

RbBaPO₄:Eu²⁺: a new alternative blue-emitting phosphor

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Abstract

A novel blue-emitting phosphor on a phosphate-based host matrix, $RbBaPO_4:Eu^{2+}$ (RBP), was synthesized by a solid-state reaction. This phosphor could be excited efficiently by ultra violet-visible light in the 220–400 nm range to exhibit a highly efficient emission peak in the range of 410–420 nm. In addition, the photoluminescence properties of the RbBaPO₄:Tb³⁺ and RbBaPO₄:Ce³⁺ also described.

Keywords: Phosphors; Photoluminescence; Eu²⁺activator; XRD

Introduction

In particular, rare-earth-element doped-phosphates with the general formula of $ABPO_4$ (where A = Li^+, Na^+, K^+, Rb^+ and Cs^+ and $B = Ca^{2+}, Sr^{2+}$ and Ba^{2+}) have been investigated for use in n-UV LEDs owing to their excellent thermal and hydrolytic stability and their compatibility with efficient luminescent host materials[1] .The optical properties of the correlative color temperature (CCT) and the color rendering index (CRI) of the phosphor-converted w-LED were investigated[2].In this paper we studied the photoluminescence properties of the RbBaPO₄ (RBP) phosphor doped with Eu²⁺. In addition, the photoluminescence properties of the RbBaPO4:Tb³⁺ and RbBaPO4:Ce³⁺ also described.

Experimental

Polycrystalline RbBaPO₄ was prepared by a conventional solid-state reaction. Stiochiometric quantities of freshly prepared dry CaHPO₄ and Rb₂CO₃ (99%, Aldrich) along with dopant Eu₂O₃(99.9%) were thoroughly ground and fired at 350° C for 1 h and 950° C for 8 hrs with intermediate re-grindings. The final product was heated in slightly reducing atmosphere at 950 C for 1 hr in burning charcoal and then quenched.

Phase structure of crystalline powders was checked by analyzing the diffraction spectra. X- ray diffraction patterns were recorded on Philips PANalytical X'pert Pro diffractometer. Photoluminescence (PL) spectra in the spectral range 220 -700 nm were recorded at room temperature on Hitachi F - 4000 spectro- fluorimeter wi th spectral slit widths of 1.5 nm.

Results and discussion

Fig. 1. XRD pattern of $RbBaPO_4was$ studied. A good match was observed with ICDD files 81-0647. The desired compounds are thus formed by the procedure as described above The excitation and emission spectra of the RBP phosphor are presented in Fig. 2. The excitation spectra extended from 220 nm to 400 nm, indicating that the phosphor was suitable for n-UV excitation.



International Journal of Luminescence and its applications Volume 4(I), 14/02/2014, ISSN 2277 – 6362 concentration of Eu²⁺ increases. A non-radiative energy



Fig 1.XRD of RbBaPO4

Two broad distinct bands were observed in the excitation spectrum with maxima at approximately 270 nm and 338 nm. The first peak was assigned to absorption in the host lattice and the second to the $4f^7 \rightarrow 4f^65d^1$ transition of the Eu²⁺ activators. The spectra emission showed the allowed $4f^{6}5d^{1} \rightarrow 4f^{7}$ transition in Eu²⁺. The emission spectra of the RBP phosphor exhibited an intense blue-emitting band with the maxima at 415 nm and excited at 365 nm .Based on the crystallographic information, it was found that RBP exhibited an orthorhombic structure with space groups Pnma. One phosphorous atom is coordinated with four oxygen atoms in a rigid tetrahedral structure and there is only one Ba2+ site in the RBP structure[3].Based on the effective ionic radius of the cation ($R_{Eu2+} = 1.17^{\circ}A$ and $R_{Ba2+} = 1.35^{\circ}A$), Eu^{2+} could substitute for one Ba2+ site in the RBP host lattice.[4]

Therefore, it was expected that one emission band would be observed for the RBP phosphors. As shown in Fig. 2. The emission spectrum of the RBP phosphors contained only a single symmetric emission band. This implied that Eu^{2+} occupied one emission center in the RBP lattice as mentioned above [5].

