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Comparative investigations of gadolinium based borate glasses doped with Dy³⁺ for white light generations

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ABSTRACT

Gadolinium-based borate glasses doped with Dy³⁺ ions were developed by melt quenching technique for white light generation. The title glasses were examined by XRD, optical absorption spectra and Photoluminescence spectra. From photoluminescence emission spectra, the higher intensity peak was observed at 575 nm (⁴F_{9/2} → ⁶H_{13/2}) for present glass samples. The experimental decay rate (τ_{exp}) of ⁴F_{9/2} transition of Dy³⁺ ions were found to be a decline in increasing of Dy₂O₃ content. The Inokuti-Hirayama (IH) model is used to explain the non-exponential decay time by putting S = 6, which confirmed that the energy is transfer through cross-relaxation is of dipole–dipole nature among the Dy₂O₃. The values of color coordinates match with the range of white light of chromaticity (CIE) diagram. The color chromaticity coordinates (u, v) and color correlated temperature (CCT) values for present glasses were correlated with standards, which are closely related to the standard, therefore, the prepared glasses might be helpful for different photonic applications such as white LEDs.

1. Introduction

In recent time, different glass substances are extensively studied to enhance their luminescence characteristics, which is used for the development of various luminescence and optical devices in the Solid State Lighting. Solid State lighting like W-LEDs, liquid crystal displays, traffic signals, cellular displays etc., are supposed to show an important aspect in the future. These materials save manifold of power energy and lower carbon emissions by approximately twenty-eight million metric tons in a year, worldwide [1]. In the present study white LEDs were considered as an important candidate for lighting source because of their important applications like bunched size, shock resistance, attractive design prospects, higher reliability, higher transparency and long decay time [2] friendless of environment and high capability, correlated with conventional incandescent and fluorescence lamps [3]. For this purpose Li₂O-Gd₂O₃-MO-B₂O₃ (where MO = Bi³⁺, Ba) glass matrix were selected as a host glass materials for the present work, because of greater chemical strength, greater RE ion solubility, small coefficient of heat expansion, important absorption of gamma (γ-ray) and X-rays for radiation shielding glasses, less phonon energy

(1100 cm⁻¹) less than the visible light. Therefore, its effect is considered negligible on visible light emission [4,5]. In addition, borate containing bismuth and barium oxides glasses have got special interest because of their interesting applications such as laser host, white-LEDs, lamp phosphors, radiation shielding, surgical lasers, and other photonic devices. Boric acids combined with lithium, barium and bismuth oxides form a stable host [6]. Gd₂O₃ combined with borate is may be network modifier and preferred as a host network in the recent investigation due to their greater permittivity and a higher energy gap (E_g = 5.4 eV), better heat stability that make it as a favorable devices [7]. Therefore Li₂O-Gd₂O₃-MO-B₂O₃ (where MO = Bi³⁺, Ba) host glass activated with some rare earth (RE) ions are mostly used as a nonlinear optical material, thermoluminescence, photonic devices, and solid-state lighting material [8,9]. Presently, dysprosium ions (Dy³⁺) doped in glass materials are extensively reported because of the possibility in white light generation, due to their emission in blue (482 nm) and yellow (575 nm) light [10]. There are many important application of Dy³⁺ ion activated in glassy materials, which including white light origination as a single phase, luminescence lamps, and electron trapping devices and light transformation devices. Furthermore, Dy³⁺ ion is the most important

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and used extensively as activator ions for describing the local environment in the luminescent substance [11]. Several researcher studies the properties of Dy^{3+} in different glass composition such as Zhang et al., [3] investigate the Dy^{3+} activated and co-doped with Ce^{3+} ion in calcium aluminum silicon borate glasses and study its luminescence characterization for light-emitting materials (LED) applications. Azizan et al. [12] study the spectroscopic and physical properties of Dy^{3+} activated in lithium potassium borate glasses for application in the field of SSL, optoelectronic materials and white light generation (W-LEDs) purpose. Jayasankar et al. [13] briefly study the borate and fluoroborate doped with Dy^{3+} ions and find their luminescence characterizations and discuss the energy transfer by IH model for different application in the lasing and lighting field. The alkaline earth (lithium and potassium) borate doped with Dy^{3+} glasses were investigated by Xiong et al. [14], in fluorescence radiation for the developing optical sources. The Dy^{3+} activated fluoro-phosphate glasses have been activated by Babu et al. [15] and study its luminescence properties for solid-state lighting applications. Vijayakumar and Marimuthu [16] study the Dy^{3+} doped glasses in oxyfluoro-borophosphate and investigated the luminescence and structural properties for lasing transition and white light emitting diodes (w-LEDs). Mishra et al. [11] study the barium silicate with Dy_2O_3 activated glasses for the purpose of white light emission devices and color reliability. The briefly, promises and challenging study were carried out by Bergh et al. [1] for SSL applications. Recently Zaman et al. [17] investigated the lithium gadolinium bismuth borate glasses doped with dysprosium ion and characterize its laser and luminescence properties for lightning emitting devices. The Dy^{3+} activated silicate glass materials are reported by Sun et al. [2] and study its spectroscopic properties by simulation method for white light. The aim of the recent research study is to develop gadolinium-based borate glasses doped with Dy^{3+} and investigated their luminescence properties for white light generations.

2. Experimental detail

2.1. Synthesis of LGBiBDy and LGBaBDy glasses

The glass samples which have general composition $Li_2O-Gd_2O_3-MO-B_2O_3-Dy_2O_3$ where $MO = Bi_2O_3$, BaO is synthesized through melt quenching process. Ratio of the chemical composition is 45/50 $Li_2O-15Gd_2O_3-10/5MO-(30-y) B_2O_3: yDy_2O_3$ (where $y = 0.0, 0.3, 0.5, 1.0, 1.5, 2.0$ and 2.5 mol %) label as LGBaBDy and LGBiBDy. The starting chemicals including H_3BO_3 (boric acid), Li_2CO_3 (lithium carbonate), $BaCO_3$ (barium carbonate), Gd_2O_3 (gadolinium oxides), Bi_2O_3 (bismuth oxides) and Dy_2O_3 (dysprosium (III) oxide) have been selected of purity 99.99%. The proposed ratios of chemicals weighted for 10 g samples and well mixed. The mixed chemicals are loaded in an alumina crucible, which is heated up to $1200^\circ C$ for 3 h using the electrically heated furnace. The developed transparent glasses have been finally annealed on $500^\circ C$ up to 3 h to abolish any internal stresses. The prepared glasses are cut smoothly and polished for further investigation. Photographs of the LGBiBDy and LGBaBDy glasses are given in Fig. 1(a) and (b).

