Enhanced white light emission and energy transfer studies of Dy\(^{3+}/\)Ce\(^{3+}\) co-doped YAl\(_3\)(BO\(_3\))\(_4\) phosphors for white light emitting diodes

G.V. Lokeswara Reddy\(^1\), L. Rama Moorthy\(^{1,2}\), T. Chengaiah\(^1\), B.C. Jamalaiah\(^{1,3}\)

\(^1\)Department of Physics, Sri Venkateswara University, Tirupati 517 502, India  
\(^2\)Department of Physics, Chadalawada Venkata Subbaiah Engineering College, Tirupati 517 506, India  
\(^3\)Department of Materials and Ceramics Engineering, CICECO, University of Aveiro, Campus Santiago, 3810-193 Aveiro, Portugal

*Corresponding author. E-mail: bcjamal@hotmail.com

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

**ABSTRACT**

We reported the structure, photoluminescence and energy transfer studies of Dy\(^{3+}/\)Ce\(^{3+}\) co-doped YAl\(_3\)(BO\(_3\))\(_4\) (YAB) phosphors prepared by solid-state reaction method at 1200°C/3h. Upon 273 nm UV excitation, the YAB:Ce\(^{3+}\) phosphor exhibits a sharp emission band with peak maximum at 380 nm related to the parity and spin allowed Ce\(^{3+}-\)5d \(\rightarrow\) 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 \(2^4F_5/2,\,7/2\) states, respectively. The incorporation of Ce\(^{3+}\) 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\(^{3+}\):\(2\)F\(_{9/2}\) \(\rightarrow\) 4\(H_{15/2,13/2,11/2}\) 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’Eclairage (CIE) chromaticity coordinates. The YAB-Dy\(^{3+}/\)Ce\(^{3+}\) 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.

**Gopireddy Venkata Lokeswara Reddy** obtained his M.Sc. degree in Physics in 1995 from Sri Venkateswara University, Tirupati 517502 India. He is pursuing his Ph.D. in Physics as a part-time research scholar under the supervision of Prof. L. Rama Moorthy, Department of Physics, Sri Venkateswara University, Tirupati. He is working in the area of synthesis and characterization of nanocryalline phosphor materials for lighting applications. Currently he is a Lecturer in Physics, Government Degree College, Proddatur, Kadapa district, India.

**Lalapet Rama Moorthy** received his Ph.D. from Sri Venkateswara University, Tirupati 517502 India. He visited Brazil, South Africa, Japan and South Korea as a visiting professor. He served as a Special Officer for examinations in Sri Venkateswara University, Tirupati during 2002. He published more than 100 research papers in various national and international journals and conferences. He guided about 15 students for their Doctoral degree. Presently, he is working as Principal at Chadalawada Venkata Subbaiah Engineering College, Renigunta Road, Tirupati 517 506, India.

**Thummala Chengaiah** received his M.Sc. and M.Phil. in Physics from Sri Venkateswara University, Tirupati 517502 India. He is currently a research student under the supervision of Prof. L. Rama Moorthy, Department of Physics, Sri Venkateswara University, Tirupati. His research interest includes preparation and optical characterization of rare earths doped nanocrystalline materials.

**Bungala Chinna Jamalaiah** has received Doctoral Degree in Physics in 2009 from Sri Venkateswara University, Tirupati under the supervision of Prof. L. Rama Moorthy. He worked as Assistant Professor in Department of Physics, Sree Vidyanikethan Engineering College, Tirupati 517102 during 2009-2010. He has two years of Post-Doctoral Research experience from South Korea. Currently, he is working as a Fundação para a Ciência e a Tecnologia (FCT) Post-Doctoral Researcher at the Centre for Materials Research and Technology, Portugal.
**Introduction**

Nowadays, the research of novel nanocrystalline phosphor materials for various photonic devices [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 4F9/2 → 6H11/2, 4F9/2 → 6H13/2, 4F9/2 → 6H15/2 transitions, respectively. However, the intensity of these transitions depends on the concentration of Dy3+ ions and site symmetry of the host lattice around the Dy3+ ions. The intensity of 4F9/2 → 6H11/2 (yellow) transition is very sensitive and strongly influenced by the host environment while the intensity of 4F9/2 → 6H15/2 (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 → 5d electric dipole transition [20,21]. Since the degeneracy of 5d orbitals depends on the crystal field strength around Ce3+, the emission wavelength of Ce3+ 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], GdAl3(BO3)4:Dy3+ [8], Ca2Al2O5:Er:Pr3+ [22], Sr2MgSi2O7:Ce3+ [23], CaSc2O6:Nd3+ [24] and Sr2Mg(BO3)4:Pr3+ [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:Dy3+/Ce3+ white-light emitting phosphors.

