LUMINESCENCE PROPERTIES OF DY^{3+} IONS DOPED IN B_2O_3-AL_2O_3-CAO-NA_2O GLASS FOR SOLID STATE LIGHTING APPLICATIONS

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Abstract

In this research, the luminescence properties of borate glasses doped with Dy_2O_3 have been investigated. The glass samples with chemical composition of (40-*x*)B_2O_3:20Al_2O_3:20CaO:20Na_2O: *x*Dy_2O_3 (where *x* = 0.00, 0.05, 0.10, 0.50, 1.00, and 2.00 mol%) were prepared by the conventional melt quenching technique. The results show that the density and molar volume tend to increase with increasing of Dy_2O_3 concentration. The excitation spectra are observed seven bands at 325, 351, 364, 387, 425, 452, and 472 nm corresponding to the transitions from the ground state $^6H_{5/2}$ to excited states $^6P_{3/2}$, $^6P_{7/2}$, ($^4I_{11/2}$+$^4P_{3/2}$), ($^4I_{13/2}$+$^4F_{7/2}$), $^4G_{11/2}$, $^4I_{15/2}$, and $^4F_{9/2}$, respectively. The emission spectra were recorded using 350 nm excitation wavelength. The emission peaks are observed at 482 ($^4F_{9/2}\rightarrow{}^6H_{15/2}$), 576 ($^4F_{9/2}\rightarrow{}^6H_{13/2}$), and 664 ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) nm. The ratio of ED transition to the MD transition is a measure of symmetry orientation of the local environment around the RE ion site which is evaluated for the present work using Yellow/Blue (Y/B) intensity ratio ($^4F_{9/2}\rightarrow{}^6H_{13/2}$)/ ($^4F_{9/2}\rightarrow{}^6H_{15/2}$) values. The tunable white light emission at the strongest excitation wavelengths are investigated through CIE 1931 diagram and calculated the correlated colour temperature. The decay curves show the decreasing of lifetimes with addition of Dy_2O_3 concentration.

Keywords: **Borate glasses, Dy^{3+} ions, lifetime, luminescenc**

Introduction

In recently years, the glasses doped with rare-earth ions (RE) have been attracted great interest among the researchers because of their interesting optical characteristics in the fields of solid-state lasers, optical amplifiers, optical detectors, and colour display etc. (Burtan *et al*., 2012; Venkataiah *et al*., 2015; Pawar *et al*., 2017). Dysprosium (Dy^{3+}) is a rare-earth ions that received considerable attention recently given their distinctive properties which are suitable for White-Light Emitting Diodes

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(W-LEDs) applications (Yan and Ju, 2016; Luewarasirikula and Kaewkhao, 2018; Khan *et al*., 2019; Ravangvong *et al*., 2019). Borate glasses based on rare earth ions are also interesting as alternative host for RE ion due to their specific properties such as low phonon energy, small band gap, low melting temperature, mechanical strength, etc. The structure of borate glass consists of both triangular (BO_3) and tetrahedral (BO_4) groups. Furthermore, these two fundamental units can be arbitrarily combined to form different B_xO_y structural groups (Terczyn´ska-Madej *et al*., 2011; Othman *et al*., 2016; Ruangthaweep *et al*., 2017). In order to study Dy^{3+} ions role in borate glass, the glass samples with Dy_2O_3 different concentration were prepared and the physical, optical and luminescence properties of these glasses were investigated. In addition, alkali ion such as Ca^{2+}(glass modifier), Al^{3+}(intermediate) and Na^{+}(glass modifier) were added in glass structure as modifier and intermediate.

Methodology

Sample Preparation

The glass samples with different Dy_2O_3 concentration were prepared in composition (40-x) B_2O_3:20Al_2O_3:20CaO:20Na_2O:$x$$Dy_2O_3$ (where x = 0.00, 0.05, 0.10, 0.50, 1.00, and 2.00 mol%) and the composition of all samples are shown in Table 1. The whole of composite was mixed and filled in a high purity alumina crucible (each batch weighs for 20 g). Then the batches were placed in an electrical furnace and then melted at 950°C for 30 minutes. After complete melting, the melt was quenched in air using a preheated stainless steel mould. The quenched glasses were annealed at 350°C for 3 h to reduce thermal stress, and cooled down to room temperature. Finally, all glass samples were cut and polished to a dimension of 1.0×1.5×0.3 cm for further investigation.

