Optical and Luminescence Properties of Trivalent Rare Earth Ion (Sm^{3+}, Dy^{3+}, and Eu^{3+}) doped Glass for Laser Gain Medium Development : A Review

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Abstract –*Recently, development of laser gain medium has been more attractive to be investigated due to the laser application in human daily life. For example, laser is used for medical treatment, surgery, security system, cutting, spectroscopy characterization and sensor. Laser is produced by the system including pump source, resonator, and an optical gain medium. This paper will be focused in a gain medium based on trivalent rare earth ions (Ln^{3+}) such as Dy^{3+}, Sm^{3+}, and Eu^{3+} doped glass. The gain medium is developed by melt and quenching technique. The raw materials are a powder that is melted at the glass transition temperature. Afterwards, the glass liquid is poured at stainless steel at room temperature and annealed for several hours. After the annealing process, the bulk glass is cut and polished for characterization. Physical, optical, and luminescence properties of the gain medium are analyzed and discussed in this paper. The CIE 1931 chromaticity diagram coordinate is calculated to define the proper coordinate of glass sample emission light. The previous research shows that Dy^{3+}, Sm^{3+} and Eu^{3+} in glass system can emit white, orange, and reddish-orange excited by 388 nm, 403 nm and 393 nm, respectively. From the results, trivalent rare earth ion doped glass possesses high potential to be developed for laser gain medium material.*

Keywords: *glass, laser, luminescence, optic, Ln^{3+}*

I. INTRODUCTION

Currently, laser development becomes more popular due to the wide laser applications such as industry, medical, military, scientific, etc. One of important parts of laser is the gain medium that emits light in the range of visible to the infrared region excited by ultraviolet. Nowadays, the popular optical gain medium is based on the crystal as host matrix. Unfortunately, the development of crystal is complicated and high-cost production. Therefore, the available optical gain medium is expensive. Glass is a suitable material to replace crystal as gain medium host. Glasses such as borate, phosphate and tellurite posses low melting point, good thermal stability, mechanical, transmission in the visible to infrared region, high transparency and rare earth (Ln^{3+}) solubility. Each glass posses its own advantages. For example, tellurite glass has lower phonon energy than other glasses and phosphate glass have long lifetime fluorescence. The addition metal alkaline such as Li_2O_3, Gd_2O_3, Bi_2O_3, ZnO, Al_2O_3, and BaO in glass host can improve the chemical and mechanical stability, increase the refractive index, and decrease the melting point [1–4]. Furthermore, Ln^{3+} doped glasses posses wider absorption and emission region than crystal. Ln^{3+} doped glasses have been investigated by [5–7]. The glass sample is developed by melt and quenching technique that is easy preparation and low-cost production. From the results, Ln^{3+} doped glasses can emit visible to infrared region. In this paper will be discussed the physical, optical and luminescence properties of Ln^{3+} (Dy^{3+}, Sm^{3+}, and Eu^{3+}) in various glass systems.

II. METHOD OF RESEARCH/EXPERIMENT

The glass sample was developed by melt and quenching technique [8,9]. The glasses formula and code were presented in Table 1. The batch calculation was used to obtain each component in gram unit. All raw materials were mixed in a crucible and stirred until homogeneity. For Eu^{3+} ion doped phosphate glass was melted at 1100 °C for 1 hours and annealed at 488 °C for 12 hours [1]. Dy^{3+} ion doped borate glass was melted at 1200 °C for 3 hours and annealed at 400 °C for 3 hours [2]. Meanwhile, Sm^{3+} ion doped borate glass was melted at 1100 °C for 3 hours and annealed at 500 °C for 3 hours [3]. After the annealing process, glass samples were cut and polished to characterize including physical, optical and luminescence properties.

Table 1. Composition and code of developed glasses [1–3].

