Photoluminescence (PL) properties of $\text{NaLi}_2\text{PO}_4:\text{Eu}^{3+}$ phosphor for solid state lighting application

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Abstract

The polycrystalline $\text{NaLi}_2\text{PO}_4:\text{xEu}$ ($\text{x}=0.001, 0.002, 0.005, 0.01$ and 0.02) phosphors were successfully synthesized via modified solid state diffusion method [MSSDM]. The structural of prepared phosphor was confirmed by using XRD (X-ray diffraction) technique. Additionally, the photoluminescence (PL) behaviors of $\text{NaLi}_2\text{PO}_4:\text{xEu}$ phosphor was studied. The XRD pattern of prepared phosphor is well matched with JCPDS file. The PL excitation of prepared phosphor was monitored at 618nm while emission was monitored at 393 nm. The effect of different concentrations of Eu^{3+} ions in NaLi_2PO_4 phosphor was studies and optimum PL intensity was obtained at $\text{x}=0.005$ mol. of Eu^{3+} ion. The CIE co-ordinates were calculated and obtained in orange- red region.

Keywords: $\text{NaLi}_2\text{PO}_4:\text{Eu}^{3+}$; Photoluminescence; JCPDS and CIE co-ordinates

1. Introduction

Since 1962, orthophosphates with the general formula ABPO_4 (where A and B are monovalent cation and divalent cation) compose a large family of mono-phosphates with different structure types depending on the relative size of the A and B ions [1]. The compounds ABPO_4 show excellent thermal and hydrolytic stability and are considered to be efficient luminescent hosts [2, 3].

Recently, phosphate compounds with the ABPO_4 (A = alkaline metals, B = alkaline earth metals) structure were reported and became an important family of luminescent host materials since their tetrahedral rigid three dimensional matrix of phosphate are desired for charge stabilization, thus resulting in excellent thermal stability.

The Phosphate compounds are usually referred as orthophosphates, have extensive utilization these days precisely in the field of lighting [4,5]. Being low-phonon energy materials [6,7] they could be important host materials for producing efficient luminescence. They possess excellent optical and ferroelectric properties along with many intriguing features such as good thermal, chemical and mechanical stability that make them unique for almost any display.

ABPO₄ doped with different rare-earth ions (Eu³⁺, Ce³⁺, Tb³⁺, Sm³⁺ etc.) LiMgPO₄:Tb³⁺[8], KMgPO₄:Tb³⁺ [9], NaMgPO₄:Eu³⁺[10], KSrPO₄:Eu³⁺ [11], KBaPO₄:Eu³⁺[12], KBaPO₄:Tb³⁺[13], KBaPO₄:Sm³⁺[14], NaCaPO₄:Eu³⁺[15], NaBaPO₄:Ce,Tb³⁺[16], NaSrPO₄:Eu³⁺[17], could emit different wavelengths, depending on various crystal fields. The Eu²⁺ activated ABPO₄ phosphors have been reported as blue-emitting phosphors excited by near UV- LEDs [18].

The NaLi₂PO₄ phosphor is belonging in ABPO₄ family. Shinde *et al.* reported luminescence properties of NaLi₂PO₄:Eu phosphor in 2011 and this phosphor was developed by using solid state reaction and time require was more than 24h [19]. Sahare *et al.* also reported photoluminescence properties of Eu doped NaLi₂PO₄ phosphor and compared its color purity with commercial red emitting Y₂O₃:Eu phosphor [20]. Sahare *et al.* reported TL and OSL properties of NaLi₂PO₄:Ce phosphor [20,21]. In 2016 Singh *et al.* reported radiation induced abnormal reduction of Eu³⁺ in NaLi₂PO₄ phosphor [22].