Measurements

The density (ρ) was measured by Archimedes' principle using a sensitive microbalance (AND, HR-200). The molar volume (V_m) of glass samples were calculated using the relation, $V_M = M_T/\rho$, where M_T is the total molecular weight of glass multi-component. The optical absorption spectra were measured by the UV-Vis-NIR Spectrophotometer (UV3600 by Bara Scientific company) in range of 600-2,000 nm wavelength. For the luminescence properties, excitation/emission spectra and lifetime of glass samples were measured using Cary Eclipse Fluorescence Spectrophotometer with excited radiation from a Xenon compact arc lamps. All measurements were carried at room temperature. The CIE (Commission Internationale d' Eclairage) 1931 chromaticity colour coordinate was also investigated using emission data to confirm the colour emission from glasses.

Result and Discussion

From direct observations, the obtained glass samples are optically transparent with faint yellow color for higher concentration of Dy_2O_3 content as shown in Figure 1.

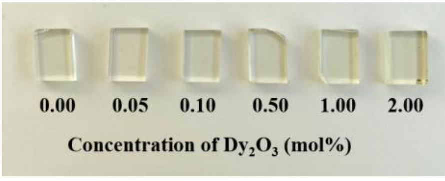

Figure 1. Glass samples doped with different Dy_2O_3 concentrations

Density and Molar Volume

The parameters like density and molar volume of present glasses are shown in Figure 2. The obtained density values are within the range of 2.4988-2.6731 g/cm^3. The densities of the glass samples increase slightly with increasing of Dy_2O_3 concentrations. This increase can be explained on the basis of molecular weight of glass formers, modifiers as well as intermediates. The low molecular weight oxide (B_2O_3 = 372.99 g/mol) was replaced by high molecular weight oxide (Dy_2O_3 = 372.99 g/mol) in the glass matrix. This result in their enhancement of density in the glass structure. The

Table 1. Chemical compositions of the glass samples

Sample	Concentration of Dy_2O_3	Glass composition (mol%)				
		B_2O_3	Al_2O_3	CaO	Na_2O	Dy_2O_3
0.00Dy	0.00	40.00	20	20	20	0.00
0.05Dy	0.05	39.95	20	20	20	0.05
0.10Dy	0.10	39.90	20	20	20	0.10
0.50Dy	0.50	39.50	20	20	20	0.50
1.00Dy	1.00	39.00	20	20	20	1.00
2.00Dy	2.00	38.00	20	20	20	2.00

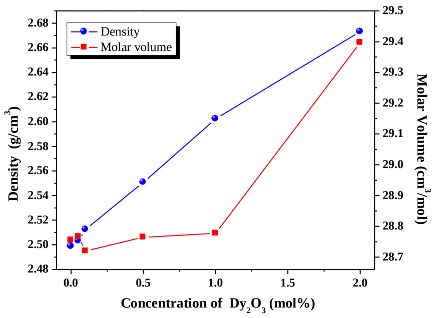

Figure 2. The density and molar volume of glass samples as a function of Dy_2O_3 concentration