2.2. Instrumentation and parameters

The density of the LGBiBDy and LGBaBDy glasses have been estimated with help of Archimedes method. Distilled water is used as a reference.

$$\rho = \frac{M_A}{(M_A - M_B)} \times 0.999g/cm^3 \quad (1)$$

Where " M_A " is mass of the glass in air and " M_B " is mass in water. The optical refractive index (n) have been obtained with the help of an Abbe refractometer (ATAGO) sodium vapor lamp wavelength (λ) of 589.3 nm is used as a source light. Shimadzu Diffractometer XRD-6100 with the software of diffraction analysis and the source is Cu radiation (40 kV, 30 mA) of 2θ from 10° to 80° , steps of 0.02° at a speed of $5^\circ/min$. The absorption spectra have been recorded by a Shimadzu 3600 UV-VIS-NIR spectrophotometer. The range of this spectrometer is (200–1800 nm). A spectrometer which is used for photoluminescence (excitation and emission) spectrum is Cary Eclipse fluorescence Spectrophotometer of Agilent technologies. All calculations have been taken at room temperature.

3. Results and discussion

3.1. Physical parameters

Density is an important, informative and simplest property of the materials and can be used for measuring the structure of glass samples. The obtained values of density (ρ), molar volume (V_m) and optical refractive index (n) of the LGBiBDy and LGBaBDy are listed in Table 1. These values of the prepared materials are increased by increasing the concentration of Dy^{3+} ion. The increasing density and molar volume of title samples show the compactness in the glass structure. This behavior of the present glass samples is due to the transfer of $[BO_3]^{-3}$ into BO^{-4} by adding modifier. It is also due to the replacement of B_2O_3 by Dy_2O_3 ion, the density of Dy_2O_3 is $7.8 g/cm^3$ and B_2O_3 is $2.46 g/cm^3$ that's why the density of the developed glasses was increased. The refractive of the title glasses also increases by increasing the concentration of Dy^{3+} ion as shown in Table 1. Which is due to the increase in the density of the synthesized samples. When density increased the structure of the glass samples is compact and velocity of light in that material is less which as a result increased the optical refractive index (n) of the developed samples. These three parameters of the LGBiBDy glass is greater than LGBaBDy glasses. It is due to the bismuth oxide (Bi_2O_3) which have greater density and higher refractive index as compared with barium oxide (BaO).

3.2. X-ray diffraction (XRD) analysis

XRD spectra of LGBaBDy and LGBiBDy for $X = 0$ mol% of Dy^{3+} concentration have been measured. Fig. 2 shows the XRD spectra which have no prominent band have been observed at two-theta (2θ), which is the amorphous nature of synthesized samples.

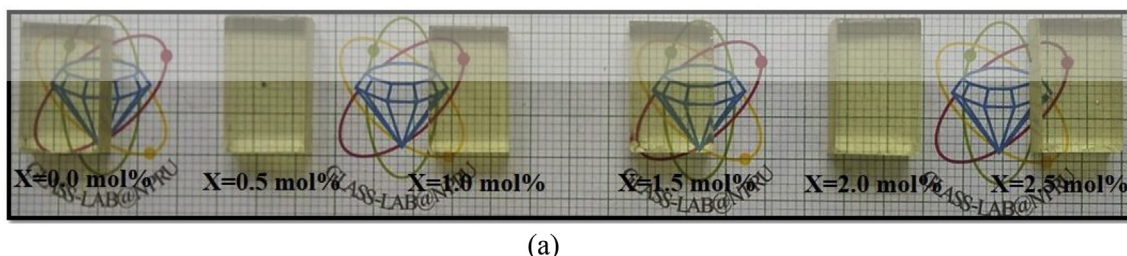


Fig. 1a. Digital photograph of LGBiBDy glasses.

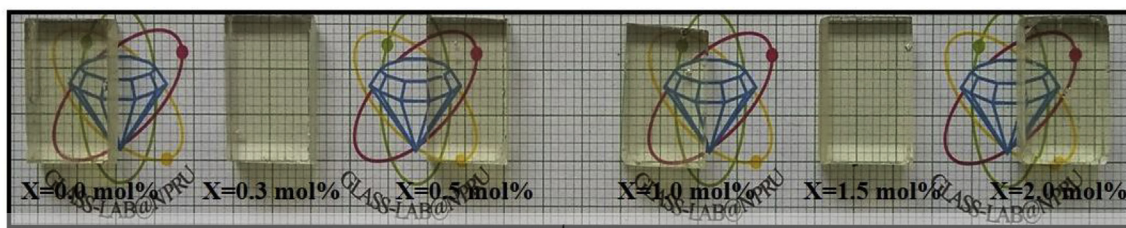


Fig. 1b. Digital photographs of LGBaBDy glasses.

Table 1

The physical parameters of Dy³⁺ doped LGBiBDy and LGBaBDy glass at room temperature.

Physical properties	LGBiBDy 1.5	LGBaBDy 1.5
Density, ρ (g/cm ³)	3.26 ± 0.015	3.18 ± 0.029
Thickness (cm)	0.44	0.40
Refractive index (n)	1.60 ± 0.002	1.59 ± 0.0023
Molecular weight, M (g/mol)	118	108
Molar volume Vm (cm ³ /mol)	36 ± 0.019	34 ± 0.021

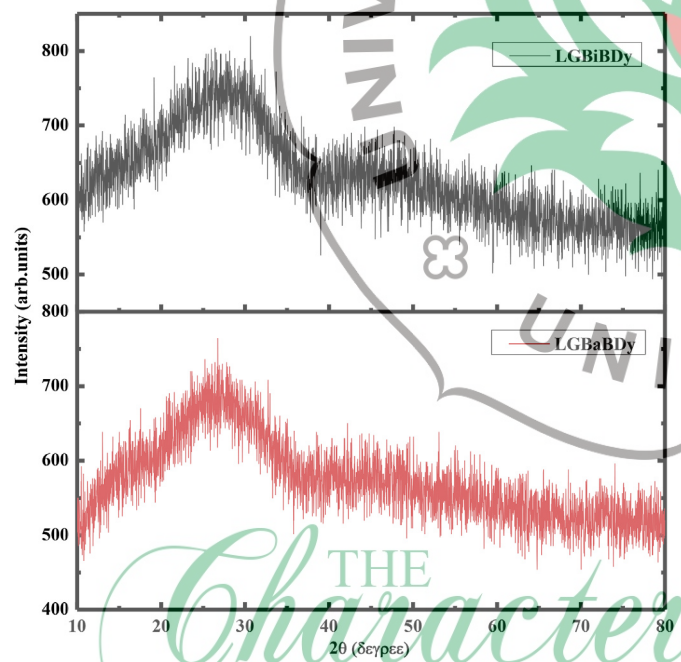


Fig. 2. X-ray diffraction (XRD) of LGBaBDy and LGBiBDy glass samples.