In the present paper, we have reported the preparation and characterization of NaLi₂PO₄:xEu³⁺ (x=0.001, 0.002, 0.005, 0.01 and 0.02) phosphor synthesized via modified solid state reaction. The synthesized material was characterized using the powder X-Ray Diffraction. After synthesis and characterization of synthesized NaLi₂PO₄:Eu³⁺ material, photoluminescence properties of this phosphor was studied in detail using fluorescence spectrometer. Also the concentration quenching of Eu³⁺ activators was calculated.

2. Experimental

Synthesis Method

The Eu³⁺ activated NaLi₂PO₄ phosphors were successfully synthesized by using Modified Solid State Diffusion method. During synthesis, the stoichiometric amounts of high purity starting materials were used. The detail of molar ratio of constituent used for phosphor synthesis was given in **Table 1**. The starting materials were taken in a proper stoichiometric ratio together in china basin and adding small amount of acetone and clear solution was obtained. This mixture was heated on hot plate at 50°C for 30 min and then sample was placed in muffle furnace with the instalment of heating and heating profiles is given in **Table 2**. The sample was suddenly quenched at room temperature and between two intermediate regrounding.

Table 1: Molar ratio of ingredients used for material preparation and corresponding chemical reaction

S.N.	Products	Corresponding reaction with balanced molar ratios of precursors
1	$\text{Na}_{(1-x)}\text{Li}_2\text{PO}_4 : x\text{Eu}$ ($x = 0.001, 0.002, 0.005, 0.01$ and 0.02).	$\text{Na}_{(1-x)}\text{NO}_3 + 2x\text{LiNO}_3 + \text{NH}_4\text{H}_2\text{PO}_4 + x(\text{Eu}_2\text{O}_3 + \text{HNO}_3) \{ \text{In stock solution form } 1\text{gm}=100\text{ml} \} \xrightarrow{\Delta} \text{Na}_{(1-x)}\text{Li}_2\text{PO}_4 : x\text{Eu} + \text{Gaseous products } (\text{H}_2\text{O}, \text{NH}_3 \text{ and } \text{NO}_2) \text{ (} x = 0.001, 0.002, 0.005, 0.01, 0.02 \text{). } \Delta \text{ (Heating) } = 100^\circ\text{C for } 30\text{min}, 200^\circ\text{C for } 2\text{h}, 400^\circ\text{C for } 2\text{h}, 800^\circ\text{C for } 3\text{h. Then sample was grounded in agate mortar and heated at } 1000^\circ\text{C for next } 5\text{h. The sample was suddenly quenched at room temperature and sample was grounded in agate mortar.}$

The phase purity of prepared phosphors were checked by means of X-ray powder diffraction (PXRD) using a Rigaku miniflex II diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5405 \text{ \AA}$) operated at 5 kV. The structural and morphological characteristics i.e., particle size and shape of powdered samples were studied using a Scanning Electronic Microscope (SEM). In this study, samples in powder form (100-150 μm) were placed directly into a SEM for imaging. The measurements were performed using a ZEISS EVO/18 Research at Department of Physics RTM Univesisty Nagpur. The PL and PL excitation (PLE) spectra were measured on (Hitachi F-7000) fluorescence spectrophotometer with a 450W Xenon lamp.

3. Results and Discussion:

3.1 X-ray diffraction (XRD) pattern

The XRD pattern of prepared $\text{NaLi}_2\text{PO}_4:\text{Eu}^{3+}$ phosphor is shown in **Fig. 1**. The peak positions in the diffraction pattern of the synthesized material is compared them with the standard data available in the literature (JCPDS # 80-2110) [23]. No separate peaks corresponding to any impurity phase are observed at concentration (0.005mole) showing that the impurity has a good solubility in the matrix.

Fig.1. X-ray diffraction pattern of $\text{NaLi}_2\text{PO}_4:\text{Eu}^{3+}$ phosphor matched with JCPDF file(JCPDS # 80-2110)

3.2 Surface Morphology

The SEM micro images of Eu^{3+} doped NaLi_2PO_4 phosphor is as display in **Fig. 2**. It was observed that microstructure of the phosphor consist of irregular grains with heavy agglomeration. The average size of as-prepared particles was found to be in the range 1-5 μm .