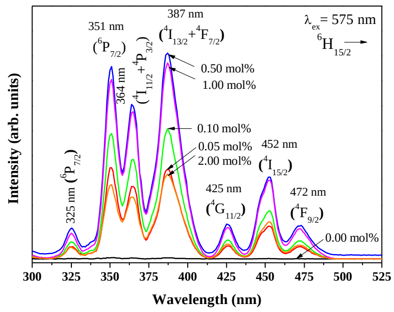

Figure 4. Excitation spectra of glass samples under 575 nm emission wavelength

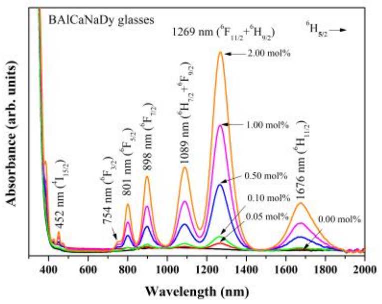

Figure 3. The absorption spectra of glass samples

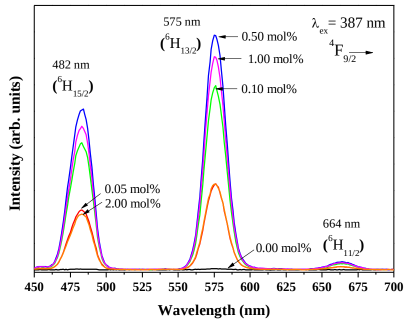

Figure 5. Emission spectra of glass samples under 387 nm excitation wavelength

molar volume of the glasses also increases with increasing of Dy_2O_3 content. When Dy^{3+} ions were added into the glass network, then there was a position transformation from network former to network modifier. This indicates that the number of non-bridging oxygen (NBO) has increased by breaking the of B-O networks (Meejitpaisan *et al*., 2016; Rajagukguk *et al*., 2016).

Absorption Spectra

The optical absorption spectra of glass samples in VIS and NIR regions were analysed by the UV-VIS-NIR spectrophotometer at room temperature in the range of 300-2000 nm, as shown in Figure 3. All transitions in the absorption spectrum of Dy^{3+} originated from the ground state $^6H_{5/2}$ to the various excited states. The seven absorption bands at 452, 754, 801, 898, 1,089, 1,269 and 1,676 nm can be attributed to the energy transitions from $^6H_{5/2}$ ground state to $^4I_{15/2}$, $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, ($^6H_{7/2}$ + $^6F_{9/2}$), ($^6F_{11/2}$+ $^6H_{9/2}$) and $^6H_{11/2}$ respectively (Chanthima *et al*., 2017). Furthermore, the absorbance intensity of Dy^{3+} was observed to increase gradually with increasing of Dy_2O_3 concentration.

Luminescence Properties

The observed excitation and emission spectra of glass samples are shown in Figures 4 and 5, respectively. The excitation spectra were obtained by monitoring in the wavelength region of 300-525 nm with emission wavelength at λ = 575 nm. The seven excitation bands are located at 325, 351, 364, 387, 425, 452, and 472 nm which attribute to transitions from the ground state $^6H_{15/2}$ to excited states $^6P_{3/2}$, $^6P_{7/2}$, ($^4I_{11/2}$+$^4P_{3/2}$), ($^4I_{13/2}$+$^4F_{7/2}$), $^4G_{11/2}$, $^4I_{15/2}$, and $^4F_{9/2}$, respectively. The excitation peak at 387 nm show the highest intensity and was selected to investigate the emission spectra.

The emission spectra of the glass samples were recorded in the wavelength region of 450-750 nm. The three emission peaks are observed at 483 (blue), 575 (yellow) and 664 (red) which corresponding to the Dy^{3+} emission transitions such as $^4F_{9/2}\rightarrow{}^6H_{15/2}$, $^4F_{9/2}\rightarrow{}^6H_{13/2}$, and $^4F_{9/2}\rightarrow{}^6H_{11/2}$ transitions, respectively (Chanthima *et al*., 2017). The results show that the intensity of these luminescence bands increase with increasing of Dy_2O_3 concentration from 0.05 to 0.50 mol% and reaches maximum at 0.50 mol%. Nevertheless, the emission intensity decreases with increasing of Dy_2O_3 concentration from 0.50 to 2.00 mol%. This is well-known as concentration quenching effect (CQE) due to the photon re-absorption between closer Dy^{3+} neighbours with increment of Dy_2O_3 concentration. The energy level diagrams for the luminescence of the Dy^{3+} ions as shown in Figure 6.

