: Synthesizing high-quality, rare-earth activated phosphate phosphors often requires precise control over the composition, crystallinity, and particle size to achieve optimal luminescence. Techniques like solid-state reactions, sol-gel processes, and hydrothermal synthesis are commonly used, but they can be complex and require high temperatures.
- **Quenching at High Concentrations**: Concentration quenching can occur if too much of the dopant is added to the phosphate matrix. This limits the amount of active material that can be included in the phosphor and necessitates careful optimization to balance brightness and efficiency.

Recent Advances

Nanophosphors: Research on nanoscale rare-earth activated phosphate phosphors has shown promise for improved light scattering, higher surface area, and enhanced performance in biomedical applications like imaging and drug delivery.

Co-Doping Strategies: Co-doping with different rare-earth ions can fine-tune emission properties and improve the energy transfer between dopants, leading to enhanced performance in lighting and display technologies.

Environmentally Friendly Phosphors: There is growing interest in developing phosphate phosphors with lower toxicity, especially for use in environmentally sensitive applications like consumer electronics and bio-imaging.

Applications

There are numerous applications of rare earth activated phosphate based phosphors.

White LEDs: By combining blue-emitting phosphors like Ce^{3+} with red- or green-emitting phosphors, white light can be generated for energy-efficient lighting solutions.

Displays and Lasers: Phosphates doped with rare-earth elements like Eu^{3+} and Tb^{3+} are used in color displays and laser materials due to their sharp emission lines and high brightness.

Bio-imaging and Sensing: Phosphors that emit in the near-infrared (NIR) region, such as Yb^{3+}- or Nd^{3+}-doped phosphates, are increasingly being explored for bioimaging applications because of their deeper tissue penetration and low scattering in biological tissues.

Conclusion

Rare-earth activated with rare-earth elements like Eu^{2+}, Eu^{3+}, Ce^{3+}, Tb^{3+}, Dy^{3+} and others, Lithium based phosphate phosphors hold significant promise for future optical technologies due to their versatile luminescence properties, stability and wide range of potential applications. While challenges such as material cost and synthesis complexity remain, ongoing research is addressing these issues, making them an increasingly viable option for modern lighting, white light emitting diodes (LEDs), optical devices, displays, lasers, bio-imaging and sensing applications.

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