Fig. 2 Surface morphology of prepared $\text{NaLi}_2\text{PO}_4:\text{Eu}^{3+}$ phosphor

3.3 Photoluminescence properties

The combined excitation and emission spectra of $\text{NaLi}_2\text{PO}_4:\text{Eu}^{3+}$ phosphor is shown in **Fig. 3**. The excitation was monitored at 618 nm and emission was monitored at 393 nm. The excitation spectra consist of series of sharp lines at 310, 363, 377 and 394 nm correspond to the $^7\text{F}_0 \rightarrow ^5\text{H}_3$, $^7\text{F}_0 \rightarrow ^5\text{D}_4$, $^7\text{F}_0 \rightarrow ^5\text{L}_7$ and $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transitions respectively. Out of all these peaks, the excitation at 394 nm is the strongest, as shown in **Fig. 3**. On the other hand emission spectra consist of two sharp peaks 595 nm and 618 nm with one weak peak at 653 nm. The emission at 595 nm corresponds to the $^5\text{F}_0 \rightarrow ^7\text{D}_1$ (magnetic dipole), the emission at 618 nm corresponds to the $^5\text{F}_0 \rightarrow ^7\text{D}_2$ (electric dipole) and weak emission at 653 nm corresponds to the $^5\text{F}_0 \rightarrow ^7\text{D}_3$ transition of Eu^{3+} ions [24]. The PL emission intensity was studied as a function of concentration of Eu^{3+} (0.001 to 0.02 moles).

From **Fig. 4** it is observed that 0.05 mol is the optimum concentration for the prepared phosphor. The luminescence intensity is observed to be decreased when the concentration of Eu^{3+} ions is increased beyond this optimum value, due to well-known phenomenon of concentration quenching. **Fig. 5** gives the energy level scheme to explain the emission process in $\text{NaLi}_2\text{PO}_4:\text{Eu}^{3+}$ phosphor.

Fig.3. Combine excitation and emission spectra of $\text{NaLi}_{1.995}\text{PO}_4:0.005\text{Eu}^{3+}$ phosphor

Fig. 4: Emission spectra $\text{NaLi}_{(2-x)}\text{PO}_4:x\text{Eu}^{3+}$ ($x=0.001, 0.002, 0.005, 0.01$ & 0.02) phosphor

Fig. 5: Energy-level scheme of Eu^{3+} ion

3.4 CIE chromaticity diagram

Fig.6 portray the emission color of $\text{NaLi}_{(2-x)}\text{PO}_4:x\text{Eu}$ ($x=0.005$ mol) phosphor calculated from their PL spectra by monitoring the 618 nm emission by using Commission Internationale de Eclairage (CIE) diagram [25]. The color coordinates of the phosphor are nearly same when it is excited at 393 nm excitation wavelength and correspond to (0.6872, 0.3125) for the phosphor with $\text{Eu} = 0.005$ mol. This indicates that europium activated $\text{NaLi}_{(2-x)}\text{PO}_4:x\text{Eu}$ is a promising candidate with red emission when excited in the near UV region. However, using it at 393 nm excitation proves beneficial as it is mercury free lamp.

Fig. 6 CIE colour coordinates for $\text{NaLi}_2\text{PO}_4:\text{Eu}^{3+}$ phosphor

4. Conclusions

The polycrystalline $\text{NaLi}_2\text{PO}_4:\text{Eu}^{3+}$ phosphors were successfully synthesized by modified solid state diffusion method. The XRD pattern of prepared $\text{NaLi}_2\text{PO}_4:\text{Eu}^{3+}$ phosphor was in good agreement with the JCPDS standard file with card no.# 80-2110. PL excitation spectra consist of series of sharp lines at 310, 363, 377 and 394 nm reveals that the phosphors could be excited by near-UV LEDs. The as-prepared phosphors demonstrated strong red emission at 618 nm with additional sharp peak at 595 nm. The CIE chromaticity coordinates of the as-prepared phosphors were determined to be (0.6872, 0.3125). The obtained results advocate that $\text{NaLi}_2\text{PO}_4:\text{Eu}^{3+}$ phosphor is a potential candidate for red-emitting near-UV LEDs.