Composition	Code	Ref
$60.5P_2O_5$:$14K_2O$:13.5SrO:11 Al_2O_3:$1Eu_2O_3$	PKSAEu10	[1]
$50Li_2O$: $15Gd_2O_3$: $5Bi_2O_3$: $28.5B_2O_3$: $1.5Dy_2O_3$	LGBiBDy15	[2]
10ZnO: $10Al_2O_3$: 20BaO: $59.7B_2O_3$: $0.3Sm_2O_3$	ZABBSm0.3%	[3]

III. RESULTS AND DISCUSSIONS

A. Physical Properties

Physical properties consist of density and molar volume. The properties show the improvement of glass structure due to the addition of dopant or modifier. The glass density calculates following Archimedes law. The glasses were weighed in the air (w_a) and liquid (w_l). The formula to calculate the glass density (ρ_g) and molar volume (V_M) is expressed in equations

$$\rho_g=(w_a/(w_a-w_l))\ x\ \rho_l\ , \qquad (1)$$

$$V_M=M_T/\ \rho_g\ , \qquad (2)$$

where ρ_l is the density of immersed liquid such as water or xylene, and M_T is defined by equation

$$M_T=X_1Z_1+X_2Z_2+...+X_nZ_n\ , \qquad (3)$$

where X_1, X_2, X_3, ..., X_n are mol fraction of each compound and Z_1, Z_2, Z_3, ..., Z_n is a molecular mass of each compound. Table 2 presents the density of molar volume of Dy^{3+}, Sm^{3+} and Eu^{3+} doped glasses. LGBiBDy15 possesses higher density than ZABBSm0.3% and PKSAEu10 glass. It is indicating that the glass structure of LGBiBDy15 glass is the densest among samples. Meanwhile, the highest of molar volume is own by the PKSAEu10 glass. The molar volume of Sm^{3+} ion doped borate glass increase by the addition of Sm^{3+} ion from 0.5 mol% to 2.5 mol% due to the increasing of NBO intensity in the glass structure [1–3].

Table 2. Density (ρ_g, g/cm^3) and molar volume (V_M, cm^3/mol) of LGBiBDy15, ZABBSm0.3% and PKSAEu10 glasss [1–3].

Glass code	ρ_g	V_M	Ref
PKSAEu10	2.71	47.00	[1]
LGBiBDy15	3.27	36.12	[2]
ZABBSm0.3%	2.72	28.02	[3]

B. Optical Properties

Optical properties of glass sample are obtained from absorption spectra. Fig. 1 shows the absorption spectra of ZABBSm0.3% glass. The absorption spectra were observed under wavelength of 350 nm to 1800 nm. Several absorption bands rise from $^6H_{5/2}$ level to $^6P_{7/2}$, $^4I_{13/2}$, $^6F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$, $^6F_{1/2}$, and $^6H_{13/2}$ levels. These transitions are centred at 398 nm, 477 nm, 947 nm, 1080 nm, 1227 nm, 1375 nm, 1477 nm, 1526 nm and 1584 nm, respectively. The hypersensitive transition occurs at $^6H_{5/2}\rightarrow{}^6P_{7/2}$ transition (398 nm) and $^6H_{5/2}\rightarrow{}^6F_{7/2}$ transition (1227 nm) for ultraviolet and near-infrared region, respectively [3]. These transitions are quite similar to other reported Sm^{3+}:glasses [10,11].

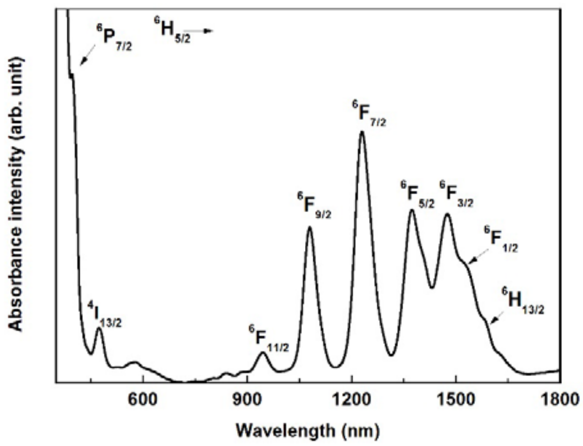


Fig 1. Absorption spectrum of ZABBSm0.3% glass from ultraviolet to infrared region [3].

