www.amlett.com, www.amlett.org, DOI: 10.5185/amlett.2013. 3453

Enhanced white light emission and energy transfer studies of Dy³⁺/Ce³⁺ co-doped YAI₃(BO₃)₄ phosphors for white light emitting diodes

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Received: 28 March 2013, Revised: 15 May 2013 and Accepted: 26 May 2013

ABSTRACT

We reported the structure, photoluminescence and energy transfer studies of Dy³⁺/Ce³⁺ co-doped YAl₃(BO₃)₄ (YAB) phosphors prepared by solid-state reaction method at 1200°C/3h. Upon 273 nm UV excitation, the YAB:Ce³⁺ phosphor exhibits a sharp emission band with peak maximum at 380 nm related to the parity and spin allowed $Ce^{3+}:Sd \rightarrow 4f$ transition. When excited with 352 nm, the broad emission band of Ce^{3+} contains two components at 390 and 417 nm due to the electric dipole transitions from 5d excited state to the two splitting ground ${}^{2}F_{5/2,7/2}$ states, respectively. The incorporation of Ce³⁺ enhances the luminescence intensity of Dy^{3+} due to efficient energy transfer from Ce^{3+} to Dy^{3+} . The emission spectra of Dy^{3+}/Ce^{3+} co-doped phosphors under 273 nm excitation display the $Dy^{3+.4}F_{9/2} \rightarrow {}^{6}H_{15/2,13/2,11/2}$ and the $Ce^{3+.5d} \rightarrow 4f$ transitions. The emission colour can be tuned from blue-to-white as a function of Ce^{3+} concentration and/or excitation wavelength. Colour perception has been analyzed by evaluating the Commission International de l'Eclairagein (CIE) chromaticity coordinates. The YAB:Dy³⁺/Ce³⁺ phosphors can be significant for current generation UV excited white light emitting diodes. Copyright © 2013 VBRI press.

Keywords: Phosphors; white light emission; solid state reaction; optical properties; luminescence.





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Introduction

Nowadays, the research of novel nanocrystalline phosphor materials for various photonic [1-3] and biomedical applications [4-6] has been the subject of intense investigation. To enhance the efficiency of white-light emitting diodes (w-LEDs), special attention has been paid in the development of frequency converting phosphors pumped through ultra violet (UV) LEDs and capable of emitting the three primary colours [7, 8]. One of the best possible methods to generate white light is utilizing the LED chips coated with appropriate tri-colour phosphor which absorbs the UV light emitted by the LED chip and converts it into visible light. Among the available phosphors, the YAl₃(BO₃)₄ (YAB) is one of the suitable host lattice for RE activated tri-colour phosphors. The YAB phosphors are significant for UV-LEDs due to their high thermal and chemical stability. Further, the YAB phosphors have more advantages over the other available phosphors owing to their wide isomorphous substitutions, UV transparency, non-linear optical properties and environmental friendly nature [9-14].

Trivalent dysprosium (Dy³⁺) exhibits blue (~470-500 nm), yellow (~570-600 nm) and red (~650-680 nm) emissions through ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$, ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$, ${}^4F_{9/2} \rightarrow$ ⁶H_{11/2} transitions, respectively. However, the intensity of these transitions depends on the concentration of Dy³⁺ ions and site symmetry of the host lattice around the Dy^{3+} ions. The intensity of ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ (yellow) transition is very sensitive and strongly influenced by the host environment while the intensity of ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ (blue) transition is insensitive and hardly varies with the host environment. The relative yellow-to-blue (Y/B) intensity ratio gives the information regarding the site symmetry around the Dy³⁺ ion in which it is situated [15]. Additionally, the emission colour of luminescence of Dy³⁺ is very close to the white and it can extensively be used as an activator ion in designing the LED based white light sources [16-19]. It is well known that the Ce³⁺ acts as efficient sensitizer of luminescence for certain RE ions because of its intense and broad absorption band due to the parity and spin allowed $4f \rightarrow 5d$ electric dipole transition [20,21]. Since the degeneracy of 5d orbitals depends on the crystal field strength around Ce^{3+} , the emission wavelength of Ce^{3+} can be controlled from UV to visible by selecting an appropriate host. As a sensitizer, the Ce³⁺ effectively enhance the luminescence of LaPO₄:Dy³⁺ [2], $GdAl_3(BO_3)_4:Dv^{3+}$ Ca₂Al₃O₆F:Tb³⁺ [8], [22], Sr₂MgSi₂O₈:Tb³⁺ CaSc₂O₄:Nd³⁺ [23], [24] and $Sr_2Mg(BO_3)_2$: Pr^{3+} [25] phosphors. Till date there were few reports on the Dy³⁺/Ce³⁺ co-doped white light phosphors and as our knowledge concerned, no reports are available on the YAB: Dy^{3+}/Ce^{3+} white-light emitting phosphors.

