

A Brief Synthesis Methods and Luminescence Development of Rare Earth Activated Borophosphate Phosphor Materials

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Abstract

Rare-earth activated phosphors are capable of producing luminescent materials which are developed to overcoming the drawback of traditional based phosphors. Most changes happened in efficiencies of lighting for colors in the novel area research. This article focuses on brief discussions on synthesis methods, luminescence developments and also summarizing the current state of researches for the potential applications of rare-earth activated borophosphate phosphor materials in diverse technological fields. Its highlights of multifunctional phosphor materials converted into high intensity of white LEDs. Finally we address the chemical composition with rare-earths and synthesis techniques in the phosphor materials to production of high luminescence intensity.

Keywords: Borophosphate Phosphor, Rare-earth and Luminescence

Introduction:

Phosphors have great applied value in the areas of displays, microwave electronics, solid state lasers, sensors and amplifiers [1]. Most phosphors are made up of a host composition and a dopant ion added in carefully controlled quantities. In order to enhance the luminous efficiency of a phosphor, the dopant ion concentration in a host material should be as high as possible to increase the absorption cross-section [2]. The synthesis methods and luminescence development of rare earth activated borophosphate phosphor materials represent a critical area of research within the field of luminescent materials and also promising the optical properties, making them attractive candidates for various applications such as solid-state lighting, displays, and biomedical imaging. This synthesis and luminescence development process involves the preparation of borophosphate host matrices and the incorporation of rare earth ions through various techniques. Understanding the synthesis routes and their impact on the luminescence properties is crucial for tailoring the optical characteristics of these materials to meet specific application requirements. Through systematic investigation, researchers aim to optimize the synthesis methods to enhance the luminescence efficiency, color purity, and stability of rare earth activated borophosphate

phosphors, thereby advancing their technological applications like phosphor-converted white LEDs, and bioimaging probes, citing examples of recent advancements and commercial products. Moreover, it offers insights into future research directions, including the exploration of novel synthesis routes, the development of multifunctional phosphor materials, and the integration of rare earth activated borophosphate phosphors into emerging technologies.

Materials and synthesis techniques:

In this paper we have discussed several kinds of methods and materials which have been synthesized already. Some of them are listed in Table 1.

Table 1. Rare-earth activated borophosphate luminescent materials

Year	Synthesized Phosphate Phosphors	Starting precursors	Synthesis Methods – Emission color	Excitations	Emissions	Reference Number
2001	La(BO ₃ , PO ₄) : Ce, Tb, Gd	BPO ₄ , La ₂ O ₃ , CeO ₂ , Tb ₄ O ₇ , Gd ₂ O ₃	single-step calcinations in a carbon reducing atmosphere	254nm- Gd ³⁺ 284nm - Ce ³⁺ Range 230–280 nm- Tb ³⁺	312nm- Gd ³⁺ 321nm & 342nm - Ce ³⁺ Range 350–480 nm- Tb ³⁺	3
2015	MBPO ₅ (M= Ca, Sr): Eu, Ce	SrCO ₃ , CaCO ₃ , H ₃ BO ₃ , (NH ₄)H ₂ PO ₄ , (Eu ₂ O ₃)/ Ce(NO ₃) ₃	Solid state synthesis Method	354nm-nUV region- SrBPO ₅ :Eu ²⁺ 247nm- CaBPO ₅ : Eu ³⁺ 312nm- MBPO ₅ :Ce ³⁺	422nm-blue region- SrBPO ₅ :Eu ²⁺ 612nm-orange-red emission- CaBPO ₅ :Eu ³⁺ 375nm- MBPO ₅ :Ce ³⁺	4
2016	Y:BaBPO ₅ , Gd:BaBPO ₅ and La:BaBPO ₅	[NH ₄]H ₂ PO ₄ , BaCO ₃ , H ₃ BO ₃ , RE oxides of Y, Gd & La	Conventional solid state method	-	-	5