3.3. Typical absorption spectra

The optical absorption spectrum of LGBaBDy and LGBiBDy glasses at 2.0 mol% of Dy³⁺ concentration are presented in Fig. 3. From absorption pattern, seven prominent signatures have been exhibit, which is assigned originating from the ⁶H_{15/2} 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} corresponding to 450, 750, 798, 896, 1085, 1265 and 1670 nm wavelength respectively. From all these absorption peaks, the transition (⁶F_{11/2} + ⁶H_{9/2}) of wavelength 1265 nm is the highest intensity among all these seven transitions and is hypersensitive transitions. These absorption transitions were good agreement with the location of the peaks of absorption spectra with the previous study [17–20].

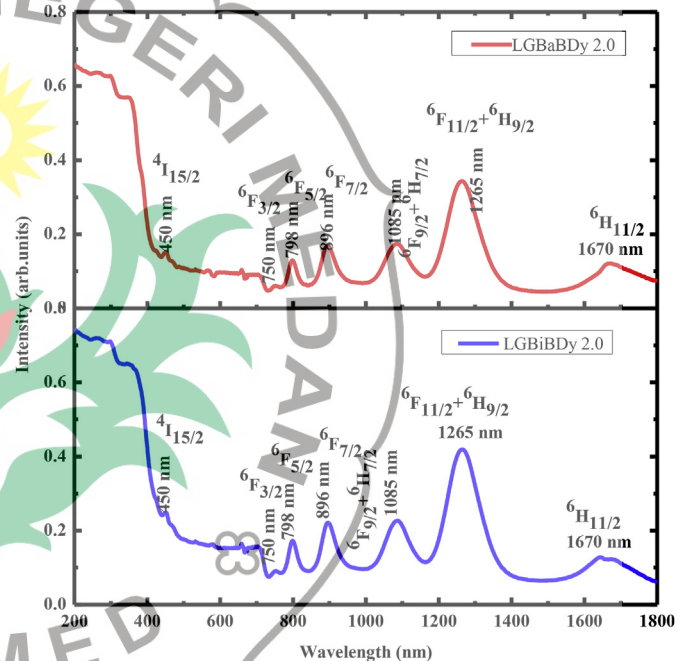


Fig. 3. Absorption spectra of LGBaBDy 2.0 and LGBiBDy 2.0 glass samples.

3.4. Photoluminescence spectra

Fig. 4. (a), (b), indicate excitation spectrum of LGBaBDy and LGBiBDy glasses respectively, by selecting emission wavelength at 575 nm. There are seven prominent signatures have been exhibit at 324, 350, 365, 388, 425, 452 and 472 nm due to ⁶H_{15/2} to 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} levels, respectively. The peak position for LGBaBDy and LGBiBDy are same, the highest intensity band was seen at 350 and 388 nm for LGBaBDy and LGBiBDy glasses respectively, and were chosen for the measurement of the emission spectrum of prepared glass samples. The position of the excitation band is found same with reported works [13,17,21]. Fig. 5(a) and (b) indicates that the photoluminescence emission spectrum of LGBaBDy and LGBiBDy glasses respectively activated with Dy³⁺ at various contents. The measurement has been done within the range of 400–800 nm by fixing excitation wavelength 350 nm and 388 nm for LGBaBDy and LGBiBDy glass respectively. From the luminescence emission spectrum, four prominent emission bands were obtained at ⁴F_{9/2} → ⁶H_{15/2}, ⁴F_{9/2} → ⁶H_{13/2}, ⁴F_{9/2} → ⁶H_{11/2} and ⁴F_{9/2} → ⁶H_{9/2} levels corresponding to the wavelength 482, 575, 663 and 752 nm respectively. Emission spectra of the synthesized glasses show that the luminescence emission intensity was found increased with the variation of Dy³⁺ content up to 1.5 mol%, quenching effect was obtained at 1.5 mol % of Dy³⁺ concentration for LGBaBDy and LGBiBDy glass samples. In the present report, the transition, ⁴F_{9/2} → ⁶H_{13/2} at 575 nm is the highest intensity and selected as the emission wavelength for measuring the excitation spectrum. Transition ⁴F_{9/2} → ⁶H_{13/2} is exactly electric