In order to determine the effect of the doping concentration the photoluminescence (PL), the Eu²⁺ concentrations (x) were varied as follows: RbBa_{1-x}PO4:Eu_x²⁺ with x = 0.001, 0.005, 0.01 and 0.02. Fig. 2 (inset) shows that the PL emission intensities initially increased as the concentration of Eu²⁺

increased. However, the PL intensity decreased when the concentration of Eu^{2+} exceeded x = 0.01 due to the concentration quenching effect. These results indicated that the optimum concentration of Eu^{2+} in RbBa₁₋ _xPO4: Eu_x^{2+} was x = 0.01. Concentration quenching is caused mainly by energy transfers among Eu^{2+} ions in the host lattice, the probability of which increases as the concentration of Eu^{2^+} increases. A non-radiative energy transfer from one Eu^{2^+} ion to another may occur by reabsorption of radiation, an exchange coupling, or via a multipolar interaction. The reabsorption of radiation comes into effect only when there is a broad overlap of the fluorescence spectra of the sensitizer and activator; in view of the emission and excitation spectra of the RBP phosphor, this was unlikely to occur. Therefore, the major cause of concentration quenching was likely a non-radiative energy transfer between different Eu^{2+} ions, such as an exchange coupling or a multipolar interaction[6].



Fig.2 Photoluminescence spectra of RbBaPO4:Eu²⁺
(1%).Emission at 415nm and excitation at 365nm. Inset, concentration dependence of PL intensity.

Fig.3. shows PL spectra for Ce (1%) activated RbBaPO4. The Ce³⁺ emission in RbBaPO4 (curve a) consists of a double-peaked band between 310 and 400 nm, caused by the transitions from the lowest energy level of the Ce³⁺ 5 d configuration to the spin orbit split ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ levels. The peaks are located at 338 nm and 352 nm, respectively. The excitation spectrum (curve b) observed at 254 nm.



Fig.3. Photoluminescence spectra of RbBaPO4: Ce^{3+} . Ce^{3+} concentration , 1.0%.



International Journal of Luminescence and its applications Volume 4(I), 14/02/2014, ISSN 2277 – 6362 Conclusion

(a) Emission spectra for 254 nm excitation; (b) excitation spectra for 352 nm emission.

Fig.4. Shows those photoluminescence spectra of RbBaPO4:Tb³⁺.Terbium shows strong excitation corresponding to allowed transition between ${}^{7}F_{6}$ ground state of 4f⁸ configuration to the levels of $4f^{7}5d^{1}$ configuration. Quite often, this falls in deep UV or VUV region of the spectrum. Intense UVexcited luminescence of Tb³⁺ can be observed only if f-d excitation band is located in this region, or if there is energy transfer from the sensitizer or host, which absorbs in UV region, to one of the levels of $4f^8$ configuration of Tb³⁺. From the excited state the ion relaxes in several steps to ${}^{5}D_{i}$ levels of $4f^{8}$ configuration. Line emission corresponding to f-f transitions is observed. most intense lines are around 487 nm and 545 nm corresponding to ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ and ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transitions, respectively. At low concentrations blue emission is dominant. Near UV emission around 387 nm corresponding to ${}^{5}D_{3} \rightarrow {}^{7}F_{6}$ transition is also observable. Fig. 5 (curve a) shows emission spectrum for RbBaPO4:Tb³⁺ (1 mol%). The lines emissions are observed at 379.6, 413.6, 434.8, 473, nm due to the (5D3 \rightarrow 7Fj) transition and 487 and 545 nm due to the (5D4 \rightarrow 7Fj) transition. The excitation corresponding to the transition from 7Fj level of 4f⁸ configuration to the lowest band of $4f^{7}5d^{1}$ configuration is in the extreme short wavelength region and the maximum is perhaps beyond the range of the spectrophotometer (< 220 nm).



Fig.4. Photoluminescence spectra of RbBaPO4:Tb³⁺(0.5%)

RbBaPO4:Eu²⁺ phosphors were synthesized using conventional solid-state reaction and the а of the Eu²⁺-doped photoluminescence properties RbBaPO4 phosphors were investigated. The RbBaPO4:Eu²⁺ phosphor could be excited efficiently in a broad n-UV region, and this phosphor efficiently emitted purplish-blue light, making it very suitable for use in n- UV-based LEDs. It was found that the emission of Ce³⁺ ions in this host at 352 nm. Hence, RbBaPO4:Ce³⁺ may be used as solid-state laser and scintillator.

The remarkable feature of the Tb^{3+} luminescence in RbBaPO4 is the spectral emission at very short wavelength. It is highly unusual for a phosphate host lattice to support RbBaPO₄ emission of the terbium. Normally the Tb^{3+} ion emission is in green region it can be readily seen, but in this we seen the entire visible spectral lines due to very large Stokes shift observed in Tb^{3+} emission in pure host RbBaPO₄.

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