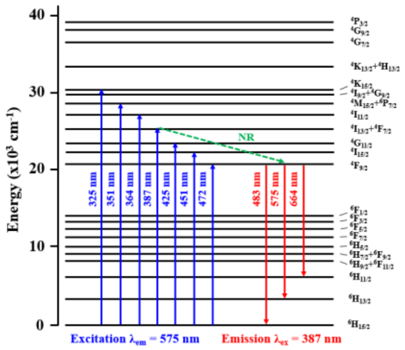

Figure 6. The energy level diagrams for the luminescence of the Dy^{3+} ions in glass samples

Table 2. Intensity ratio of yellow to blue emission

Sample	Y/B ratio	References
0.05Dy	1.4357	Present work
0.1Dy	1.4499	Present work
0.5Dy	1.4610	Present work
1.0Dy	1.4840	Present work
2.0Dy	1.5350	Present work
LBGS-0.5Dy	1.7	Khan *et al*. (2019)
LBGS-1.0Dy	1.68	Khan *et al*. (2019)
PKAZLFDy10	0.79	Vijaya *et al*. (2013)
LZBSDy0.5	2.45	Jaidass *et al*. (2018)
LZBSDy1.0	2.65	Jaidass *et al*. (2018)
L2BTAFDy	2.84	Jamalaiah *et al*. (2012)
BTLN0.5Dy	2.32	Uma *et al*. (2016)
LABD-4	1.08	Pawar *et al*. (2017)
Dy0.5	1.12	Mishra *et al*. (2016)

The yellow to blue (Y/B) intensity ratio has been used to determine the Dy^{3+}-O^{2-} bond covalence. In the present study for all the prepared glasses, the values of Y/B ratios are calculated. The present work and other reports presented the hypersensitive yellow emission, strong influence on the local environment of the glass matrix with addition of Dy^{3+} ions as shown in Table 2. The Y/B values for the present glass show increasing trend with increment of Dy^{3+} ions attributed to their structural changes. When compared with other reported literatures, the present glass samples show higher than PKAZLFDy10, LABD-4 and Dy0.5 glasses but lower than LBGS-0.5Dy, LZBSDy0.5, L2BTAFDy, and BTLN0.5Dy glasses.

The measurements of the color of light emitted by the glass samples, CIE color coordinates (x,y) of 0.5 Dy glass was analyzed by the relative ration of yellow (575 nm) to blue (483 nm) emission band which fall in white region as presented in Figure 7.

Understanding of the warm white light produced by the broadband produced can be analyzed by the correlated color temperature (CCT) values which can be calculated by using the Mc Camy's formula (McCamy, 1992).

$$CCT = -437n^3 + 3601n^2 - 6861n + 5524.31 \quad (1)$$

where, $n = (x - 0.3320)/(y - 0.1858)$ and x, y are the CIE chromaticity co-ordinates. As per the CCT ratings for a light source, if CCT values below 3200 K are referred as "warm sources" and ones above 4000 K are considered as "cool in appearance" (Su *et al*., 1993). The CCT value for 0.5 mol% Dy_2O_3 concentration is 4417K which is considered to be cool in appearance. The CCT values were compared with other reported literature as presented in Table 3 and found that the present glass sample doped with 0.5 mol% of Dy_2O_3 concentration are closer to the center of chromaticity graph (x = 0.33, y = 0.33). Hence, such closer to center of chromaticity and cool in appearance of Dy doped glass are useful for the development of white light generation devices.

The decay curve of glass samples with different concentrations of Dy^{3+} are as shown in Figure 8. The lifetimes for the $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition decreased with increasing concentration of Dy_2O_3. The decreasing behaviour of the lifetime in the present glass samples are due to the cross-relaxation energy transfer between donor Dy^{3+} ions to acceptor Dy^{3+} ions.