The structural and luminescence properties of Dy^{3+} activated YAB phosphors were reported in our previous work [26]. The concentration of Dy^{3+} has been optimized as 2% for UV excited w-LEDs. In the present work we

report the structural, optical and energy transfer (ET) studies of Dy^{3+}/Ce^{3+} co-doped YAB phosphors. The effect of concentration of Ce^{3+} (sensitizer) on the luminescence of Dy^{3+} (activator) and the ET from Ce^{3+} to Dy^{3+} ion are discussed in detail. Tunability of emission colour from blue-to-white as a function of Ce^{3+} concentration and/or excitation wavelength is explained. The YAB: Dy^{3+}/Ce^{3+} phosphors have potential applications as a UV convertible phosphor materials for current w-LEDs.

Experimental

Materials

High purity chemicals of Y_2O_3 (99.99%), Al_2O_3 (99.9%), H_3BO_3 (99.5%), Dy_2O_3 (99.99%) and Ce_2O_3 (99.99%) were obtained from Sigma-Aldrich, India. All the chemicals were used without further purification for the preparation of YAB:Dy³⁺/Ce³⁺ phosphors.

Method of preparation

Dy³⁺/Ce³⁺ co-doped YAB phosphors of chemical composition $Y_{(1-x-y)}Al_3(BO_3)_4$: yDy^{3+}/xCe^{3+} (x = 0, 0.1, 0.5, 1, 3% and y = 2%) were prepared by solid-state reaction method. The starting chemicals were grinded homogeneously in the presence of acetone using a pestle and an agate mortar. An excess of 3% of H₃BO₃ was added to compensate its evaporation while heating. The samples were fired at 200 and 600°C per 3h and sintered at 1200°C per 3h in air using alumina crucible.

Characterization

X-ray diffraction (XRD) measurements were carried out on X'Pert- Pro Materials Research Diffractometer using CuK α radiation ($\lambda = 1.5406$ Å). The photoluminescence excitation, emission and decay measurements were performed with a Jobin YVON Fluorolog-3 spectrofluorimeter. Scanning electron microscope (SEM) studies were done using Hitachi SU-70 scanning electron microscope. All the measurements were performed at room temperature.

Results and discussion

XRD and SEM analysis

The XRD profiles of undoped, Dy^{3+} , Ce^{3+} and Dy^{3+}/Ce^{3+} co-doped YAB phosphors are presented in **Fig. 1(a)**. The observed XRD peaks are well consistent with JCPDS card No. 72-1978. The YAB phosphor has huntite CaMg₃(CO₃) structure with space group R32 **[27]**. Relatively weak XRD profiles corresponding to the YBO₃ phase could be due to stoichiometric imbalance at higher temperatures or the slower reaction rate of Al₂O₃ with Y₂O₃ and B₂O₃. However, the YBO₃ phase does not affect the optical transitions of RE impurities present in YAB lattice **[26]**.

