ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 4, Issue 10, April 2015

Luminescence characters of Dy^{3+} and Ce^{3+} ions co-doped in alkali metal borate glasses

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Abstract* — Luminescence characters of Dy^{3+} and Ce^{3+} ions co-doped in alkali metal borate glasses fabricated by melting method have been studied. The energy transfer between ions Dy^{3+} and Ce^{3+} and the cross-relaxation mechanisms were discussed for BLN:Dy^{3+} glass. From the visible emission spectra, the blue to yellow-blue emission intensity ratio ($B_{Ce}/Y\text{-}B_{Dy}$) and CIE chromaticity coordinates were calculated. The results reveal that these glasses emit bright white light which is suitable for the development of W-LEDs.

***Keywords:* Dy^{3+} and Ce^{3+} ions; alkali metal borate glass, cross-relaxation, relaxation mechanism**

I. INTRODUCTION

Due to the unique structural and physicochemical properties, alkali metal borate glasses doped with RE^{3+} ions have been widely used as laser materials, optical amplifiers, optical memories, optoelectronics and magneto-optical devices [5,6]. The presence of structurally different borate units in alkali metal borate glasses is favorable for spectroscopic investigations of RE^{3+} ions. These structural differences are usually correlated to chemical composition, type of modifiers and conditions during glass preparation. Low phonon energy glasses doped with Dy^{3+} ions have been studied for optical amplifiers [5,6,7] and yellow–green up-conversion applications [9,11]. Special interest has been devoted to Dy^{3+} doped borate glasses with various chemical compositions [5]. The visible luminescence of the Dy^{3+} ion mainly consists of yellow band at 570–600 nm corresponding to the $^4F_{9/2}$-$^6H_{13/2}$ hypersensitive transition and the blue band at 470–500 nm corresponding to the $^4F_{9/2}$-$^6H_{15/2}$ transition. Dysprosium doped glasses and crystals emit intense discrete radiation in the yellow (570–600 nm) and NIR (1.35 and 3.0 mm) regions that have potential technological applications in commercial displays and telecommunications [5,6,7,8]. The intensity of the $^4F_{9/2}$-$^6H_{13/2}$ hypersensitive transition strongly depends on the host, in contrast to a less sensitive $^4F_{9/2}$-$^6H_{15/2}$ transition of Dy^{3+} and results in different yellow to blue luminescence intensity ratios that largely change with concentration and/or glass composition [6].

In these works, we prepared and studied spectroscopic properties of Dy^{3+} and Ce^{3+} ions in alkali metal borate glass. The energy transfer between ions Dy^{3+} and Ce^{3+} and the cross-relaxation mechanisms were discussed for BLN glass. From the visible emission spectra, the blue to (yellow-blue) emission intensity ratio ($B_{Ce}/Y\text{-}B_{Dy}$) and CIE chromaticity coordinates (x,y) were calculated which have been used to evaluate the white light emission of materials.

II. EXPERIMENT

Alkali metal borate glass (BLN glass) doped with Dy^{3+} or/and Ce^{3+} were prepared by conventional melt quenching technique. The stoichiometric ratio of BLN glasses is $(69\text{-}x)B_2O_3\text{-}15Na_2O\text{-}15Li_2O\text{-}1Dy_2O_3\text{-}xCe_2O_3$. The metal oxides were weighed accurately in an electronic balance mixed thoroughly and ground to a fine powder. The batches were then placed in quartz cup and melted in an electrical furnace in air at 1323 K for 1.5 hours. The melt was quenched to room temperature in air. The glasses were then annealed at 650 K for 2 hours. The glasses thus obtained were throughout, evenly, no bubble. The samples were cut, grinding, polishing blocks rounded product size: thickness d = 0.98 mm, radius r = 6.5 mm (used for the measurement of refractive index n, density, absorption and fluorescence); crushing and sorting grab particles range in size from 76 to 150 micron powder products (used for X-ray diffraction). The glass formation was confirmed by powder X-ray diffraction.

The measurement of the refractive index n is performed on the system Abbe refractometer at a wavelength of Natri lamp, 589 nm with $C_{10}H_7Br$ (1 – bromonaphthalin) used as the liquid in contact. The measurement of density made by Archimede method, using xylene as immersion liquid form. Optical absorption spectra were recorded in the wavelength regions 200 nm – 2500 nm using Varian spectrometer system Cary 5E UV-VIS-NIR, with a resolution of 1 nm. Fluorescence spectra were obtained at room temperature using Flourolog – 3 Model FL3 – 22, resolution of 0.3 nm, excitation light xenon (Vehicle).