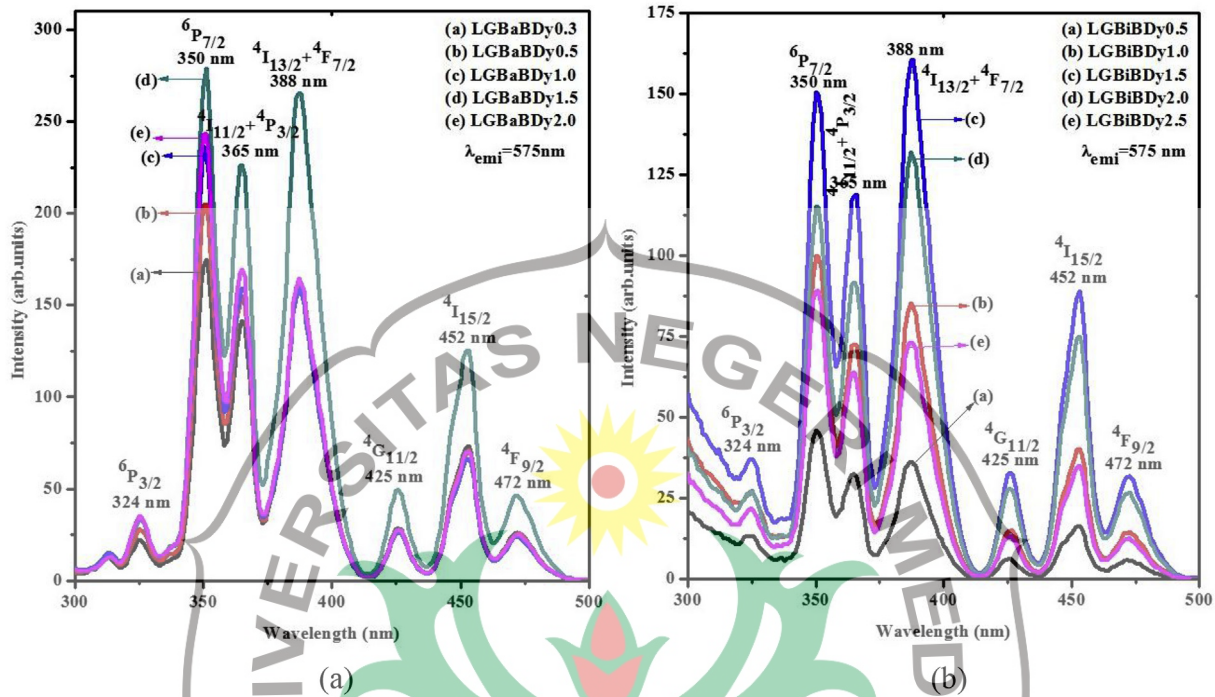


Fig. 4. PL Excitation spectrum of (a) LGBaBDy and (b) LGBiBDy glasses.

dipole (ED), while ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ level is purely magnetic dipole (MD) [18]. It is necessary for the asymmetric environment of the glass materials that ED level is more intense than the MD level. Therefore the interaction among the RE ions and the host materials will be stronger. From the present study it is concluded that the ED intensity of the LGBaBDy is higher than LGBiBDy glasses, therefore the LGBaBDy is more asymmetric from LGBiBDy glasses. Fig. 5(a) and (b) show that the intensity of the LGBaBDy glasses more as from LGBiBDy glasses, it is due to the more asymmetric nature of the LGBaBDy glasses. Therefore

the energy transfer from the host material (LGBaB) to the luminescence center (Dy^{3+}) is more than the LGBiBDy glasses. The photoluminescence spectra of the title glasses are similar to those of the previous work [13,17,21].

3.5. Lifetime

Decay profile of ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ level of LGBaBDy and LGBiBDy glasses were determined at room temperature under 350 and 388 nm

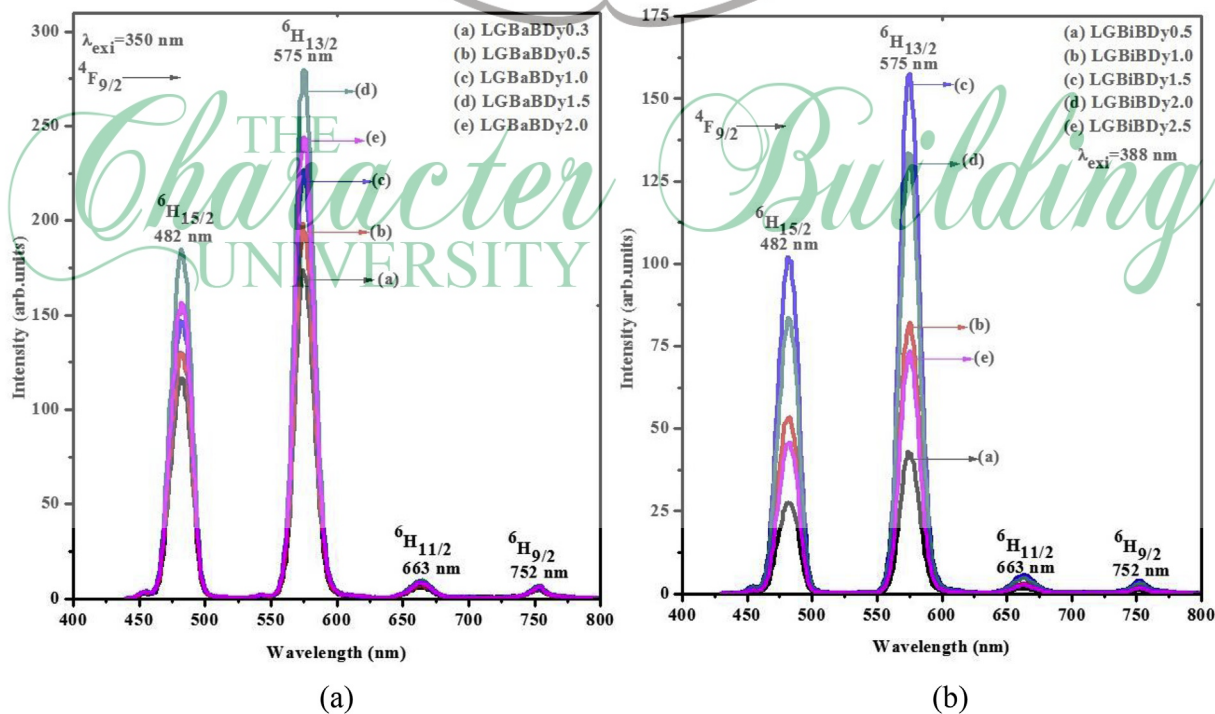


Fig. 5. Photoluminescence emission spectra of (a) LGBaBDy and (b) LGBiBDy glasses.