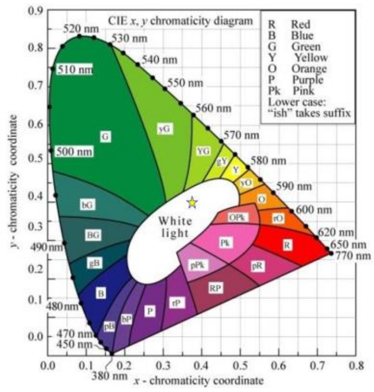

Figure 7. The CIE 1931 the chromaticity color coordinates of 0.50Dy glass

Table 3. Correlated colour temperature (CCT, K) for 0.50Dy glass

Sample	CCT (K)	References
0.05Dy	4417	Present work
LABD-4	5260	Pawar *et al*. (2017)
BBS05	6602	Mishra *et al*. (2016)
Standard white	5455	Su *et al*. (1993)
Dy0.5	3950	Krishna Reddy *et al*. (2019)
0.5DZTFB	4769	Suthanthirakumar and Marimuthu (2016)

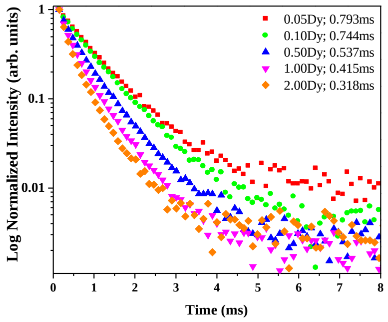

Figure 8. Decay curve of the $^4F_{9/2}$ level for Dy^+ in glass samples

Conclusions

In this work, the effect of Dy_2O_3 with different concentrations on physical and optical properties in borate glass were investigated. The results show that the density and molar volume tend to increase with increasing of Dy_2O_3 concentration. The absorption spectra of all glass sample reveal six intense bands at 754, 801, 898, 1,089, 1,269, and 1,676 nm. The excitation bands were identified at 325, 351, 364, 387, 425, 452, and 472 nm while the emission spectra exhibit three intense emission bands at 483 (blue), 575 (yellow) and 664 (red) nm. The Y/B values for the present glass show increasing trend with increasing in Dy^{3+} ions attributed to the Dy^{3+}-O^{2-} bond covalence. The CIE color coordinates (x,y) is found to be (0.37, 0.40) for all glasses which was fall on white region. The CCT value found to be 4417K which is considered to be cool in appearance. The lifetimes for the $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition decrease with increasing of Dy_2O_3 concentration. The obtained Dy^{3+} ions doped glasses can be applied as potential candidate for the solid-state white lighting material applications.

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Reference

Burtan, B., Mazurak, Z., Cisowski, J., Czaja, M., Lisiecki, R., Romanowski, W., Reben, M., and Wasylak, J. (2012). Optical properties of Nd^{3+} and Er^{3+} ions in TeO_2-WO_3-PbO-La_2O_3 glasses. Optic. Mat., 34(12):2,050-2,054.

Chanthima, N., Ruangtaweep, Y., and Kaewkhao, J. (2017). Optical properties and white emission from Dy^{3+} doped in Y_2O_3-CaO-SiO_2-B_2O_3 glasses. Key Eng. Mat., 702:62-65.

Jaidass, N., Krishna Moorthi, C., Mohan Babu, A., and Reddi Babu, M. (2018). Luminescence properties of Dy^{3+} doped lithium zinc borosilicate glasses for photonic applications. Heliyon. 4(3):e00555.

Jamalaiah, B.C., Rama Moorthy, L., and Hyo, J.S. (2012). Effect of lead oxide on optical properties of Dy_{3+} ions in PbO-H_3BO_3-TiO_2-AlF_3 glasses. J. Non-Crystall. Solid., 358(2):204-209.

Khan, I., Rooh, G., Rajaramakrishna, R., Srisittipokakun, N., Wongdeeying, C., Kiwasakunkran, N., Wantana, N., Kim, H.J., Kaewkhao, J., and Tuscharoen, S. (2019). Photoluminescence and white light generation of Dy_2O_3 doped Li_2O-BaO-Gd_2O_3-SiO_2 for white light LED. J. Alloy. Comp., 774:244-254.

Krishna Reddy, D.V., Sambasiva Rao, T., Taherunnisa, S.K., Suchocki, A., Zhydachevskyy, Y., Piasecki, M., and Rami Reddy, M. (2019). Tunable white light by varying excitations in yttrium alumino bismuth borosilicate glasses co-doped with Dy^{3+}-Eu^{3+} for cool WLED applications. J. Non-Crystall. Solid., 513:167-182.