2018	$\text{Ba}_3(\text{ZnB}_5\text{O}_{10})\text{PO}_4:\text{Eu}^{2+}$	$\text{BaCO}_3, \text{ZnO}, \text{NH}_4\text{H}_2\text{PO}_4, \text{Eu}_2\text{O}_3$	solid-state reactions	365nm -nUV	415nm-blue light	6
2020	$\text{K}_2\text{BaCa}(\text{PO}_4)_2(\text{BO}_3):\text{Eu}^{2+}$	$\text{K}_2\text{CO}_3, \text{CaCO}_3, \text{BaCO}_3, \text{NH}_4\text{H}_2\text{PO}_4, \text{Eu}_2\text{O}_3, \text{H}_3\text{BO}_3$	Solid state reactions	405nm -	447nm & 660nm -red	7
2020	$\text{CsNa}_2\text{Eu}_2(\text{BO}_3)(\text{PO}_4)_2:(\text{REE} = \text{Y}, \text{Gd})$	$\text{Cs}_2\text{CO}_3, \text{NaF}, \text{Na}_2\text{CO}_3, \text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}, \text{B}_2\text{O}_3, \text{H}_3\text{BO}_3, \text{NH}_4\text{H}_2\text{PO}_4, \text{Y}_2\text{O}_3, \text{Gd}_2\text{O}_3, \text{Eu}_2\text{O}_3$	high temperature flux method	394 nm	615 nm	8
2021	$\text{CsNa}_2\text{Ln}_2(\text{BO}_3)(\text{PO}_4)_2 (\text{Ln} = \text{Ho}, \text{Er}, \text{Tm}, \text{Yb})$	$\text{Cs}_2\text{CO}_3, \text{Na}_2\text{CO}_3, \text{NaF}, \text{B}_2\text{O}_3, \text{H}_3\text{BO}_3, \text{NH}_4\text{H}_2\text{PO}_4, \text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}, \text{Ho}_2\text{O}_3, \text{Er}_2\text{O}_3, \text{Tm}_2\text{O}_3, \text{Yb}_2\text{O}_3$	high temperature flux method with superfluous	980 nm	522 nm, 557 nm and 659 nm	9
2021	$\text{Li}_2\text{NaBP}_2\text{O}_8:\text{Tb}^{3+}$	$\text{Li}_2\text{CO}_3, \text{Na}_2\text{CO}_3, \text{H}_3\text{BO}_3, \text{NH}_4\text{H}_2\text{PO}_4, \text{Tb}_2\text{O}_3$	solid state reaction procedure	372nm	544 nm	10
2021	$\text{KNa}_4\text{B}_2\text{P}_3\text{O}_{13}:\text{Sm}^{3+}$	$\text{Sm}_2\text{O}_3, \text{H}_3\text{BO}_3, \text{NH}_4\text{H}_2\text{PO}_4, \text{K}_2\text{CO}_3, \text{Na}_2\text{CO}_3$	facile solid-state synthesis	402 nm	598 nm	11

Known and scrutinized substances:

The $\text{La}(\text{BO}_3, \text{PO}_4) : \text{Ce}^{3+}, \text{Tb}^{3+}, \text{Gd}^{3+}$ were prepared by single-step calcinations in a carbon reducing atmosphere method, identified the monoclinic system with space group of $\text{P2}_1/\text{n}$ structure, little boron substituted for phosphorus in the lattice by comparison between the two prepared powders using with $(\text{NH}_4)_2\text{HPO}_4$ and BPO_4 phosphate source. At roughly 850°C , the final product starts to develop. The ideal parameters are a firing temperature of 1200°C and a molar ratio (Li^+/BPO_4) of 0.06:1 by S. J. Ding et al [3].

Cerium and Europium doped MBPO₅(M=Ca, Sr) phosphors were synthesized by modified solid state method. This method has more advantages over than other methods. The PL emission spectra gives CaBPO₅: Eu³⁺(Red region of visible spectrum), SrBPO₅: Eu²⁺(Blue region of visible spectrum) phosphors application with different concentrations. The PL of MBPO₅(M=Ca, Sr): Ce³⁺ gives range of 230-350 nm excitation band, range of 350-500nm (375nm) emission bands are observed. It is evident that every discharge curve seems situated in the ultraviolet area, which is indicative of Ce³⁺ ion emission. Following careful examination, the PL emission spectra of Ce³⁺ ions in SrBPO₅ and CaBPO₅ phosphors may be helpful for scintillation operations by V. R. Kharabe et al [4].

Y, Gd and La doped BaBPO₅ were prepared by conventional solid state method at 900°C. In this found the unit cell parameters, morphology by rietveld refinement method and also studied the luminescent properties were achieved to support the crystal structure and nature of the compounds by G. Çelik Gül et al [5].