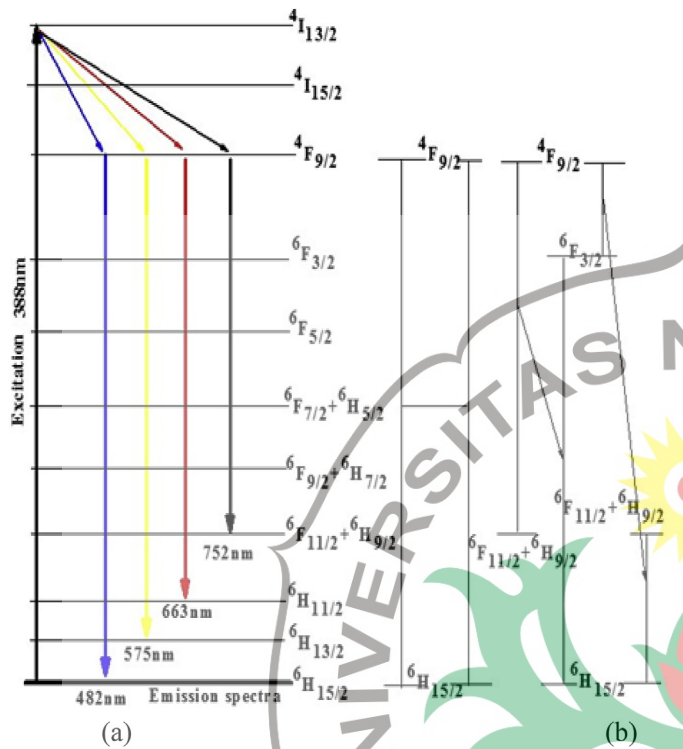


Fig. 6. Energy level diagram of the present glass samples with resonant energy level.

excitation and at 575 nm emission wavelength and is given in Fig. 7(a). The lifetime of LGBaBDy and LGBiBDy glasses decreases with the variation of Dy³⁺ concentration as given in Fig. 7(b). The increase of nonradiative relaxation rates and a decline in experimental decay times (τ_{exp}) might be because of the transfer of energy by cross-relaxation and also may be through resonant energy channels in the developed glass network [22]. To discuss the non-exponential behavior in the present glass matrix Inokuti–Hirayama (IH) model [23] were used for ion-ion interaction (among Dy³⁺ ions), and the fit is good for $S = 6$, which indicate dipole-dipole interaction, the fluorescence decay intensity “ $I(t)$ ” is explained by the following equation,

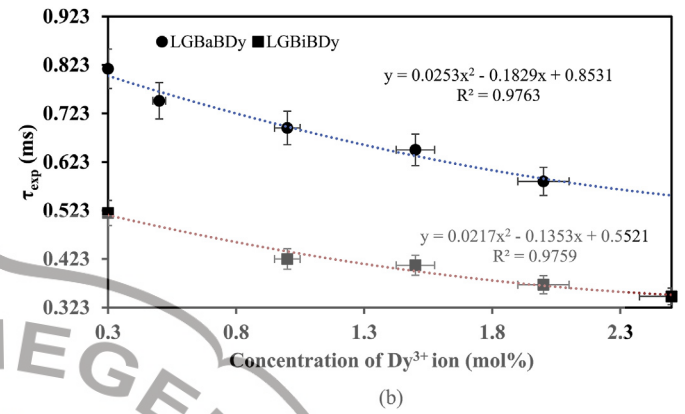


Fig. 7b. Variation of lifetime with concentration of Dy³⁺ ion in LGBaBDy and LGBiBDy glasses.

$$I(t) = I_0 \exp \left\{ -\frac{t}{\tau_0} - Q \left(\frac{t}{\tau_0} \right)^{3/S} \right\} \quad (2)$$

Where τ_0 is decay time of the donors, t is time after excitation. $S = 6$ for dipole–dipole, $S = 8$ for dipole–quadrupole and $S = 10$ quadrupole–quadrupole. Transfer energy parameter “ Q ” is related by Ref. [24],

$$Q = \frac{4\pi}{3} \Gamma \left(1 - \frac{3}{S} \right) N_0 R_0^3 \quad (3)$$

Where “ Q ” is the transfer energy parameter, “ R_0 ” is critical distance, Γ is gamma function and N_0 is the acceptor concentration. To obtain good fit among the theoretical and experimental curve the value of S are putting 6 which is given in Fig. 7(a). The dipole-dipole interaction parameter C_{DA} was determined through below relation,

$$C_{DA} = \frac{R_0^S}{\tau_0} \quad (4)$$

The obtained data of fitting factors “ Q , R_0 , and C_{DA} ” are collected in Table 2 for LGBaBDy 0.3 LGBaBDy 0.5, LGBaBDy 0.5 and LGBaBDy 1.0 glasses along with Dy³⁺ ion concentration (N), density (d) and decay rate (τ_{exp}) of ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition of the title glass network. The given quantities were correlated with those of reported investigation which includes LBDy1.0 [13], PKAlCaFDy05 [18], and PKBAFD10 [25]

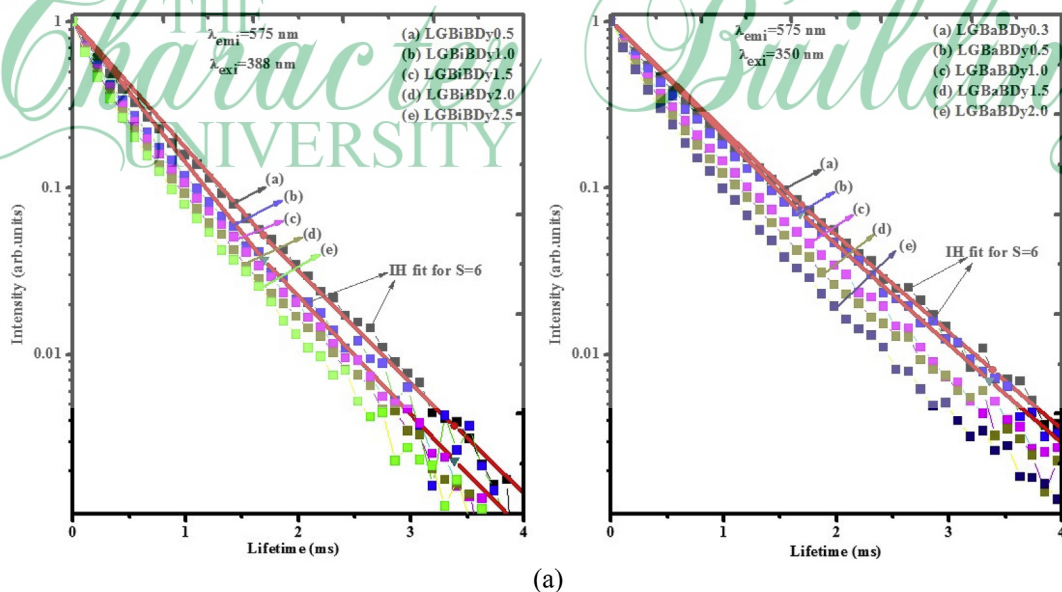


Fig. 7a. Lifetime of the ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ level for LGBaBDy and LGBiBDy glasses.