The structural and luminescence properties of Dy3+ activated YAB phosphors were reported in our previous work [26]. The concentration of Dy3+ 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 Dy3+/Ce3+ co-doped YAB phosphors. The effect of concentration of Ce3+ (sensitizer) on the luminescence of Dy3+ (activator) and the ET from Ce3+ to Dy3+ ion are discussed in detail. Tunability of emission colour from blue-to-white as a function of Ce3+ concentration and/or excitation wavelength is explained. The YAB:Dy3+/Ce3+ phosphors have potential applications as a UV convertible phosphor materials for current w-LEDs.

**Experimental**

**Materials**

High purity chemicals of Y2O3 (99.99%), Al2O3 (99.9%), H3BO3 (99.5%), Dy2O3 (99.99%) and Ce2O3 (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 Y1-x/3xAlx(BO3)4:Ce3+y Dy3+x (x = 0, 0.1, 0.5, 1, 3% and y = 2%) were prepared by solid-state reaction method. The starting chemicals were ground 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 CuKα radiation (λ = 1.5406 Å). The photoluminescence excitation, emission and decay measurements were performed with a Jobin YVON Fluorolog-3 spectrophotometer. 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, Dy3+, Ce3+ and Dy3+/Ce3+ 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 hunte CaMg2(CO3)4 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, Dy3+, Ce3+ and Dy3+/Ce3+ co-doped YAB phosphors has been calculated by Scherrer’s formula,
where $\lambda$, $\beta_{2\theta}$ and $\theta$ 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: $Dy^{3+}/Ce^{3+}$ 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: $Dy^{3+}/Ce^{3+}$ phosphor is shown in Fig. 1(b).

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

<table>
<thead>
<tr>
<th>Position</th>
<th>$\beta_{2\theta}$</th>
<th>d-spacing</th>
<th>Rel. Int.</th>
<th>(h k l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.4708</td>
<td>0.1722</td>
<td>53.82</td>
<td>30.63</td>
<td>(1 0 1)</td>
</tr>
<tr>
<td>19.1099</td>
<td>0.1722</td>
<td>46.44</td>
<td>17.96</td>
<td>(1 1 0)</td>
</tr>
<tr>
<td>25.3414</td>
<td>0.1722</td>
<td>35.15</td>
<td>39.12</td>
<td>(0 2 1)</td>
</tr>
<tr>
<td>27.0024</td>
<td>0.1378</td>
<td>33.02</td>
<td>10.43</td>
<td>(0 1 2)</td>
</tr>
<tr>
<td>31.9368</td>
<td>0.1722</td>
<td>26.02</td>
<td>32.92</td>
<td>(2 1 1)</td>
</tr>
<tr>
<td>33.3208</td>
<td>0.2066</td>
<td>26.89</td>
<td>100.00</td>
<td>(0 2 2)</td>
</tr>
<tr>
<td>38.7476</td>
<td>0.2411</td>
<td>23.24</td>
<td>31.42</td>
<td>(1 2 2)</td>
</tr>
<tr>
<td>42.4113</td>
<td>0.1378</td>
<td>21.31</td>
<td>24.89</td>
<td>(1 1 3)</td>
</tr>
<tr>
<td>46.8946</td>
<td>0.1378</td>
<td>19.37</td>
<td>10.93</td>
<td>(4 0 1)</td>
</tr>
<tr>
<td>47.9054</td>
<td>0.1722</td>
<td>18.98</td>
<td>23.89</td>
<td>(3 1 2)</td>
</tr>
<tr>
<td>51.0367</td>
<td>0.2755</td>
<td>17.90</td>
<td>12.75</td>
<td>(0 3 3)</td>
</tr>
<tr>
<td>52.0801</td>
<td>0.1033</td>
<td>17.56</td>
<td>15.73</td>
<td>(0 4 2)</td>
</tr>
<tr>
<td>54.8518</td>
<td>0.1033</td>
<td>16.73</td>
<td>14.18</td>
<td>(2 2 3)</td>
</tr>
<tr>
<td>55.8343</td>
<td>0.4822</td>
<td>16.47</td>
<td>11.99</td>
<td>(2 3 2)</td>
</tr>
</tbody>
</table>