The mean crystallite size (D_{hkl}) of undoped, Dy^{3+} -, Ce^{3+} - and Dy^{3+}/Ce^{3+} co-doped YAB phosphors has been calculated by Scherrer's formula,

(1)





Fig.1. (a) XRD profiles for Dy^{3+}/Ce^{3+} and (b) the SEM image of YAB: $Dy^{3+}_{2\%}/Ce^{3+}_{3\%}$ phosphor.

where λ , $\beta_{2\theta}$ and θ are the wavelength of X-rays used to record XRD profiles, the full width at half maximum of diffraction profiles (in radians) and the angle of diffraction, respectively. The mean crystallite size is estimated to be 39.50 nm using the $\beta_{2\theta}$ of intense peak corresponding to (2 0 2) plane. For reference, the powder XRD data of YAB: $Dy_{2\%}^{3+}/Ce_{3\%}^{3+}$ phosphor is given in **Table 1**. The studied phosphors exhibit grain like morphology with different size and shape and the particles are appeared to be agglomerated. The SEM image of YAB: $Dy_{2\%}^{3+}/Ce_{3\%}^{3+}$ phosphor is shown in **Fig. 1(b)**.

Table 1. The powder XRD data such as peak position (in °20), full width at half maximum (β_{20} in °20), lattice spacing (d-spacing in nm), relative intensity (Rel. Int. in %) and Millar planes (h k l) for YAB: $Dy_{2\%}^{3+}/Ce_{3\%}^{3+}$ phosphor.

Position	β _{2θ}	d-spacing	Rel. Int.	(h k l)	
16.4708	0.1722	53.82	30.63	(1 0 1)	
19.1099	0.1722	46.44	17.96	(1 1 0)	
25.3414	0.1722	35.15	39.12	(0 2 1)	
27.0024	0.1378	33.02	10.43	(0 1 2)	
31.9368	0.1722	28.02	32.92	(2 1 1)	
33.3208	0.2066	26.89	100.00	(2 0 2)	
38.7476	0.2411	23.24	31.42	(1 2 2)	
42.4113	0.1378	21.31	24.89	(1 1 3)	
46.8946	0.1378	19.37	10.93	(4 0 1)	
47.9054	0.1722	18.98	23.89	(3 1 2)	
51.0367	0.2755	17.90	12.75	(0 3 3)	
52.0801	0.1033	17.56	15.73	(0 4 2)	
54.8518	0.1033	16.73	14.18	(2 2 3)	
55.8343	0.4822	16.47	11.99	(2 3 2)	



Fig. 2. PLE and PL spectra for YAB: $Dy_{2\%}^{3+}$ phosphor.

Photoluminescence of YAB: Dy³⁺

The photoluminescence excitation (PLE) and photoluminescence (PL) spectra of YAB: $Dy_{2\%}^{3+}$ phosphor is shown in Fig. 2. The PLE spectrum recorded by monitoring the emission at 576 nm (${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$) transition exhibits eight bands with peak maximum at 325, 338, 352, 365, 387, 426, 453, and 475 nm corresponding to the ${}^{6}H_{15/2} \rightarrow {}^{6}P_{3/2}, {}^{4}I_{9/2}, {}^{6}P_{7/2}, {}^{6}P_{5/2}, {}^{4}F_{7/2}, {}^{4}G_{11/2}, {}^{4}I_{15/2}$, and ⁴F_{9/2} transitions, respectively [28]. Among these, the PLE band due to the ${}^{6}\text{H}_{15/2} \rightarrow {}^{6}\text{P}_{7/2}$ (352 nm) transition is found to be more intense and is used to characterize the optical transitions of Dy3+ ions. Upon 273and 352 nm UV excitations, the PL spectra of YAB:Dy³⁺ phosphor exhibits similar emission transitions at 485 nm (${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$), 576 nm (${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$) and 666 nm (${}^{4}F_{9/2} \rightarrow {}^{6}H_{11/2}$).



Fig. 3. Partial energy level diagram showing the emission and energy transfer mechanisms in Dy^{3+}/Ce^{3+} co-doped YAB phosphor.

The partial energy level diagram shown in Fig. 3 presents the emission mechanism of Dy^{3+} in YAB phosphor. In the present study, we focused our discussion on the prominent emission (${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2,13/2}$) transitions only. As seen the PL spectra, though the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ (blue) and ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ (yellow) transitions are located at the same position, their intensities vary as a function of excitation wavelength. It is noteworthy that the Dy^{3+} ion has been used as a probe to know the local site symmetry around it.