Table 2
Shows Dy³⁺ ion concentration (N, Ions/cm³ ×10²⁰), densities (d, g/cm³), experimental decay time (τ_{exp}, ms) for the ⁴F_{9/2} → ⁶H_{13/2} level, transfer energy parameter (Q), critical distance (R₀, Å), dipole–dipole type parameter (C_{DA}, × 10⁻⁴⁰ cm⁶/s), for LGBaBDy and LGBiBDy glasses.

Glass		N	d	τ _{exp}	Q	R ₀	C _{DA}
LGBaBDy0.3	Resent work	0.533	3.096	0.815	0.326	9.37	8.35
LGBaBDy0.5	Resent work	0.887	3.111	0.749	0.327	7.92	3.30
LGBaBDy1.0	Resent work	1.768	3.144	0.693	-	-	-
LGBaBDy1.5	Resent work	2.646	3.181	0.648	-	-	-
LGBaBDy2.0	Resent work	3.514	3.213	0.583	-	-	-
LGBiBDy0.5	Resent work	0.847	3.236	0.518	0.256	7.42	3.22
LGBiBDy1.0	Resent work	1.681	3.253	0.423	0.515	7.49	4.03
LGBiBDy1.5	Resent work	2.501	3.268	0.410	-	-	-
LGBiBDy2.0	Resent work	3.296	3.272	0.370	-	-	-
LGBiBDy2.5	Resent work	4.086	3.286	0.346	-	-	-
LBDy1.0	[13]	-	-	0.513	1.156	7.20	1.66
PKAlCaFDy0.5	[18]	-	-	0.786	0.346	6.85	1.27
PKBAFDy1.0	[25]	-	-	0.732	0.40	7.00	1.33

glasses. Table 2, noticed that the values of Q, R₀, and C_{DA} among the donors and acceptor (Dy³⁺) increases for LGBiBDy glass on increasing the Dy³⁺ concentration (0.5–1 mol%). The increase in the given parameters is because of the effective density of Dy³⁺ ions, which shows the transfer of energy mechanism among the Dy³⁺ ions by cross relaxation. The calculated values of C_{DA} and R₀ amongst donor and acceptor are shows declined trend for LGBaBDy glasses with Dy³⁺ content. The obtained results of critical distance (R₀) are related with the strength of donor and acceptor pairing and its trend might be because of migration of energy in the donor at higher contents of Dy³⁺ ions in LGBaBDy glass. The magnitude of lifetime of the developed and reported glasses are the order of LGBaBDy0.3 (τ = 0.815 ms) [present work] > PKAlCaFDy0.5 (τ = 0.786 ms) [18] > PKBAFDy1.0 (τ = 0.732 ms) [25] > LGBiBDy0.5 (τ = 0.518 ms) [present work] > LBDy1.0 (τ = 0.513 ms) [13]. The lifetime of all the glasses is more or less similar. The LGBaBDy glass longer decay time as compared to all other glasses. Fig. 6, explain the energy level diagram for different transitions along with resonant energy transitions and transfer of energy through the cross-relaxation process.

3.6. CIE chromaticity coordinates

The developed glasses LGBaBDy and LGBiBDy emit white light at excitation wavelengths 350 and 388 nm at specific intensity ratio yellow to blue (Y/B) of (⁴F_{9/2} → ⁶H_{13/2})/(⁴F_{9/2} → ⁶H_{15/2}) emission state as shown in Table 3. Fig. 8 shows that the obtained coordinate's values fall in the white light range in the CIE chromaticity diagram [18]. The CIE has selected for the usage of uniform color space (UCS), the other related factors (CCT, CRI etc.) are also explained in this diagram [11]. The following relation is used to calculate the values of (u, v)

Table 3

The obtained data of color coordinates (x, y), (u, v), yellow to blue ratio Y/B and color correlated temperature (CCT, K) for LGBaBDy and LGBiBDy glasses.

Glass	Color coordinates (x,y)	Color coordinates (u,v)	CCT (k)	Y/B ratio	Reference
Standard white	(0.33, 0.33)	(0.21, 0.32)	5455	-	[27]
D65	(0.31, 0.33)	(0.19, 0.32)	6504	-	[27]
YAG + Blue chips	(0.29, 0.30)	(0.19, 0.32)	5610	-	[28]
LGBaBDy0.3	(0.36, 0.40)	(0.21, 0.34)	4488	1.48	Resent work
LGBaBDy0.5	(0.36, 0.40)	(0.21, 0.34)	4466	1.52	Resent work
LGBaBDy1.0	(0.37, 0.41)	(0.21, 0.34)	4431	1.54	Resent work
LGBaBDy1.5	(0.37, 0.41)	(0.21, 0.34)	4422	1.51	Resent work
LGBaBDy2.0	(0.37, 0.41)	(0.21, 0.34)	4476	1.56	Resent work
LGBiBDy0.5	(0.37, 0.40)	(0.19, 0.34)	4424	1.54	Resent work
LGBiBDy1.0	(0.38, 0.41)	(0.19, 0.34)	4279	1.52	Resent work
LGBiBDy1.5	(0.37, 0.41)	(0.19, 0.34)	4363	1.54	Resent work
LGBiBDy2.0	(0.37, 0.41)	(0.19, 0.34)	4323	1.59	Resent work
LGBiBDy2.5	(0.37, 0.41)	(0.19, 0.34)	4356	1.60	Resent work