Kesavulu *et al.* investigated the absorption spectra of LGBiBDy15 glass is measured under wavelength of 200 nm to 1800 nm. The band absorptions appear at 452 nm, 751 nm, 799 nm, 896 nm, 1086 nm, 1266 nm and 1671 nm. The wavelengths belong to transition from ground state level $^6H_{15/2}$ to $^4I_{15/2}$, $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$, $^6F_{11/2}+{}^6H_{9/2}$ and $^6H_{11/2}$ level. The strongest absorption band is centred at 1266 nm due to $^6H_{15/2}\rightarrow{}^6F_{11/2}+{}^6H_{9/2}$ transition [2,12]. This transition is called hypersensitive transition and depends on the environment around rare earth ion in the glass system [13].

Fig. 2 is the absorption spectra of 1 mol% Eu^{3+} ion doped phosphate glass (PKSAEu10). The band absorptions of PKSAEu10 glass are 362 nm, 376 nm, 382 nm, 393 nm, 400 nm, 415 nm, 464 nm, 526 nm and 533 nm. These wavelengths are corresponded by transitions of $^7F_0\rightarrow(^5D_4,\ ^5G_3,\ ^5G_2,\ ^5L_6)$, $^7F_1\rightarrow(^5L_6,{}^5D_3)$, $^7F_0\rightarrow(^5D_2,\ ^5D_1)$ and $^7F_1\rightarrow{}^5D_1$ respectively. The hypersensitive transition is produced by $^7F_0\rightarrow{}^5L_6$ transition centred at 393 nm. For infrared region, PKSAEu10 glass absorbs the wavelength of 2209 nm and 2085 nm due $^7F_0\rightarrow{}^7F_6$ and $^7F_1\rightarrow{}^7F_6$ transition [1,8].

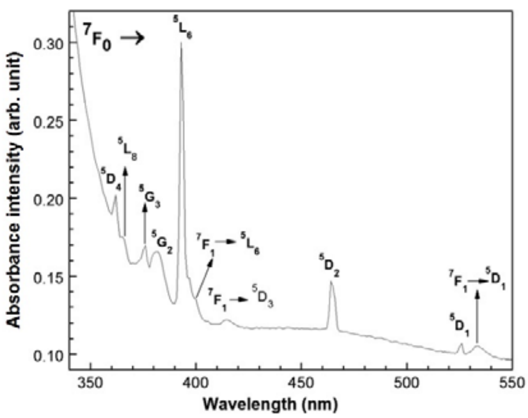
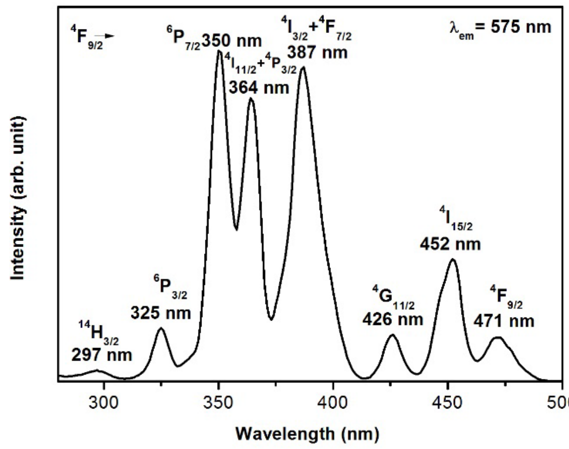


Fig 2. Absorption spectrum of PKSAEu10 in ultraviolet to the visible region with $^7F_0\rightarrow{}^5L_6$ hypersensitive transition [1].