When the Dy³⁺ ions occupy low symmetry local site with non-inversion centre, the intensity of ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ (yellow) transition is prominent than the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ (blue) transition and the Y/B intensity ratio is higher than unity. Conversely, if the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ (blue) transition is more prominent over the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ (yellow) transition, then the Dy³⁺ ions occupy higher symmetry local sites with inversion centre and corresponding Y/B intensity ratio is less than unity [15]. In case of YAB: $Dy_{2\%}^{3+}$ phosphor, the intensity of ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ transition is more prominent than the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ transition under 273 nm UV excitation. The Y/B intensity ratio of ~0.7364 indicates that the Dy³⁺ ions occupy the higher symmetry inversion site of YAB lattice. Thus, the YAB: $Dy_{2\%}^{3+}$ phosphor emits pale-blue colour with CIE chromaticity coordinates (x = 0.2047; y)= 1871) which are well located in the blue region of the CIE chromaticity diagram shown in Fig. 4.



Fig. 4. (Colour online) CIE chromaticity coordinates for YAB:Dy³⁺/Ce³⁺ phosphors with (a) $\lambda_{ex} = 273$ nm and (b) $\lambda_{ex} = 352$ nm.

The Dy³⁺ ions in LaPO₄ [2] exhibited the same emission properties under 272 nm UV excitation. When excited with 352 nm UV wavelength, the Dy³⁺ ions displaced from higher symmetry to lower symmetry sites resulting white emission [16]. In this case, the intensity of ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ transition is higher than that of ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ transition and corresponding Y/B intensity ratio is 1.1478. The CIE chromaticity coordinates (x = 0.3212; y = 0.3616) are well located within the white region (see Fig. 4).

Photoluminescence of YAB: Ce^{3+}

Fig. 5 shows the PLE and PL spectra of YAB: $Ce_{1\%}^{3+}$ phosphor. The PLE spectrum reveals three Ce³⁺ characteristic bands centered at 256, 273 and 323 nm

corresponding to the Ce³⁺:4f \rightarrow 5d transition. This spectrum is similar to that of Gd_{0.97}Al₃(BO₃)₄:Ce_{0.07} [20] and Sr_{2.99}MgSi₂O₈:0.01Ce³⁺ [23] phosphors.

Fig. 5. PLE and PL spectra for YAB: $Ce_{1\%}^{3+}$ phosphor.

To resolve the overlapping excitation bands centered at 256 and 273 nm and decompose them into individual bands the deconvolution procedure assuming the Gaussian shapes of the bands was applied to each peak to identify exactly the positions of overlapping energy levels. The PL spectrum of YAB: $Ce_{1\%}^{3+}$ displays a sharp band with peak maximum at 380 nm (5d \rightarrow 4f) under 273 nm UV excitation. However, it exhibits a broad band with two components at 390 and 417 nm when excited with 352 nm UV wavelength. These two components are due to the electric dipole transitions from 5d excited state to the two splitting ground ${}^{2}F_{5/2,7/2}$ states of Ce³⁺ ion. Also, the 5d \rightarrow 4f band shifts towards longer-wavelength side when excited with 352 nm UV wavelength. This might be due to the splitting of Ce^{3+} ground state in to their ${}^2F_{5/2}$ and ${}^2F_{7/2}$ components. The emission mechanism of Ce³⁺ ion in YAB phosphor is displayed in Fig. 3. The YAB: $Ce_{1\%}^{3+}$ phosphor emits intense blue colour with CIE chromaticity coordinates (x = 0.1642; y = 0.0131) and (x = 0.1622; y =0.0186) under 273 and 352 nm UV excitations, respectively. These chromaticity coordinates are well positioned in the blue region of CIE chromaticity diagram shown in see Fig. 4.

Photoluminescence of YAB: $Dy3+/Ce^{3+}$

The PLE spectra of Dy^{3+}/Ce^{3+} co-doped YAB phosphors monitoring the emission at 576 nm ($Dy^{3+}:^4F_{9/2} \rightarrow {}^{6}H_{13/2}$) contain the Ce³⁺ (4f \rightarrow 5d) and the Dy^{3+} (${}^{6}H_{15/2} \rightarrow {}^{6}P_{7/2}$, ${}^{6}P_{5/2}$, ${}^{4}F_{7/2}$, ${}^{4}G_{11/2}$, ${}^{4}I_{15/2}$ and ${}^{4}F_{9/2}$) characteristic bands. For reference, the PLE spectrum of YAB: $Dy^{3+}_{2\%} / Ce^{3+}_{3\%}$ phosphor is shown in **Fig. 6a**. The PLE spectrum of YAB: $Ce^{3+}_{1\%}$ phosphor (**Fig. 6b**) monitoring the prominent emission of Dy^{3+} ion at 576 nm (${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$) is similar to that obtained by monitoring the Ce³⁺ emission at 380 nm (5d \rightarrow 4f) as presented in **Fig. 5**.