References

1. C. C. Lin, Z. R. Xiao, G. Y. Guo, T. S. Tang, R. S. Liu *J. Am. Chem. Soc.* **132** (2010) 3020.
2. R. R. Patil, S. V. Moharil *Phys. Stat. Sol. A* **187** (2001) 557.
3. R. R. Patil, S. V. Moharil, S. M. Dhopte, P. L. Muthal, V. K. Kondawar, *Phys. Stat. Sol. A* **199** (2003) 527.
4. C. P. Grey, F. I. Poshni, A. F. Gualtieri, P. Norby, J. C. Hanson, D. R. Corbin, *J. Am. Chem. Soc.*, **119**, (1997) 1981
5. J. Zhou, L. Sun, J. Shen, J. Gu, C. Yan, *Nanoscale*, **3**, (2011) 1977.
6. E. Davis, *Nature* **417**, (2002) 813.
7. J. M. Thomas, *Angew. Chem. Int. Ed.* **38**, (1999) 3589.
8. C.B. Palan, N.S. Bajaj, A. Soni, S.K. Omanwar *Bull. Mater. Sci.* **39**, (2016) 1157.
9. C.B. Palan, N.S. Bajaj, A. Soni, S.K. Omanwar *Journal of Luminescence* **176** (2016), 106
10. Y. Gao, Q. Long, R. Nong, T. Wang, Y. Huang, S. Liao, H. Zhang *Journal of ELECTRONIC MATERIALS* **46**, (2017).911
11. C.B. Palan, N.S. Bajaj, S.K. Omanwar *AIP Conference Proceedings* **1728** (2016) 020474
12. S.K. Ramteke A.N. Yerpude S.J. Dhoble N.S. Kokode *Luminescence*. (2020) 1.
13. W. Zhijun, P. L. Li, Z.P. Yang, Q.L. Guo *Journal of Inorganic Materials* **26**(5), (2011) 503
14. S.K. Ramteke, A.N. Yerpude, S.J. Dhoble, N.S. Kokode *Luminescence*. **35**, 6 (2020);969
15. Li Chen , Zhan Hui Zhang ,Chun Tong , De Fu Cheng, Zhi Liang Huang *Phys. Status Solidi A*, **209**, 7 (2012) 1313
16. Zhang Qiuhong, Ni Haiyong, Wang Lingli, Xiao Fangming *Advanced Materials Research* **4** (2014) 6
17. Jia Yue Sun, Xiang Yan Zhang, Ji Cheng Zhu, Yi Ning Sun, Hai Yan Du **502** (2012) 128
18. M. Kim, M. Kobayashi, H. Kato, M. Kakihana *Optics. Photonics. J.* **3** (2013) 13
19. K. N. Shinde, S. J. Dhoble *Luminescence* **28** (2012) 93.
20. P. D. Sahare, M. Singh, P. Kumar *J. Radioanal. Nucl. Chem.* **302** (2014) 517.
21. P. D. Sahare, N. Ali, N. S. Rawat, S. Bahl, P. Kumar **174** (2016) 22.
22. M. Singh, P. D. Sahare, P. Kumar, S. Bahl *Columbia Int. Publ. J. Lumin. Appl.* **3** (2016) 1.
23. P. D. Sahare, M. Singh *Indian J. Phys.* **88** (2014) 621.
24. K. A. Koparkar, N. S. Bajaj, S. K. Omanwar *Electron. Mater. Lett.* **11** (2015) 303.
25. R.G. Bora, C.B. Palan, N.S. Sawala, G.V. Korpe, S.K. Omanwar *Journal of Materials Science: Materials in Electronics* **29** (2018) 541