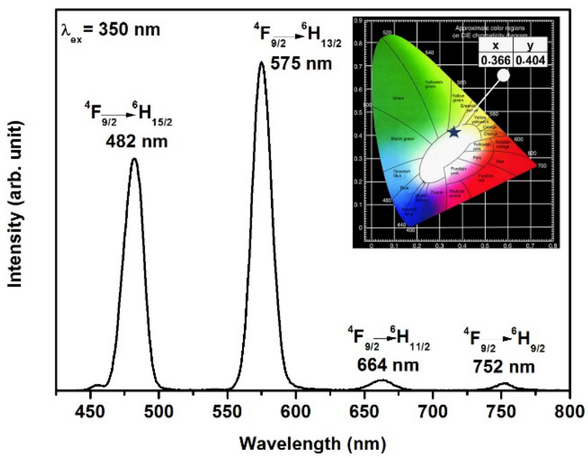
C. Photoluminescence Properties

Photoluminescence properties consist of excitation and emission spectra. Fig. 3(a) shows the excitation spectra of borate glass doped 0.5 mol% Dy^{3+} ion that was developed by Djamal, et al. Excitation spectra were measured in the range of 250 to 500 nm with λ_{em} = 575 nm. Several peaks occur due to transition from $4F_{9/2}$ to $^{14}H_{3/2}$, $^6P_{3/2}$, $^6P_{7/2}$, $^4I_{11/2}$+$^4P_{3/2}$, $^4I_{3/2}$+$^4F_{7/2}$, $^4G_{11/2}$ and $^4I_{15/2}$ level. These transitions are correlated by wavelengths such as 297 nm, 325 nm, 350 nm, 364 nm, 387 nm, 426 nm, 452 nm and 471 nm, respectively. The strongest emission was generated from $^4F_{9/2} \rightarrow {}^6P_{7/2}$ transition centred at 350 nm. This wavelength can be utilized to excite the glass sample. Fig. 3(b) presents the emission spectra. The glass sample produces several transitions originated from $^4F_{9/2}$ level and leads to $^6H_{15/2}$ (482 nm), $^6H_{13/2}$ (575 nm), $^6H_{11/2}$ (664 nm) and $^6H_{9/2}$ (752 nm). The $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition yield emission in the blue and yellow region. The combination of two colours generates a white colour that is proved by the colour coordinate of CIE 1931 chromaticity. The colour coordinate of glass sample is x = 0.366 and y = 0.404 that is lied down at white region [5]. Therefore, borate glass doped 0.5 mol% Dy^{3+} ion is a suitable material for the gain medium of WLED or white laser. It is well known that white colour of semiconductor LED is obtained from several materials with a different bandgap that produces red, green and blue colour (RGB). However, the glasses only doped by a Dy^{3+} ion is capable to generate white colour.

On the other hand, several transitions occur in the excitation spectra of ZABBSm0.3% with λ_{em} = 598 nm. The transitions are originated from $^6H_{5/2}$ level to $^4I_{9/2}$, $^4D_{3/2}$, $^6P_{7/2}$, $^4L_{13/2}$, $^6P_{5/2}$, $^4M_{17/2}$ and $^4I_{13/2}$+ $^4M_{15/2}$+ $^4I_{11/2}$ level centred at 344 nm, 361 nm, 374 nm, 401 nm, 416 nm, 439 nm and 476–561 nm, respectively. The strongest intensity of excitation spectra come from 401 nm ($^6H_{5/2} \rightarrow {}^4L_{13/2}$). Meanwhile, the emission spectra under λ_{ex} = 402 nm lead the transition from $^4G_{5/2}$ level to $^6H_{5/2}$ (561 nm), $^6H_{7/2}$ (597 nm), $^6H_{9/2}$ (644 nm) and $^6H_{11/12}$ (706 nm). The strongest emission intensity is produced by $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition centred at 507 nm. The CIE 1931 chromaticity coordinate of ZABBSm0.3% is 0.593 and 0.407 for x and y-axis, respectively. The coordinate is fallen down at orange region [3]. Therefore, glass doped Sm^{3+} ion is a potential material for orange emitting devices application.

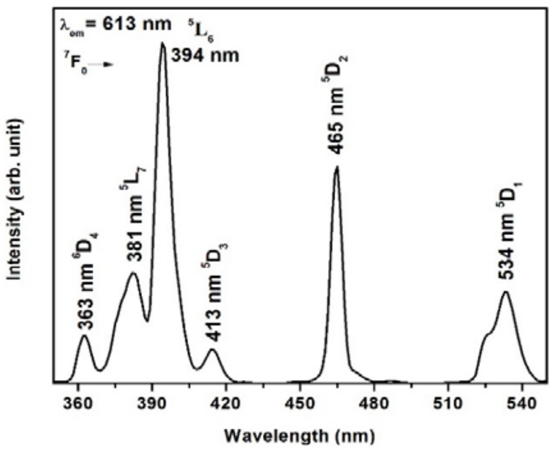


(a)