The intensity of PLE band of Ce^{3+} (4f \rightarrow 5d) increases with the increase of Ce^{3+} concentration. On the other hand,

the intensity of Dy^{3+} bands increases up to 0.5%Ce³⁺ and then decrease for further increase of Ce^{3+} concentration due to the dominant intensity of $4f \rightarrow 5d$ excitation band indicating the uniform distribution of Dy³⁺ and Ce³⁺ ions in YAB host lattice. The intensity variation of $Ce^{3+}:4f \rightarrow 5d$ and Dy^{3+} :⁶ $H_{15/2} \rightarrow {}^{6}P_{7/2}$ transitions with Dy^{3+}/Ce^{3+} concentration is shown in Fig. 6 (c). Further, the presence of $Ce^{3+}:4f \rightarrow 5d$ excitation band in the PLE spectrum of Dy^{3+}/Ce^{3+} co-doped phosphors suggest the ET from Ce^{3+} to Dy³⁺ ions, which is expected to occur considering that the emission of Ce³⁺:5d \rightarrow 4f overlaps the Dy³⁺:⁶H_{15/2} \rightarrow ⁶P_{5/2}, ${}^{4}F_{7/2}$, ${}^{4}G_{11/2}$, ${}^{4}I_{15/2}$, ${}^{4}F_{9/2}$, absorption (PLE) transitions. Fig. 6 (d) describes the overlap of Dy^{3+} absorption (PLE) transitions and Ce³⁺ emission transitions. This overlap has been well accepted to be favourable for an efficient ET from Ce³⁺ to Dy³⁺.

Fig. 6. (a) PLE spectra for YAB: $Dy_{2\%}^{3+}/Ce_{3\%}^{3+}$, and YAB: $Ce_{1\%}^{3+}$ (b) phosphors. (c) The variation of intensity of $4f \rightarrow 5d$ and ${}^{6}H_{15/2} \rightarrow {}^{6}P_{7/2}$ transitions as a function of Dy^{3+}/Ce^{3+} concentration and (d) he overlap region of Dy^{3+} absorption (solid black-line) and Ce^{3+} emission (dashed red-line) transitions.

Upon 273 nm UV excitation, the PL spectra of Dy^{3+}/Ce^{3+} co-doped YAB phosphors consist not only the $Ce^{3+}:5d \rightarrow 4f$ (380 nm) transition but also $Dy^{3+}.^4F_{9/2} \rightarrow {}^{6}H_{15/2}$ (485 nm), $Dy^{3+}.^4F_{9/2} \rightarrow {}^{6}H_{13/2}$ (576 nm) and $Dy^{3+}.^4F_{9/2} \rightarrow {}^{6}H_{11/2}$ (666 nm) transitions. When excited with 273 nm UV wavelength, a part of excited Ce^{3+} ions radiate to the $Ce^{3+}.^2F_{5/2}$ ground state through 380 nm emission and the rest of Ce^{3+} ions transfer their energy to Dy^{3+} ions. The excited Dy^{3+} ions decay quickly by means of non-radiative (NR) transitions to the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{J}$ (J = 15/2, 13/2, 11/2) transitions. The PL spectra normalized to the intensity of $Ce^{3+}:5d \rightarrow 4f$ transition is shown in **Fig. 7(a)**.