A series of Ba₃(ZnB₅O₁₀)PO₄:Eu²⁺ phosphors were developed and identified the nine-coordinated 'Ba' site occupied by Eu²⁺ ions. A bright blue emission peak appeared at 415nm. After calculation of the parameters observed quenching mechanism was attributable to the dipole-dipole interaction, and the activation energy for thermal quenching (DE) was 0.223 eV. Moreover, the internal QE of the composition-optimized Ba_{2.95}(ZnB₅O₁₀)PO₄: 0.05Eu²⁺ was determined as 30.1%. In view of the above results, the reported blue-emitting Ba₃(ZnB₅O₁₀)PO₄: Eu²⁺ phosphors are potential candidates for applications in n-UV-pumped white LEDs by J. Sun et al [6].

In this work, successfully synthesize borophosphate K₂BaCa(PO₄)_{2-x}(BO₃)_x:0.03Eu²⁺ full-visible-spectrum phosphors by using the phosphate K₂BaCa(PO₄)₂:0.03Eu²⁺ cyan phosphor as a host and also discover a new insight concealed behind the Eu²⁺ activator's site selection. It has been observed that reducing the partial co substitution of (PO₄)³⁻ by (BO₃)³⁻ units lowers both steric barrier of Eu in Ca sites as well as the formation energy EF(Ca) of Eu substituting Ca sites. The most remarkable findings found here are that the introduction of (BO₃)³⁻ units creates a unique pathway for Eu²⁺ substitution, which leads to partial Eu²⁺ to the empty Ca sites before producing an unusual red emission at 660 nm and achieving the spectrum tuning from cyan to white-light. Remarkably, a prototype WLED with simply this full-visible-spectrum phosphor (x = 0.4) shows high quality colour reproduction (Ra = 90.4, R9 = 93.8). The comprehensive explanation of site-selective occupation of Eu²⁺ activator in this work should enhance comprehension of the basic mechanism of single-composition white-light emission. Furthermore, we stress that the suggested anion-group co substitution approach, which is based on the (BO₃)³⁻ substituting (PO₄)³⁻ groups, can be a very flexible approach to materials design and, as such, could be applied to different domains for the development of novel borophosphate compounds by X. Sheng et al [7].

High temperature flux method was used to prepared the two new rare-earth borophosphates CsNa₂REE₂(BO₃)(PO₄)₂ (REE = Y, Gd) and found their crystal structure by SC-XRD method. By separating Na⁺ and Cs⁺ ions described the structure to built up from identical [REE₂(BO₃)(PO₄)₂]_∞ 1D rows. As these compounds exhibit minimal absorption beyond 400 nm in their UV-Vis diffuse reflectance spectra, they can be used as luminous host lattices. Then, under 394 nm stimulation, Eu³⁺ ions were added to create a series of phosphors CsNa₂REE₂(1-x)Eu_{2x}(BO₃)(PO₄)₂ (REE = Y, Gd; x = 0–1). These phosphors exhibit strong red emission because of the distinctive ⁵D₀ → ⁷F_J (J = 4, 3, 2, 1, 0) transitions of Eu³⁺. Surprisingly, for fluorescence energy migration between interline Eu³⁺, the [REE₂(BO₃)(PO₄)₂]_∞ rows have a spacing of more than 6.9 Å, which largely separates the intraline Eu³⁺

ions. Since the Eu^{3+} has a low critical distance for dipole–dipole energy transfer, this indicates that the Eu^{3+} is sufficiently separated to escape concentration quenching. Thus, in $\text{CsNa}_2\text{REE}_{2(1-x)}\text{Eu}_{2x}(\text{BO}_3)(\text{PO}_4)_2$ phosphors, the concentration quenching effect, which often severely restricts the luminous efficiency, is not an issue. The light intensity increases as the concentration of Eu^{3+} rises under 394 nm illumination. Consequently, the highest emission is produced by the stoichiometric phosphor $\text{CsNa}_2\text{Eu}_2(\text{BO}_3)(\text{PO}_4)_2$, which has a high Eu^{3+} concentration of roughly 7.27×10^{21} ions per cm^3 . Moreover, the $\text{CsNa}_2\text{Eu}_2(\text{BO}_3)(\text{PO}_4)_2$ phosphor has exceptional thermal stability between 30°C and 200°C, holding onto almost 96% of its initial intensity at 200°C and 66.1% of that intensity at 300°C. Because of its exceptional heat stability and lack of concentration quenching, red phosphor can be used in high-power LEDs by D. Zhao et al [8]