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

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

**Photoluminescence of YAB: Dy$^{3+}$**

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

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 ($^4F_{9/2} \rightarrow ^4I_{15/2, 13/2}$) transitions only. As seen the PL spectra, though the $^4F_{9/2} \rightarrow ^4H_{15/2}$ (blue) and $^4F_{9/2} \rightarrow ^4H_{13/2}$ (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 Dy$^{3+}$ ions occupy low symmetry local sites with non-inversion centre, the intensity of $^4F_{9/2} \rightarrow ^4H_{15/2}$ (yellow) transition is more prominent than the $^4F_{9/2} \rightarrow ^4H_{13/2}$ (blue) transition and the Y/B intensity ratio is higher than unity. Conversely, if the $^4F_{9/2} \rightarrow ^4H_{13/2}$ (blue) transition is more prominent over the $^4F_{9/2} \rightarrow ^4H_{15/2}$ (yellow) transition, then the Dy$^{3+}$ ions occupy higher symmetry local sites with inversion centre and corresponding Y/B intensity ratio is less than unity [15]. In case of YAB: $^{3+}$ Dy$^{3+}$, phosphor, the intensity of $^4F_{9/2} \rightarrow ^6H_{15/2}$ transition is more prominent than the $^4F_{9/2} \rightarrow ^6H_{13/2}$ transition under 273 nm UV excitation. The Y/B intensity ratio of -0.7364 indicates that the Dy$^{3+}$ ions occupy the higher symmetry inversion site of YAB lattice. Thus, the YAB: $^{3+}$ Dy$^{3+}$ 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](image-url)

(Colour online) CIE chromaticity coordinates for YAB:Dy$^{3+}$/Ce$^{3+}$ phosphors with (a) $\lambda_e = 273$ nm and (b) $\lambda_e = 352$ nm.

The Dy$^{3+}$ ions in LaPO$_4$ [2] exhibited the same emission properties under 272 nm UV excitation. When excited with 352 nm UV wavelength, the Dy$^{3+}$ ions displaced from higher symmetry to lower symmetry sites resulting white emission [16]. In this case, the intensity of $^4F_{9/2} \rightarrow ^4H_{13/2}$ transition is higher than that of $^4F_{9/2} \rightarrow ^4H_{15/2}$ 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$^{3+}$ phosphor. The PLE spectrum reveals three Ce$^{3+}$ characteristic bands centered at 256, 273 and 323 nm corresponding to the Ce$^{3+}$:4f $\rightarrow$ 5d transition. This spectrum is similar to that of Gd$_{0.97}$Al$_3$(BO$_3$)$_3$:Ce$^{3+}$ [20] and Sr$_2$Ge$_2$Si$_2$O$_7$:0.01Ce$^{3+}$ [23] phosphors.

![Fig. 5](image-url)

PLE and PL spectra for YAB: Ce$^{3+}$ 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$^{3+}$ 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 $^2F_{3/2, 5/2}$ states of Ce$^{3+}$ ion. 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 $^2F_{3/2}$ and $^2F_{5/2}$ components. The emission mechanism of Ce$^{3+}$ ion in YAB phosphor is displayed in Fig. 3. The YAB: Ce$^{3+}$ 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: Dy$^{3+}$/Ce$^{3+}$

