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Eu^{3+}doped Borosilicate Glass for Solid-State Luminescence Material

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Abstract

The Eu^{3+} doped potassium borosilicate (KBSi:Eu^{3+}) glasses were prepared by the melt quenching technique. The physical, optical and luminescence properties of glasses were investigated. Glass density and molar volume increase with increasing of Eu_2O_3 concentration. Glasses absorbed photons in the visible light and near infrared region. Since 394 nm excitation, glasses emitted the strong light with 613 nm in milliseconds of lifetime. CIE 1931 chromaticity diagram exhibits that emission from KBSi:Eu^{3+} glass is reddish-orange light. In summary, this KBSiEu glass performs the interesting property for using in the photonic devices such as solid-state laser and LEDs.

Keywords: Borosilicate glass; Europium; Photoluminescence.

Introduction

Rare earth (RE) -doped glasses are interesting materials for optical devices such as display devices, fiber amplifiers, ultraviolet (UV) detectors and lasers. Among the rare earth elements, europium (Eu) is a special element as used dopant ion, because it shows the property of valence fluctuation such as the valence state is divalent or trivalent.(1-3) Therefore, it shows different characteristics of luminescence. Trivalent europium have been of strong interest for photo-conversion due to the $4f^6$ electronic configuration of Eu^{3+} which results to the characteristic red photoluminescence (PL) with high quantum efficiency.(3) From publication papers, the PL spectrum of Eu^{3+} usually exhibits a variety of sharp PL lines in the orange to red spectral region occurring from the $^5D_0$ to the ground levels transitions.(1-4) Eu^{3+} doped materials are important for light emitting diodes (LEDs), solid-state laser, scintillators and plasma display panels.(1-3) Borosilicate glasses perform the low melting temperature, low coefficients of thermal expansion and can be used in the relatively high temperatures.(5) Adding potassium into glass network, it can improve chemical and electrical resistance of glass material.(6)

In this paper, we report the physical, optical and luminescence properties of Eu^{3+} doped potassium borosilicate glasses with different Eu^{3+} concentrations (0.05, 0.10, 0.50, 1.00 and 1.50 mol%).

Experimental

The potassium borosilicate glasses doped with europium ions of 25 K_2O:10 SiO_2: (65-x) B_2O_3:x Eu_2O_3 (where is x = 0.05, 0.10, 0.50, 1.00 and 1.50 mol%) composition were synthesized by melt quenching technique. High purity starting materials K_2CO_3 (Potassium carbonate), SiO_2 (Silicon dioxide), H_3BO_3 (Boric acid) and Eu_2O_3 were used. In the first step, 15 g batches of homogeneously mixed host composition were melted at temperature of 1,200 °C for 3 h in alumina crucibles. The obtained glasses were annealed at 500 °C for 3 hours to relieve thermal stresses and strains. Finally, the glass samples were cut and then finely polished in order to study their properties. The densities (ρ) were measured by Archimedes's principle, glasses were weighted in air and water as an immersion liquid using a 4-digit sensitive microbalance (AND, HR 200).

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After that the molar volumes (V_m) were calculated from relation $V_m = M_T/\rho$ where M_T is total molecular weight of composition. The UV-VIS-NIR absorption spectra of glass samples were measured using UV-VIS-NIR spectrometer (Shimadzu, UV3600) in the range 200-2,500 nm. The emission, excitation and lifetime were measured using by a fluorescence spectrophotometer (Cary eclipse) with xenon lamp as a light source.

Results and discussion

The density of glasses tends to increase with increasing of Eu_2O_3 concentration, as shown in Figure 1. The Eu_2O_3 addition in glass network, it replaced borate and the molecular weight of Eu_2O_3 is 351.93 g/mol while that of B_2O_3 is 69.62 g/mol. The increased density of the samples is due to higher molecular weight of europium than any other component of the given glass system. The molar volume of BiBSi:Eu^{3+} glasses tend to increase with increasing of Eu_2O_3 doped concentration, as shown in Figure 2.

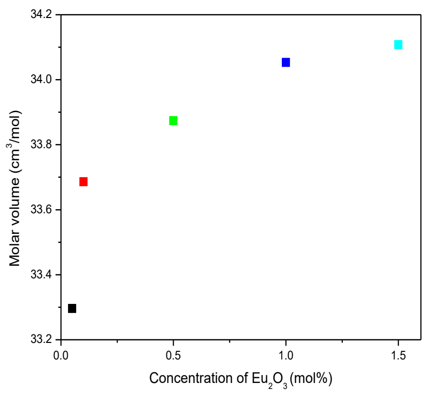

Figure 1. Densities of the KBSi: Eu^{3+} glasses

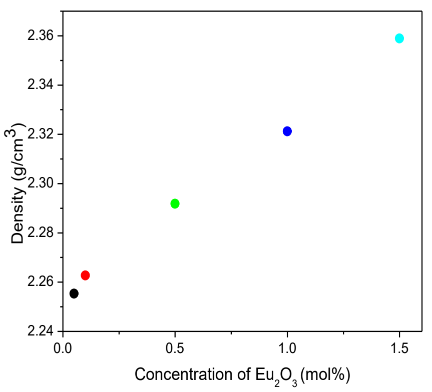

Figure 2. Molar volume of the KBSi: Eu^{3+} glasses.