From these spectra it is known that the luminescence intensity of $Ce^{3+}:5d \rightarrow 4f$ and $Dy^{3+}:^4F_{9/2} \rightarrow {}^6H_J$ transitions increases with the increase of Ce^{3+} concentration. The increase in intensity of Ce^{3+} and Dy^{3+} emission transitions could be attributed to the increased concentration of Ce^{3+} and effective ET from Ce^{3+} to Dy^{3+} , respectively. The

variation in intensity of Ce³⁺:5d \rightarrow 4f (I_{Ce}) and Dy³⁺:⁴F_{9/2} \rightarrow ⁶H_{13/2} (I_{Dy}) transitions as a function of Dy³⁺/Ce³⁺ concentration is illustrated in **Fig. 7(b**). Moreover, the increase in Dy³⁺-to-Ce³⁺ intensity ratio $\left(\frac{I_{Dy}}{I_{Ce}} = \frac{4F_{9/2} \rightarrow ^{6}H_{13/2}}{5d \rightarrow 4f}\right)$ also reveals the ET from Ce³⁺ to Dv³⁺

 $\langle I_{Ce} - 5d \rightarrow 4f \rangle$ also reveals the ET from Ce³⁺ to Dy³⁺ ion. The variation of I_{Dy}/I_{Ce} intensity ratio as a function of Ce³⁺ concentration is described in **Fig. 7(c)**.

Fig. 7. (a) The PL spectra for YAB: $Dy_{2\%}^{3+}/Ce_{x\%}^{3+}$ with $\lambda_{ex} = 273$ nm, (b) variation of intensity of $4f \rightarrow 5d$ and ${}^{6}H_{15/2} \rightarrow {}^{6}P_{7/2}$ transitions, (c) (I_{Ce}/I_{Dy}) intensity ratio as a function of Dy^{3+}/Ce^{3+} concentration, (d) PL spectra of YAB: $Dy_{2\%}^{3+}/Ce_{x\%}^{3+}$ with $\lambda_{ex} = 352$ nm and (e) $Log(I/C_{ce})$ of $Ce^{3+}:5d \rightarrow 4f$ verses $log(C_{Ce})$ in YAB: Dy^{3+}/Ce^{3+} phosphors.

In the present investigation, when the concentration of Ce^{3+} is raised from 0.1 to 3% the intensity of ${}^{4}F_{9/2} \rightarrow {}^{6}H_{J}$ transitions in YAB:Dy³⁺/Ce³⁺ phosphors increases monotonically than that of the YAB:Dy³⁺ phosphor under 273 nm UV excitation and corresponding Y/B intensity ratios are summarized in **Table 2**.

Table 2. Yellow-to-blue (Y/B) intensity ratios and the chromaticity coordinates (x-, y-) for YAB: $Dy_{2\%}^{3+} / Ce_x^{3+}$ phosphors at different excitations.

YAB doping	λ_{ex} = 273 nm			λ _{ex} = 352 nm		
	Y/B	x-	у-	Y/B	x-	у-
<i>x</i> = 0.1%	1.2610	0.2680	0.2459	1.0198	0.2151	0.1323
<i>x</i> = 0.5%	1.2520	0.2639	0.2371	0.8953	0.2017	0.1052
<i>x</i> = 1.0%	1.2402	0.2597	0.2266	0.6474	0.1990	0.1023
<i>x</i> = 3.0%	1.2092	0.2614	0.2316	0.7575	0.1946	0.0962

As seen in **Fig. 7(a)**, the intensity of the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ transition is more prominent than the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ transition and the Y/B ratio is higher than unity (it is quite different than YAB:Dy³⁺ emission under the same excitation). These results suggest that the Dy³⁺ ions occupy the lower symmetry local sites with non-inversion centre in