The PLE spectra of Dy$^{3+}$/Ce$^{3+}$ co-doped YAB phosphors monitoring the emission at 576 nm (Dy$^{3+}$: $^4F_{9/2} \rightarrow ^6H_{13/2}$) contain the Ce$^{3+}$ (4f $\rightarrow$ 5d) and the Dy$^{3+}$ ($^4I_{15/2} \rightarrow ^4P_{1/2, 3/2}$, $^4F_{7/2}$, $^4G_{11/2, 11/2}$, $^4I_{15/2}$ and $^4F_{9/2}$) characteristic bands. For reference, the PLE spectrum of YAB: Dy$^{3+}$/Ce$^{3+}$ phosphor is shown in Fig. 6a. The PLE spectrum of YAB: Ce$^{3+}$ phosphor (Fig. 6b) monitoring the prominent emission of Dy$^{3+}$ ion at 576 nm ($^4F_{9/2} \rightarrow ^4H_{13/2}$) is similar to that obtained by monitoring the Ce$^{3+}$ 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\textsuperscript{3+} bands increases up to 0.5% Ce\textsuperscript{3+} and then decrease for further increase of Ce\textsuperscript{3+} concentration due to the dominant intensity of 4f \rightarrow 5d excitation band indicating the uniform distribution of Dy\textsuperscript{3+} and Ce\textsuperscript{3+} ions in YAB host lattice. The intensity variation of Ce\textsuperscript{3+}:4f \rightarrow 5d and Dy\textsuperscript{3+}:H\textsubscript{15/2} \rightarrow \Phi_{9/2} transitions with Dy\textsuperscript{3+}/Ce\textsuperscript{3+} concentration is shown in Fig. 6 (c). Further, the presence of Ce\textsuperscript{3+}:4f \rightarrow 5d excitation band in the PLE spectrum of Dy\textsuperscript{3+}/Ce\textsuperscript{3+} co-doped phosphors suggest the ET from Ce\textsuperscript{3+} to Dy\textsuperscript{3+} ions, which is expected to occur considering that the emission of Ce\textsuperscript{3+}:5d \rightarrow 4f overlaps the Dy\textsuperscript{3+}:H\textsubscript{15/2} \rightarrow \Phi_{9/2}, \Phi_{11/2}, \text{4F} \rightarrow \text{4I}, \text{F} \rightarrow \text{I}, absorption (PLE) transitions. Fig. 6 (d) describes the overlap of Dy\textsuperscript{3+} absorption (PLE) transitions and Ce\textsuperscript{3+} emission transitions. This overlap has been well accepted to be favourable for an efficient ET from Ce\textsuperscript{3+} to Dy\textsuperscript{3+}.

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

From these spectra it is known that the luminescence intensity of Ce\textsuperscript{3+}:5d \rightarrow 4f and Dy\textsuperscript{3+}:\Phi_{9/2} \rightarrow \text{6H}\textsubscript{11/2} transitions increases with the increase of Ce\textsuperscript{3+} concentration. The increase in intensity of Ce\textsuperscript{3+} and Dy\textsuperscript{3+} emission transitions could be attributed to the increased concentration of Ce\textsuperscript{3+} and effective ET from Ce\textsuperscript{3+} to Dy\textsuperscript{3+}, respectively. The variation in intensity of Ce\textsuperscript{3+}:5d \rightarrow 4f (I\textsubscript{Ce}) and Dy\textsuperscript{3+}:\Phi_{9/2} \rightarrow \text{6H}\textsubscript{11/2} (I\textsubscript{Dy}) transitions as a function of Dy\textsuperscript{3+}/Ce\textsuperscript{3+} concentration is illustrated in Fig. 7(b). Moreover, the increase in Dy\textsuperscript{3+}-to-Ce\textsuperscript{3+} intensity ratio \((\text{I}_{\text{Dy}}/\text{I}_{\text{Ce}})\) also reveals the ET from Ce\textsuperscript{3+} to Dy\textsuperscript{3+} ion. The variation of I\textsubscript{Dy}/I\textsubscript{Ce} intensity ratio as a function of Ce\textsuperscript{3+} concentration is described in Fig. 7(c).

In the present investigation, when the concentration of Ce\textsuperscript{3+} is raised from 0.1 to 3% the intensity of \Phi_{9/2} \rightarrow \text{6H}\textsubscript{J} transitions in YAB:Dy\textsuperscript{3+}/Ce\textsuperscript{3+} phosphors increases monotonically than that of the YAB:Dy\textsuperscript{3+} phosphor under 273 nm UV excitation and corresponding Y/B intensity ratios are summarized in Table 2.