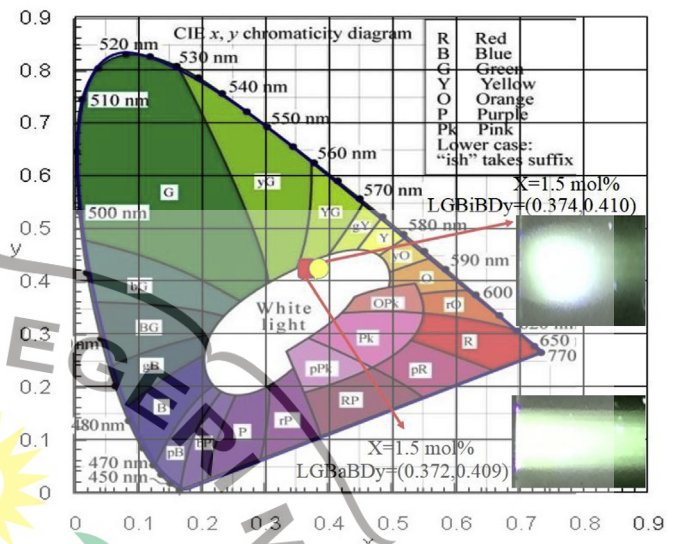


Fig. 8. The CIE diagram shows the chromaticity color coordinates for various Dy³⁺ ion concentration in LGBaBDy and LGBiBDy glasses. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

coordinates:

$$u = \frac{4x}{-2x + 12y + 3} \tag{5}$$

$$v = \frac{6y}{-2x + 12y + 3} \tag{6}$$

The obtained values of chromaticity coordinates (u, v) for LGBaBDy and LGBiBDy samples are listed in Table 3. Nature of emitted light is investigated by the color correlated temperature (CCT), which can be obtained from McCamy relation as mention below [26].

$$CCT = -449n^3 + 3525n^2 - 6823n + 5520.33 \tag{7}$$

Where the values of $n = \frac{x-x_e}{y-y_e}$ where x_e and y_e are the epicenter [20]. The obtained results of the CCT for the LGBaBDy and LGBiBDy glasses are given in Table 3. The color coordinates (x, y), (u, v) and CCT values are compared with standard equal energy white illuminated, CIE standard D65 illuminated and YAG + Blue chips, which are closely related as shown Table 3. Therefore it is suggested that LGBaBDy and LGBiBDy glasses are useful for the white light generation by commercial UV LED chip under excitation wavelengths 350 and 388 nm.

4. Conclusion

Optical and transparent quality of LGBaBDy and LGBiBDy glasses with various contents of Dy₂O₃ ions have been developed through melt quenching process for W-LED application in solid state lighting. The glassy phase of synthesized devices is confirmed from the XRD pattern. From optical absorption measurements, the higher intensity and hypersensitive transition are at 1265 nm (⁶H_{15/2} → ⁶F_{11/2} + ⁶H_{9/2}). The photoluminescence emission spectra which is excited by UV or blue light (350 and 388 nm), four prominent peaks have been observed, corresponding to 482, 575, 663, 755 nm and higher intensity transition is ⁴F_{9/2} → ⁶H_{13/2} (575 nm) for Dy³⁺ doped LGBaBDy and LGBiBDy glasses. Similar emission were observed from previous literature for Dy³⁺ doped in other glasses [29–32]. Concentration quenching is found at 1.5 mol% of Dy³⁺ contents in LGBaBDy and LGBiBDy glasses. The experimental lifetime of ⁴F_{9/2} transition of LGBaBDy and LGBiBDy samples is found to decreasing on increasing concentration of Dy³⁺ ion. Non-exponential lifetime is fitted by Inokuti-Hirayama (IH) model for S = 6, which shows the transfer of energy by cross-relaxation among Dy³⁺ ions, which is a dipole-dipole type. Color coordinates (x, y), (u, v) and CCT values of synthesized samples are compared with standard equal energy white illuminated, CIE standard D65 illuminated and YAG + Blue chips, which are close related. Hence, the LGBaBDy and LGBiBDy samples are might be used for white light generation (W-LEDs), which is friendly environment and financial saving.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.solidstatesciences.2018.12.020>.