Luewarasirikula, N. and Kaewkhao, J. (2018). Dy^{3+}-doped Ba-Na-B white light-emitting glass for w-LED applications. Matrials Today: Proceedings, 5(6)13,963-13,970.

McCamy, C.S. (1992). Correlated color temperature as an explicit function of chromaticity coordinates. Color Res Appl., 17(2):142-144.

Meejitpaisan, P., Kedkaew, C., Ruangthaweep, Y., and Kaewkhao, J. (2016). Investigated on photoluminescence properties of Sm^{3+} ions in gadolinium calcium phosphate glasses. Key Eng. Mat., 702:57-61.

Mishra, L., Sharma, A., Vishwakarma, A.K., Jha, K., Jayasimhadri, M., Ratnam, B.V., Jang, K., Rao, A.S., and Sinha, R.K. (2016). White light emission and color tunability of dysprosium doped barium silicate glasses. J. Lumines., 169:121-127.

Othman, H.A., Elkholy, H.S., and Hager, I.Z. (2016). FTIR of binary lead borate glass: Structural investigation. J. Molec. Struc., 1,106:286-290.

Pawar, P.P., Munishwar, S.R., Gautam, S., and Gedam, R.S. (2017). Physical, thermal, structural and optical properties of Dy^{3+} doped lithium alumino-borate glasses for bright W-LED. J. Lumine., 183:79-88.

Rajagukguk, J., Kaewkhao, J., Djamal, M., Hidayat, R., Suprijadi and Ruangtaweep, Y. (2016). Structural and optical characteristics of Eu^{3+} ions in sodium-lead-zinc-lithium-borate glass system. J. Molec. Struc., 1,121:180-187.

Ravangvong, S., Chanthima, N., Rajaramakrishna, R., Kim, H.J., Sangwaranatee, N., and Kaewkhao, J. (2019). Dy^{3+} ions doped (Na_2O/NaF)-Gd_2O_3–P_2O_5 glasses for solid state lighting material applications. Solid State Sci., 97:105972.

Ruangthaweep, Y., Kaewkhao, J., Hansupho, S., and Huaikrachao, W. (2017). Physical and optical properties of Ni^{2+} ions in borate glass. J. Thai Interdiscipl. Res., 12(3):19-22.

Su, Q., Pei, Z., Chi, L., Zhang, H., Zhang, Z., and Zou, F. (1993). The yellow-to-blue intensity ratio (Y/B) of Dy^{3+} emission. J. Alloy. Comp., 192(1-2):25-27.

Suthanthirakumar, P. and Marimuthu, K. (2016). Investigations on spectroscopic properties of Dy^{3+} doped zinc telluro-fluoroborate glasses for laser and white LED applications. J. Molec. Struc., 1,125:443-452.

Terczyn´ska-Madej, A., Cholewa-Kowalska, K., and Łaczka, M. (2011). Coordination and valence state of transition metal ions in alkali-borate glasses. Opt. Mat., 33(12):1,984-1,988.

Uma, V., Maheshvaran, K., Marimuthu, K., and Muralidharan, G. (2016). Structural and optical investigations on Dy^{3+}

doped lithium tellurofluoroborate glasses for white light applications. J. Lumines., 176:15-24.

Venkataiah, G., Jayasankar, C.K., Krishnaiah, K.V., Dharmaiah, P., and Vijaya, N. (2015). Concentration dependent luminescence properties of Sm^{3+}-ions in tellurite-tungsten-zirconium glasses. Opt. Mat., 40:26-35.

Vijaya, N., Upendra Kumar, K., and Jayasankar, C.K. (2013). Dy^{3+}-doped zinc fluorophosphate glasses for white luminescence applications. Spectroc. Acta Part A: Molec. Biomolec. Spectros., 113:145-153.

Yan, H. and Ju C. (2016). Structure and luminescence of Dy^{3+} doped CaO-B_2O_3-SiO_2 glasses. Physica. B., 493:68-71.