<table>
<thead>
<tr>
<th>YAB doping</th>
<th>(\lambda_{\text{ex}} = 273) nm</th>
<th>(\lambda_{\text{ex}} = 352) nm</th>
<th>Y/B</th>
<th>x'</th>
<th>y'</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.1%</td>
<td>1.2610</td>
<td>0.2860</td>
<td>0.2459</td>
<td>1.0168</td>
<td>0.2151</td>
</tr>
<tr>
<td>x = 0.5%</td>
<td>1.2520</td>
<td>0.2539</td>
<td>0.2371</td>
<td>0.8953</td>
<td>0.2017</td>
</tr>
<tr>
<td>x = 1.0%</td>
<td>1.2402</td>
<td>0.2597</td>
<td>0.2266</td>
<td>0.6474</td>
<td>0.1990</td>
</tr>
<tr>
<td>x = 3.0%</td>
<td>1.2092</td>
<td>0.2614</td>
<td>0.2316</td>
<td>0.7575</td>
<td>0.1946</td>
</tr>
</tbody>
</table>

As seen in Fig. 7(a), the intensity of the \Phi_{9/2} \rightarrow \text{6H}\textsubscript{J} transition is more prominent than the \Phi_{9/2} \rightarrow \text{6H}\textsubscript{J} transition and the Y/B ratio is higher than unity (it is quite different than YAB:Dy\textsuperscript{3+} emission under the same excitation). These results suggest that the Dy\textsuperscript{3+} ions occupy the lower symmetry local sites with non-inversion centre in

---

**Table 2.** Yellow-to-blue (Y/B) intensity ratios and the chromaticity coordinates (x', y') for YAB: Dy\textsuperscript{3+}/Ce\textsuperscript{3+} phosphors at different excitations.

---

**Fig. 6.** (a) PLE spectra for YAB: Dy\textsuperscript{3+}/Ce\textsuperscript{3+}, and YAB: Ce\textsuperscript{3+} phosphors. (b) The variation of intensity of 4f \rightarrow 5d and \Phi_{9/2} \rightarrow \Phi_{9/2} transitions as a function of Dy\textsuperscript{3+}/Ce\textsuperscript{3+} concentration and (c) the overlap region of Dy\textsuperscript{3+} absorption (solid black-line) and Ce\textsuperscript{3+} emission (dashed red-line) transitions.

**Fig. 7.** (a) The PL spectra for YAB: Dy\textsuperscript{3+}/Ce\textsuperscript{3+} with \(\lambda_{\text{ex}} = 273\) nm, (b) variation of intensity of 4f \rightarrow 5d and \Phi_{9/2} \rightarrow \Phi_{9/2} transitions, (c) (I\textsubscript{Ce}/I\textsubscript{Dy}) intensity ratio as a function of Dy\textsuperscript{3+}/Ce\textsuperscript{3+} concentration, (d) PL spectra of YAB: Dy\textsuperscript{3+}/Ce\textsuperscript{3+} with \(\lambda_{\text{ex}} = 352\) nm and (e) Log(I/C\textsubscript{Ce}) of Ce\textsuperscript{3+}:5d \rightarrow 4f versus log(C\textsubscript{Ce}) in YAB:Dy\textsuperscript{3+}/Ce\textsuperscript{3+} phosphors.
YAB: Dy<sup>3+</sup>/Ce<sup>3+</sup> phosphors. The changes in local sites from higher to lower symmetry under 273 nm UV excitation by the addition of Ce<sup>3+</sup> is mainly due to the sensitization of Ce<sup>3+</sup> ions. The emission mechanism and ET process in Dy<sup>3+</sup>/Ce<sup>3+</sup> co-doped phosphors are illustrated in partial energy level diagram shown in Fig. 3. In order to confirm the ET from Ce<sup>3+</sup> to Dy<sup>3+</sup>, the PL measurements was also carried out for Dy<sup>3+</sup>/Ce<sup>3+</sup> co-doped phosphors with 352 nm UV excitation. Upon this excitation, the PL spectra shown in Fig. 7d display both Ce<sup>3+</sup>:5d → 4f and Dy<sup>3+</sup>:4F<sub>9/2</sub> → 6H<sub>j</sub> transitions. The broad band due to the Ce<sup>3+</sup>:5d → 4f transition has two components similar to that of YAB: Ce<sup>3+</sup> phosphor under 352 nm excitation (see Fig. 5).