YAB:Dy³⁺/Ce³⁺ phosphors. The changes in local sites from higher to lower symmetry under 273 nm UV excitation by the addition of Ce³⁺ is mainly due to the sensitization of Ce³⁺ ions. The emission mechanism and ET process in Dy³⁺/Ce³⁺ co-doped phosphors are illustrated in partial energy level diagram shown in Fig. 3. In order to confirm the ET from Ce^{3+} to Dy^{3+} , the PL measurements was also carried out for Dy³⁺/Ce³⁺ co-doped phosphors with 352 nm UV excitation. Upon this excitation, the PL spectra shown in **Fig. 7d** display both Ce³⁺:5d \rightarrow 4f and Dy³⁺:⁴F_{9/2} \rightarrow ⁶H_J transitions. The broad band due to the $Ce^{3+}:5d \rightarrow 4f$ transition has two components similar to that of YAB: $Ce_{1\%}^{3+}$ phosphor under 352 nm excitation (see Fig. 5). From the PL measurements, it is clear that the luminescence intensity of $Dy^{3+}:{}^{4}F_{9/2} \rightarrow {}^{6}H_{J}$ transitions in Dy^{3+}/Ce^{3+} co-doped phosphors is higher than that of the Dy³⁺- doped phosphor and increases as a function of Ce³⁺ concentration. These results also manifest the ET from Ce³⁺ to Dy³⁺ ions under 352 nm UV excitation.

The CIE chromaticity coordinates of YAB:Dy³⁺/Ce³⁺ phosphors have been determined using the relative intensity of emission transitions and summarized in **Table 2**. Upon 273 nm UV excitation, the Dy³⁺/Ce³⁺ co-doped phosphors emit white luminescence due to non-inversion lower symmetry sites around the Dy³⁺ ions. However, when excited with 352 nm UV wavelength, the Dy³⁺/Ce³⁺ co-doped phosphors emits blue luminescence owing to the reason that the Dy³⁺ ions are embedded in the higher symmetry inversion sites. **Fig. 4(a)** and **(b)** clearly describes the location of CIE chromaticity coordinates under 273 and 352 nm excitations, respectively. Based on the PL results, we suggest that the YAB: $Dy_{296}^{3+}/Ce_{x96}^{3+}$ (x =0.1, 0.5, 1 and 3%) phosphors under 273 nm UV excitation can be potential for white light applications.

Energy transfer mechanism

By assuming the random distribution of ions, the average distance (R_{ran}) between Dy³⁺ and Ce³⁺ ions has been calculated using the following formula [29].

$$R_{ran} = 2 \left[\frac{3}{4 \pi (C_{Dy} + C_{Ce})} \right]^{1/3}$$
(2)

where C_{Dy} and C_{Ce} are the concentrations of $Dy_{2\%}^{3+}$ and Ce^{3+} ions, respectively. The concentration of $Dy_{2\%}^{3+}$ is estimated to be 1.023×10^{20} ions/cm³. The Ce^{3+} ions concentrations are 2.406, 13.636, 27.271, and 81.012×10^{20} ions/cm³ for x = 0.1, 0.5, 1, and 3%, respectively and corresponding values of R_{ran} are 26.32, 25.44, 24.52, and 21.84 Å. The decrease of average distance between Dy^{3+} and Ce^{3+} ions induce the ET from Ce^{3+} to Dy^{3+} ions. The critical distance (R_c) between Dy^{3+} and Ce^{3+} luminescent centers for which the ET is possible has been determined using the following equation [**30**]:

$$R_c = 2 \left(\frac{3V}{4\pi x_c N}\right)^{1/3} \tag{3}$$

where V is the volume of the unit cell, x_c is the critical concentration of Dy³⁺ (acceptor) ions when the luminescence intensity of Ce³⁺ (donor) ions decreases to its half value and N is the number of available crystallographic sites per unit cell. For YAB: $Dy_{2\%}^{3+}/Ce_{x\%}^{3+}$ phosphors, the values of V and N are 541.94 Å³ and 3, respectively. The evaluated value of R_c is ~25.84 Å and is found very close to the R_{ram} . Based on these values we suggest that the ET from Ce³⁺ to Dy³⁺ ions is possible for all concentrations of Ce^{3+} . In general, the ET is related to the multi-polar interactions such as exchange, dipole-dipole (d-d), dipolequadrupole (d-q) and quadrupole-quadrupole (q-q), between donor (Ce^{3+}) and acceptor (Dy^{3+}) ions. In order to identify the type of interaction through which ET takes place between Ce^{3+} and Dy^{3+} , the intensity of $Ce^{3+}:5d \rightarrow 4f$ transition is integrated from the PL spectra of YAB:Dy³⁺/Ce³⁺ phosphors. The relationship between the integrated luminescence intensity (I) and doping concentration (C) is given as [31]:

$$I \propto a^{(1-\frac{s}{3})} \Gamma\left(1+\frac{s}{3}\right) \tag{4}$$

$$a = C \Gamma \left(1 + \frac{s}{3}\right) \left[X_0 \frac{(1+A)}{\gamma} \right]^{3/s}$$
(5)

where γ is the intrinsic transition probability of sensitizer, s is the index of electric multi-pole which take the values 3, 6, 8, and 10 for exchange, d-d, d-q and q-q interactions, respectively. The factors *A* and *X*₀ are the constants and Γ is the Euler's function. After mathematical operation, the above two equations can be simplified as

$$\log\left(\frac{I}{C}\right) = -\frac{s}{3}\log C + \log f \tag{6}$$

where f is the independent of the doping concentration. The value of s can be obtained from the log(I/C_{Ce}) verses log(C_{Ce}) plot shown in **Fig. 7** (e). According to the slope of the fitted line (y = -0.853 x + 1.869), the slope parameter (s/3) is found to be 0.853 (i.e., nearly unity) and the index (s) of the electric multi-pole is 3. According to the Van Uitert [**32**], the obtained value of s = 3 for YAB:Dy³⁺/Ce³⁺ phosphors indicates that the ET from Ce³⁺ to Dy³⁺ takes place through exchange interaction mechanism.

Decay analysis

Fig. 8 shows the decay curves of ${}^{4}F_{9/2}$ emission level of Dy³⁺ ion in YAB:Dy³⁺/Ce³⁺ phosphors monitoring the emission and excitation wavelengths at 576 nm and 273 nm, respectively.

The inset figure illustrates the decay profile of YAB: $Dy_{2\%}^{3+}$ phosphor under the same experimental constrains. These decay profiles are well fitted to a single exponential function, $I = I_0 e^{-t/\tau}$, where *I* is the intensity at time t, I_0 is the intensity at t = 0 and τ is the lifetime. From these decay profiles the lifetime has been determined by taking the first e-folding times of the intensity of decay curves. The lifetime values are 432, 474, 488, 491 and 580 μ s for x = 0, 0.1, 0.5, 1 and 3% phosphors, respectively. The increase in lifetime of ${}^{4}F_{9/2}$ state of Dy³⁺ with the increase of Ce³⁺ ion concentration evidences the ET from Ce³⁺ to Dy³⁺ ion in YAB phosphors under 273 nm UV excitation.

Fig. 8. Decay profiles of Dy^{3+} : ${}^{4}F_{9/2}$ emission level in YAB: $Dy^{3+}_{2\%}$ / $Ce^{3+}_{x\%}$ phosphors.

Conclusion

The structural, photoluminescence and energy transfer studies of YAB:Dy3+/Ce3+ phosphors prepared by solid state reaction method at 1200°C/3h were reported. Upon 273 and 352 nm UV excitations, the YAB:Ce³⁺ phosphor emits intense blue colour corresponding to the $5d \rightarrow 4f$ transition. The YAB: $Dy_{2\%}^{3+}$ phosphor shows pale-blue and white emissions under 273 and 352 nm UV excitations, respectively. The PLE spectra of YAB:Dy3+/Ce3+ phosphors contain Ce³⁺ and Dy³⁺ characteristic transitions. The incorporation of Ce³⁺ enhances the luminescence intensity of Dy³⁺ ions due to efficient ET from Ce³⁺ to Dy³⁺ ions. Upon 273 nm UV excitation, the YAB: Dy3+/Ce3+ phosphors emit enhanced white light. In YAB:Dy³⁺/Ce³⁺ phosphors char the ET from Ce^{3+} to Dy^{3+} take place through exchange interaction mechanism. Based on the experimental results, we suggest that the YAB:Dy³⁺/Ce³⁺ phosphors emit enhanced white luminescence by the sensitization of Ce³⁺ and they exhibit great potential for UV excited w-LEDs.

Acknowledgements

One of the authors Dr. B.C. Jamalaiah would like to thank the Fundação para a Ciência e a Tecnologia (FCT), Ministério da Educação e Ciência, PORTUGAL for supporting him as a Post-Doctoral Researcher wide Ref. No. SFRH/BPD/76581/2011.

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