III. RESULTS AND DISCUSSION

A. Luminescence of Dy^{3+} in BNL glass

Fig.1 shows the luminescence spectrum of BLN:Dy^{3+} glass in the spectral region of 400-800 nm consists of four bands centered at around 486, 577, 664 and 755 nm which are assigned to the $^4F_{9/2}\rightarrow{}^6H_{15/2}$, $^4F_{9/2}\rightarrow{}^6H_{11/2}$, $^4F_{9/2}\rightarrow{}^6H_{13/2}$ and $^4F_{9/2}\rightarrow{}^6H_{9/2}$ transitions, respectively. The emissions at 486 nm and 577 nm are observed to be strong, which correspond to the $^4F_{9/2}\rightarrow{}^6H_{15/2}$ (blue) and $^4F_{9/2}\rightarrow{}^6H_{11/2}$ (yellow) transitions, respectively, whereas the emissions at 664 nm ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) and 755 nm ($^4F_{9/2}\rightarrow{}^6H_{9/2}$) are found to be very

ISSN: 2277-3754
ISO 9001:2008 Certified
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Volume 4, Issue 10, April 2015

weak. The yellow-to-blue emission intensity ratio (Y/B) has been used to evaluate the symmetry of the local environment of the RE^{3+} ions [1,2,5,6].

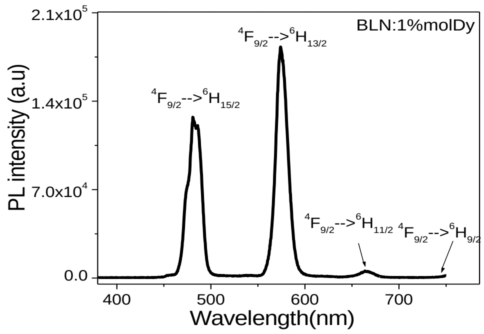

Fig. 1. The emission spectrum of BNL: 1% Dy^{3+} glass, λ_{ex} = 386 nm.

The greater of this ratio, the higher the asymmetry. With the BLN:Dy^{3+} glass, the Y/B ratio (1.3) is greater than some other hosts [5,6,8]. This can be attributed to lower symmetry of the coordination structure surrounding the Dy^{+3} ions.

B. Luminescence of Ce^{3+} in BLN glass

Fluorescence spectrum of Ce^{3+} doped BLN glass is shown in Fig 2. Broad band emission with maximum around 405 nm (violet luminescence) characteristic of displacement 4f-5d. The 4f–5d transitions have high energies and only those of Ce^{3+}, Pr^{3+} and Tb^{3+} are commonly observed. Fig. 3 shows the crystal-field splitting of both the $4f^1$ ($^2F_{5/2}$,$^2F_{7/2}$) and $5d^1$ ($^2D_{3/2}$,$^2D_{5/2}$) electronic configurations of Ce^{3+} in D_{3h} symmetry [1,10].

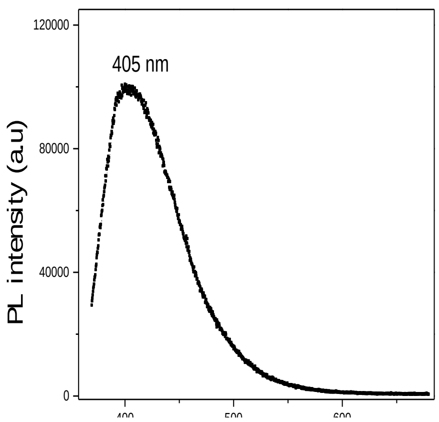

Fig.2. Fluorescence spectra of Ce^{3+}doped BLN glasses, λ_{ex} = 350 nm

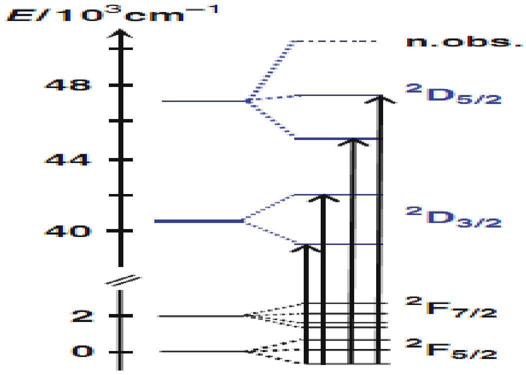

Fig.3. Assignment (D_{3h} symmetry)

In the displayed spectrum, the third transition to $^2D_{5/2}$ is not observed because it lies at too high energy. Conversely, the Ce^{3+} luminescence can be tuned from about 300 to 500 nm, depending on the matrix into which the metal ion is inserted, because of large crystal-field effect on the $5d^1$ excited state.

C. Luminescence of BLN:Dy^{3+},Ce^{3+} glass

Fig. 4 presents the emission spectra of $Dy^{3+}$and Ce^{3+} co-doped in BLN glasses. Curves is proves that both Ce^{3+} and Dy^{3+} ions are the luminescent center in the BLN glass. The emission spectrum exhibits a broad band around the peak wavelength of 405 nm corresponding to 4f–5d transition in Ce^{3+} ions and other bands corresponding to f-f transitions in Dy^{3+} ions.