From the PL measurements, it is clear that the luminescence intensity of Dy<sup>3+</sup>:4F<sub>9/2</sub> → 6H<sub>j</sub> transitions in Dy<sup>3+</sup>/Ce<sup>3+</sup> co-doped phosphors is higher than that of the Dy<sup>3+</sup> doped phosphor and increases as a function of Ce<sup>3+</sup> concentration. These results also manifest the ET from Ce<sup>3+</sup> to Dy<sup>3+</sup> ions under 352 nm UV excitation. The CIE chromaticity coordinates of YAB:Dy<sup>3+</sup>/Ce<sup>3+</sup> phosphors have been determined using the relative intensity of emission transitions and summarized in Table 2. Upon 273 nm UV excitation, the Dy<sup>3+</sup>/Ce<sup>3+</sup> co-doped phosphors emit white luminescence due to non-inversion lower symmetry sites around the Dy<sup>3+</sup> ions. When excited with 352 nm UV wavelength, the Dy<sup>3+</sup>/Ce<sup>3+</sup> co-doped phosphors emits blue luminescence owing to the reason that the Dy<sup>3+</sup> 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<sup>3+</sup>/Ce<sup>3+</sup> (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<sub>ran</sub>) between Dy<sup>3+</sup> and Ce<sup>3+</sup> ions has been calculated using the following formula [29].

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

(2)

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

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

(3)

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

\[
I \propto a \left(1 + \frac{s}{3}\right) \Gamma \left(1 + \frac{s}{3}\right)
\]

(4)

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

(5)

where \(\gamma\) 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 \(\Gamma\) is the Euler’s function. After mathematical operation, the above two equations can be simplified as

\[
\log\left(\frac{I}{C}\right) = -\frac{s}{3} \log C + \log f
\]

(6)

where \(f\) is the independent of the doping concentration. The value of \(s\) can be obtained from the log(I/C<sub>0</sub>) versus log(C<sub>0</sub>) 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 \(\left(3\right)\) of the electric multi-pole is 3. According to the Van Uitert [32], the obtained value of \(s = 3\) for YAB:Dy<sup>3+</sup>/Ce<sup>3+</sup> phosphors indicates that the ET from Ce<sup>3+</sup> to Dy<sup>3+</sup> takes place through exchange interaction mechanism.

**Decay analysis**

Fig. 8 shows the decay curves of 4F<sub>9/2</sub> emission level of Dy<sup>3+</sup> ion in YAB: Dy<sup>3+</sup>/Ce<sup>3+</sup> phosphors monitoring the emission and excitation wavelengths at 576 nm and 273 nm, respectively.

The inset figure illustrates the decay profile of YAB: Dy<sup>3+</sup>/Ce<sup>3+</sup> phosphor under the same experimental constrain. 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 \(\tau\) 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 μs for x = 0, 0.1, 0.5, 1 and 3% phosphors, respectively. The increase in lifetime of 4f9/2 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 Dy3+: 4F9/2 emission level in YAB: Dy3+/Ce3+ 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 → 4f transition. The YAB: Dy3+/Ce3+ 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, the ET from Ce3+ to Dy3+ 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 Ce4+ and they exhibit great potential for UV excited w-LEDs.

Acknowledgements

One of the authors Dr. B.C. Jamaliah 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.

Reference


DOI: 10.1039/b912115c


DOI: 10.1016/j.jlumin.2012.07.014


DOI: 10.1039/c1ra00651g


DOI: 10.10029781118523025.ch7


DOI: 10.100297811831974.ch3


DOI: 10.1016/j.jallcom.2012.06.125


DOI: 10.1088/0957-4484/18/4/145602


DOI: 10.1039/c2jm21500k


DOI: 10.1016/j.mseb.2008.11.024


DOI: (PFI) S0022-2313(02)00533-1


DOI: 10.1063/1.124364


DOI: 10.1016/j.optmat.2008.02.005


DOI: 10.1007/s10853-005-5482-y


DOI: 10.1016/j.matchemphys.2011.05.062


DOI: 10.1016/j.jlumin.2011.01.015


DOI: 10.1016/j.jssc.2011.05.027


DOI: 10.1016/j.optmat.2011.06.018


DOI: 10.1016/j.materresbull.2009.07.021


DOI: 10.1016/j.mseb.2006.11.010


DOI: 10.1063/1.3460806


DOI: 10.1021/jz304722g


DOI: 10.1016/j.optlastec.2012.02.005


DOI: 10.1016/j.jallcom.2010.08.064


DOI: 10.1016/j.jlumin.2010.09.035


DOI: 10.1016/j.ceramint.2012.09.034
DOI: 10.1007/s11051-007-9349-9
DOI: 10.1063/1.1669893
DOI: 10.1088/0953-8984/20/39/395205
DOI: 10.1016/0375-9601(68)90486-6
DOI: 10.1149/1.2424184