References

- [1] A. Bergh, G. Craford, A. Duggal, R. Haitz, The promise and challenge of solid-state lighting, *Phys. Today* 54 (2001) 42, <https://doi.org/10.1063/1.1445547>.
- [2] X.Y. Sun, S.M. Huan, X.S. Gong, Q.C. Gao, Z.P. Ye, C.Y. Cao, Spectroscopic properties and simulation of white-light in Dy³⁺-doped silicate glass, *J. Non-Cryst. Solids* 356 (2010) 98.
- [3] Pan-pan Zhang, Yong-ping Pun, Xiao-juan Zhu, Han-yu Zheng, Jiao-jiao Zhao, Yu-rong Wu, Yan-jie Luo, Yu-wen Liu, Luminescence properties of Dy³⁺ doped and Dy³⁺/Ce³⁺ co-doped CaO-Al₂O₃-SiO₂-B₂O₃ glass for LED applications, *Ceram. Int.* 41 (2015) S729–S733.
- [4] R. Kaur, S. Singh, O.P. Pandey, FTIR structural investigation of gamma irradiated BaO-Na₂O-B₂O₃-SiO₂ glasses, *Physica B* 407 (2012) 4765.
- [5] Qiaqiao Chen, Nengli Dai, Zijun Liu, Yingbo Chu, Baoyuan Ye, Haiqing Li, Jinggang Peng, Zuowen Jiang, Jinyan Li, Fang Wang, Luyun Yang, White light luminous properties and energy transfer mechanism of rare earth ions in Ce³⁺/Tb³⁺/Sm³⁺ co-doped glasses, *Appl. Phys. A* 115 (2014) 1159.
- [6] S. Lakshmi Srinivasa Rao, G. Ramadevudu, Md Shareefuddin, Abdul Hameed, M. Narasimha Chary, M. Lakshminpathi Rao, Optical properties of alkaline earth borate glasses, *Int. J. Eng. Sci. Technol.* 4 (2012) 25–35.
- [7] Ragab M. Mahani, Samir Y. Marzouk, AC conductivity and dielectric properties of SiO₂-Na₂O-B₂O₃-Gd₂O₃ glasses, *J. Alloy. Comp.* 579 (2013) 394–400.
- [8] G. Zanella, R. Zannoni, R. Dall'igna, P. Polato, M. Bettinelli, Development of a terbium lithium glass for slow neutron detection, *Nucl. Instrum. Methods* 359 (1995) 547–550.
- [9] Xin-Yuan Sun, Pan Gao, Shuai WU, Hong-Shu WU, H.U. Qiang-Lin, Xiang Zhang, Yan Huang, Tao Ye, Luminescent properties and energy transfer of Ce³⁺ activated Li₂O-B₂O₃-Gd₂O₃ scintillating glasses under VUV-UV and X-ray excitation, *Nucl. Instrum. Methods Phys. Res. B* 350 (2015) 36–40.
- [10] L.H. Cheng, X.P. Li, J.S. Sun, H.Y. Zhong, Y. Tian, J. Wan, Investigation of the luminescence properties of Dy³⁺-doped α-Gd₂(MoO₄)₃ phosphors, *Physica B* 405 (2010) 4457–4461.
- [11] Lokesh Mishra, Anchal Sharma, Amit K. Vishwakarma, Kaushal Jha, M. Jayasimhadri, B.V. Ratnam, Kiwan Jang, A.S. Rao, R.K. Sinha, White light emission and color tenability of dysprosium doped barium silicate glasses, *J. Lumin.* 169 (2016) 121–127.
- [12] S.A. Azizan, S. Hashim, N.A. Razak, M.H.A. Mhareb, Y.S.M. Alajerami, N. Tamchek, Physical and optical properties of Dy³⁺: Li₂O-K₂O-B₂O₃ glasses, *J. Mol. Struct.* 1076 (2014) 20–25.
- [13] C.K. Jayasankar, V. Venkatramu, S. Surendra Babu, P. Babu, Luminescence properties of Dy³⁺ ions in a variety of borate and fluoroborate glasses containing lithium, zinc, and lead, *J. Alloy. Comp.* 374 (2004) 22–26.
- [14] H.H. Xiong, L.F. Shen, E.Y.B. Pun, H. Lin, High-efficiency fluorescence radiation of Dy³⁺ in alkaline earth borate glasses, *J. Lumin.* 153 (2014) 227–232.
- [15] S. Babu, V. Reddy Prasad, D. Rajesh, Y.C. Ratnakaram, Luminescence properties of Dy³⁺ doped different fluoro-phosphate glasses for solid state lighting applications, *J. Mol. Struct.* 1080 (2015) 153–161.
- [16] M. Vijayakumar, K. Marimuthu, Structural and luminescence properties of Dy³⁺ doped Oxyfluoro-borophosphate glasses for lasing materials and white LEDs, *J. Alloy. Comp.* 629 (2015) 230–241.
- [17] F. Zaman, J. Kaewkhao, N. Srisittipokakun, N. Wantana, H.J. Kim, G. Rooh, Investigation of luminescence and laser transition of Dy³⁺ in Li₂O-Gd₂O₃-Bi₂O₃-B₂O₃ glasses, *Opt. Mater.* 55 (2016) 136–144.
- [18] Sk Nayab Rasool, L. Rama Moorthy, C.K. Jayasankar, Optical and luminescence properties of Dy³⁺ ions in phosphate based glasses, *Solid State Sci.* 22 (2013) 82–90.
- [19] Yaser saleh Mustafa Alajerami, Suhairul Hashim, Wan Muhammad Saridan, Wan Hassan, Ahmad Termizi Ramli, Azman Kasim, Optical properties of lithium magnesium borate glasses doped with Dy³⁺ and Sm³⁺ ions, *Physica B* 407 (2012) 2398–2403.
- [20] Raghda Saefi Eddin Said Dawoud, Suhairul Hashim, Yasser Saleh Mustafa Alajerami, M.H.A. Mhareb, N. Tamchek, Optical and structural properties of lithium sodium borate glasses doped Dy³⁺ ions, *J. Mol. Struct.* 1075 (2014) 113–117.
- [21] B. Shanmugavelu, V.V. Ravi Kanth Kumar, Luminescence studies of Dy³⁺ doped bismuth zinc borate glasses, *J. Lumin.* 146 (2014) 358–363.
- [22] Ch Basavapoornima, C.K. Jayasankar, Spectroscopic and photoluminescence properties of Sm³⁺ ions in Pb-K-Al-Na phosphate glasses for efficient visible lasers, *J. Lumin.* 153 (2014) 233–241.
- [23] M. Inokuti, F. Hirayama, Influence of energy transfer by the exchange mechanism on donor luminescence, *J. Chem. Phys.* 43 (1965) 1978.
- [24] Ki-Soo Lim, P. Babu, Sun-Kyun Lee, Van-Thai Pham, D.S. Hamilton, Infrared to visible up-conversion in thulium and holmium doped lutetium aluminum garnet, *J. Lumin.* 102103 (2003) 737–743.
- [25] R. Praveena, R. Vijaya, C.K. Jayasankar, Photoluminescence and energy transfer studies of Dy³⁺-doped fluorophosphate glasses, *Spectrochim. Acta, Part A* 70 (2008) 577–586.
- [26] C.S. McCamy, Correlated color temperature as an explicit function of chromaticity coordinates, *Color Res. Appl.* 17 (2) (1992) 142–144.
- [27] Q. Su, Z. Pei, L. Chi, H. Zhang, Z. Zhang, F. Zou, The yellow-to-blue intensity ratio (Y/B) of Dy³⁺ emission, *J. Alloy. Comp.* 192 (1993) 25.
- [28] Z. Ci, Q. Sun, S. Qin, M. Sun, X. Jiang, X. Zhang, Y. Wang, Warm white light generation from a single phase Dy³⁺ doped Mg₂Al₄Si₆O₁₈ phosphor for white UV-LEDs, *Phys. Chem. Chem. Phys.* 16 (2014) 11597.
- [29] J. Kaewkhao, N. Wantana, S. Kaewjaeng, S. Kothan, H.J. Kim, Luminescence characteristics of Dy³⁺ doped Gd₂O₃-CaO-SiO₂-B₂O₃ scintillating glasses, *J. Rare Earths* 34 (2016) 583–589.
- [30] N. Luewarasirikul, H.J. Kim, P. Meejitpaisan, J. Kaewkhao, White light emission of dysprosium doped lanthanum calcium phosphate oxide and oxyfluoride glasses, *Opt. Mater.* 66 (2017) 559–566.
- [31] E. Kaewnuam, H.J. Kim, J. Kaewkhao, Development of lithium yttrium borate glass doped with Dy³⁺ for laser medium, W-LEDs and scintillation materials applications, *J. Non-Cryst. Solids* 464 (2017) 96–103.
- [32] L. Shamshad, G. Rooh, K. Kirdsiri, N. Srisittipokakun, B. Damdee, H.J. Kim, J. Kaewkhao, Photoluminescence and white light generation behavior of lithium gadolinium silicoborate glasses, *J. Alloy. Comp.* 695 (2017) 2347–2355.