A single crystal of new series of $\text{CsNa}_2\text{Ln}_2(\text{BO}_3)(\text{PO}_4)_2$ ($\text{Ln} = \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$) phosphors were prepared by high temperature flux method with superfluous $\text{Cs}_2\text{O}-\text{NaF}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ constituents as flux and Ln_2O as solute. Then, using the SC-XRD technique, the symmetry of orthorhombic space group crystal structure was determined. The chemical formula is $\text{CsNa}_2\text{Ln}_2(\text{BO}_3)(\text{PO}_4)_2$, despite having a complex structure, may be understood by itself since it states that the cations Cs^+ , Na^+ , and Yb^{3+} are segregated and separated in an anion matrix by BO_3 and PO_4 groups. The groups BO_3 and PO_4 are segregated from one another, and they are joined by Yb atoms via sharing O atoms to form a three-dimensional open framework of $[\text{Yb}_2(\text{BO}_3)(\text{PO}_4)_2]_\infty$. Two different types of tunnels that run along the c-axes and are filled with Na^+ and Cs^+ cations to maintain charge neutrality are delimited by the anion matrix $[\text{Yb}_2(\text{BO}_3)(\text{PO}_4)_2]_\infty$. The four chemicals' UV-VIS-NIR and infrared (IR) spectra have been investigated. Using Er^{3+} as the trigger and the Yb compound $\text{CsNa}_2\text{Yb}_2(\text{BO}_3)(\text{PO}_4)_2$ as the host matrix, a number of UC materials were produced. Because of the $\text{Yb}^{3+}: {}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ transition, the $\text{CsNa}_2\text{Yb}_2(\text{BO}_3)(\text{PO}_4)_2$ host is able to efficiently absorb the 980 nm light source. The energy is then transferred to the Er^{3+} activator, which produces UC emissions. For $\text{Yb}_{2-x}\text{Er}_x$, the doping concentration (x) was optimized to be 0.03. As an exciting source, 980 nm light was used, and the temperature dependency emission intensity for $\text{CsNa}_2\text{Yb}_2(\text{BO}_3)(\text{PO}_4)_2$ were measured in the range of 303–573 K. The maximum relative temperature sensing sensitivity was calculated to be a high value of 0.011 K^{-1} at 303 K. Therefore, one might expect that the UC phosphor $\text{CsNa}_2\text{Yb}_{2-x}\text{Er}_x(\text{BO}_3)(\text{PO}_4)_2$ could be a promising candidate for UC temperature sensors by Dan Zhao et al [9]

At 610 °C, polycrystalline product series of $\text{LNBP}:\text{Tb}^{3+}$ were produced. It photoluminescence exhibits under 372 nm near UV excitation based on doping concentration. The shift of the Tb^{3+} ion from ${}^5\text{D}_4$ to ${}^7\text{F}_5$ is reflected in the main emission peak at 544 nm. The reported excitation and emission intensity reaches its maximum at 0.03 mol of Tb^{3+} doping. The concentration of Tb^{3+} doped light regulates the color shift of the light emission, which ranges from white to yellowish-green to yellow-green. The concentration quenching mechanism is known to be the dipole–dipole interaction. Based on the findings, it can be concluded that a potential component for near UV-based white LEDs is Tb^{3+} -activated LNBP phosphor with good thermal stability by J. Zhu et al [10]

In this, series of $\text{KNBP}:\text{Sm}^{3+}$ was synthesized for orange-red phosphor based on new alkali metal borophosphate via facile solid-state synthesis procedure. The synthesized series of $\text{KNBP}:\text{xSm}^{3+}$ micro particles maintain the orthorhombic structure of the KNBP matrix even though dopant Sm^{3+} occupies the Na^+ site. After 402 nm NUV irradiation, the phosphor displays the characteristic 4f–4f transitions of Sm^{3+} at 645 nm (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$), 598 nm (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$) and 562 nm (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$). The electric dipole-dipole interaction has significance for concentration quenching at the ideal 0.75 mol% concentration of

Sm³⁺. With an activation energy of 0.31 eV, the phosphor exhibits good thermostability, as demonstrated by the operating temperature-dependent photoluminescence. The discovered parameters validate the prospective use of the high CP and low CCT KNBP: Sm³⁺ phosphor in solid-state lighting and display devices by Z. Fang et al [11]

Conclusion:

In this research paper on the synthesis methods and luminescence development of rare earth activated borophosphate phosphor materials would typically summarize the findings and their full potential of significances and various applications. It might emphasize the effectiveness of certain synthesis techniques in producing high-quality phosphors with desirable luminescent properties. Additionally, it could discuss any new insights gained into the luminescence mechanisms of these materials and their potential applications in various fields such as lighting, displays, or optoelectronic devices. The conclusion may also highlight valuable resource avenues by addressing key challenges and proposing future research directions for researchers, engineers, and technologists working in the field of luminescent materials.

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