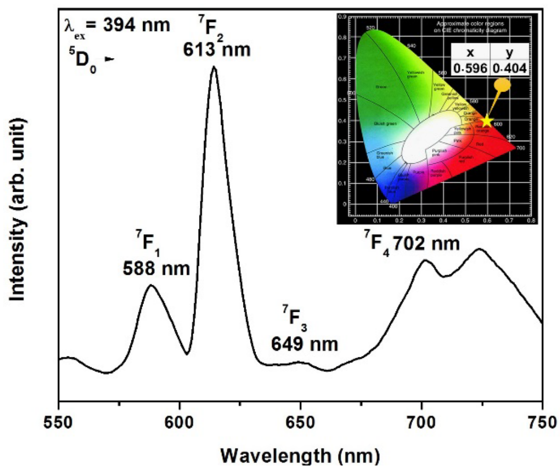


(b)

Fig 3. Photoluminescence properties of borate glass doped 0.5 mol% Dy^{3+} ion : (a) excitation spectra under λ_{em} = 575 nm and (b) emission spectra under λ_{ex} = 350 nm and CIE 1931 chromaticity of inset graph [5].



(a)



(b)

Fig 4. Photoluminescence of oxyfluoride boro-tellurite glass doped 1.5 mol% Eu^{3+} ion : (a) excitation spectra under λ_{em} = 613 nm and (b) emission spectra excited by λ_{ex} = 394 nm with CIE 1931 chromaticity coordinate [4].

Excitation spectra of oxyfluoride boro-tellurite glass doped 1.5 mol% Eu^{3+} ion is presented in Fig. 4(a). The excitation spectra with λ_{em} = 613 nm were measured in the range of 345 nm – 555 nm. The electrons originated from ground state $^7F_0$ to $^6D_4$ (363 nm), $^5L_7$ (381 nm), $^5L_6$ (394 nm), $^5D_3$ (413 nm), $^5D_2$ (465 nm) and $^5D_1$ state (534 nm) are represented in Fig. 4(a). The highest peak of excitation spectra come from $^7F_0 \rightarrow ^5L_6$ transition centred at 394 nm. Fig. 4(b) shows the emission spectra of Eu^{3+} ion in oxyfluoride boro-tellurite glass with λ_{ex} = 394 nm. The electrons from metastable level $^5D_0$ pull down to $^7F_1$, $^7F_2$, $^7F_3$ and $^7F_4$ level. The transitions generate emission in the wavelength of 588 nm (orange), 613 nm (red), 649 nm (deep red) and 702 nm (deep red), respectively. The strongest emission is generated by $^5D_0 \rightarrow ^7F_2$ transition centred at 613 nm. The color coordinate of CIE 1931 chromaticity of glass doped Eu^{3+} ion is fall down in reddish-orange region (x = 0.596 and y = 0.404) [4]. Kiran, *et al*. was developed Eu^{3+} ion in borophosphate glass. The glass sample was excited by λ_{ex} = 385 nm. The glass produces red emission with coordinate of 0.577 and y = 0.373 [14]. This is indicating that the emission coordinate depends on the glass host and excitation wavelength.

IV. CONCLUSIONS

Laser gain medium based on glass doped trivalent rare earth ions such as LGBiBDy15, ZABBSm0.3%, and PKSAEu10 is developed by melt and quenching technique. The density pattern of glass sample is LGBiBDy15>ZABBSm0.3%>PKSAEu10. This indicates that LGBiBDy15 glass has the highest density among glass samples. The optical and photoluminescence of glass samples can be seen in Table 3.

Table 3. The highest absorption bands (λ, nm), the excitation (λ_{ex}, nm), emission wavelength (λ_{em}, nm) and colour of glass samples.

Dopant	λ	λ_{ex}	λ_{em}	Emission color
Dy^{3+}	398	388	575	White
Sm^{3+}	452	403	598	Orange
Eu^{3+}	393	393	609	Reddish-orange/red

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