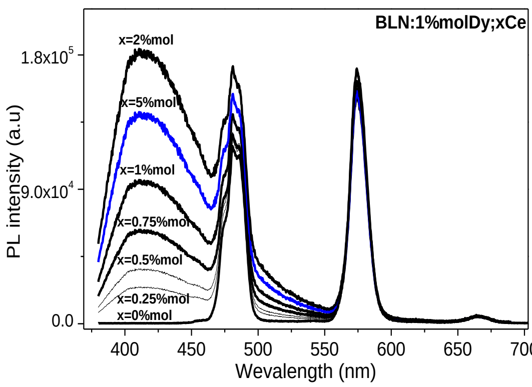

Fig. 4. Fluorescence spectra of Dy^{3+}, Ce^{3+} co-doped in BNL glass, λ_{ex} = 350 nm.

The luminescence measurement of the above samples system have been carried out and it is interested to find the relation between three factors: the ratio (B_{Ce}/Y-B_{Dy}), the concentration of Dy and Ce and the color coordination of samples. At the same concentration of Dy at 1%mol, by changing the concentration of xCe (with x= 0,25; 0,5; 0,75; 1,0; 2,0 và 5,0 %mol), the photo luminescence spectra shows that the intensity of wide range at 405 nm peak was changed depends on the concentration of Ce. It leads to the ratio (B_{Ce}/Y-B_{Dy}) between the PL intensity of wide range at 405nm

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peak (B_{Ce}) and the wide ranges at 486nm, 577nm ($Y\text{-}B_{Dy}$) is increased. To evaluates xCe^{3+} (with x = 0,25; 0,5; 0,75; 1,0; 2,0 và 5,0) doped BLN glass performance on color luminescent emission, Commission International Eclairage 1931 (CIE) chromaticity coordinates for BLN:1Dy,xCe glass were calculated and represented in table 1.

Table 1. The CIE coordinates (x,y) of BLN:1Dy,xCe

Concentration Ce (%mol)	x	y
0	0.365	0.315
0,25	0,330	0,329
0,50	0,327	0,328
0,75	0,315	0,327
1,0	0,298	0,328
2,0	0,257	0,326
5,0	0,285	0,327

Table 1 shows that the same concentration of Ce at 0%mol only luminescence of Dy^{3+}, the *x* and *y* values of CIE chromaticity coordinates were obtained as 0.315 and 0.362, respectively. By increased the concentration of Ce from 0,25; to 5,0%mol, it leads to the ratio ($B_{Ce}/Y\text{-}B_{Dy}$) is increased. From CIE coordinates of BLN:1Dy,xCe in the table 1, the worth indicate that the sample BLN:1Dy,0,25Ce glows with color coordinates which are closest to the white light ideal point (0.333; 0.333) (represented in fig 5)[3,4,11].

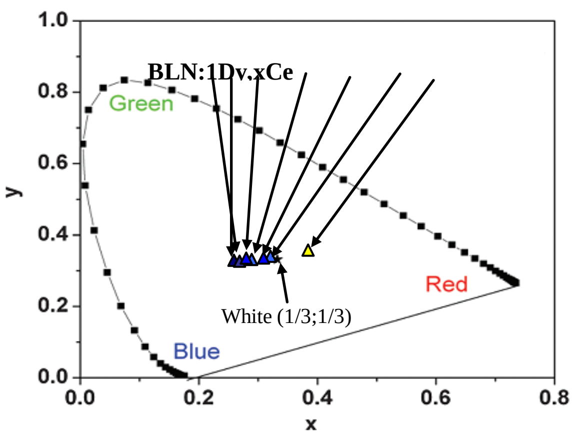

Fig.5. CIE chromaticity diagram for 1%mol Dy^{3+},xCe^{3+} co-doped in BLN glass

V. CONCLUSION

Optical spectroscopic of Dy^{3+} and Ce^{3+} ions co-doped alkali metal borate glasses have been studied. The luminescence spectra of the BLN:1Dy,xCe^{3+} glass to comprise: Broad band emission with maximum around 405 nm (violet luminescence) characteristic of 4f–5d transitions have high energies and only those of Ce^{3+} are commonly observed. The emissions at 486 nm and 577 nm are observed to be strong, which correspond to the $^4F_{9/2}\rightarrow{}^6H_{15/2}$ (blue) and $^4F_{9/2}\rightarrow{}^6H_{11/2}$ (yellow) transitions in Dy^{3+} ions.

The luminescence measurement of the above samples system have been carried out and it is interested to find the relation between three factors: the ratio ($B_{Ce}/Y\text{-}B_{Dy}$), the concentration of Dy and Ce and the color coordination of samples. The worth indicate that the sample BLN:1Dy,0,25Ce glows with color coordinates which are closest to the white light ideal point (0.333; 0.333). The CIE chromaticity diagram has shown that BLN: 1Dy,0,25Ce glasses emit bright white light which is suitable for the development of W-LEDs.

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