This can be explained that Eu^{3+} destroy the bridges that connect oxygen ions and generate non-bridging oxygen (NBOs) increasing in network glass. These NBOs produce interstitial space and decrease the concentration of borate units. Therefore, the resulting network gets loose and the connectivity of borate network decreases. The gradual increase in the molar volume can be attributed to opening up of glass structure.

Figure 3(a) and 3(b) presents the absorption spectra of KBSi:Eu^{3+} glasses were recorded in 200-2,500 nm wavelength, glasses absorb light in visible light and near infrared region which originating from the $^7F_0$ and $^7F_1$ to higher energy level. In visible light region, glasses absorbed photon with 362, 379, 394 and 465 nm wavelength, which causes energy transitions $^7F_0 \rightarrow {}^5D_4$, $^7F_0 \rightarrow {}^5G_2$, $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5D_2$ transitions, respectively.[1-4] The absorption bands at 2,094 and 2,211 nm of photon which represents a change in energy levels $^7F_0 \rightarrow {}^7F_6$ and $^7F_1 \rightarrow {}^7F_6$, respectively.[1-4] The absorption intensity increase with the increase in Eu_2O_3 concentrations and the most prominent absorption of Eu_2O_3 ion is 394 nm, which is located in VIS region.

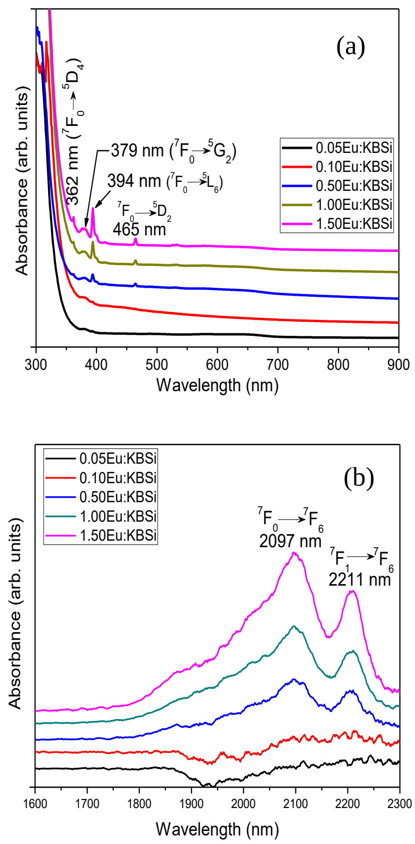

Figure 3. The Absorption spectra of the KBSi:Eu^{3+} glasses.

The excitation spectra of KBSi:Eu^{3+} glasses have been recorded by selecting emission wavelength as 613 nm as shown in Figure 5. From the excitation spectra, seven bands were observed at 362, 381, 394, 414, 464, 525 and 532 nm assigned to the $^7F_0 \rightarrow {}^5D_4$, $^7F_0 \rightarrow {}^5G_2$, $^7F_0 \rightarrow {}^5L_6$, $^7F_1 \rightarrow {}^5D_3$, $^7F_0 \rightarrow {}^5D_2$, $^7F_0 \rightarrow {}^5D_1$ and $^7F_1 \rightarrow {}^5D_2$ transitions, respectively.(1-4) The band at 394 nm wavelength exhibited the highest excitation in visible light. This wavelength then was selected to excite glasses for study the emission spectra as shown in Figure 4. The emission spectra of KBSi:Eu^{3+} glasses in the range of 500 to 750 nm as shown in the Figure 5.

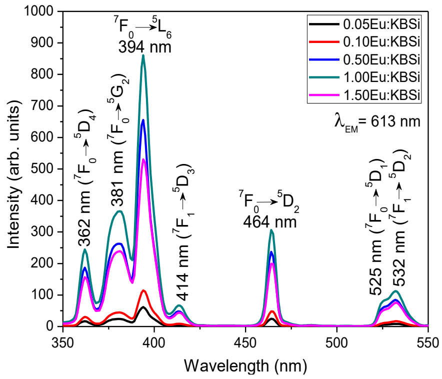

Figure 4. Excitation spectra of KBSi:Eu^{3+} glasses in the range of 350 to 550 nm.

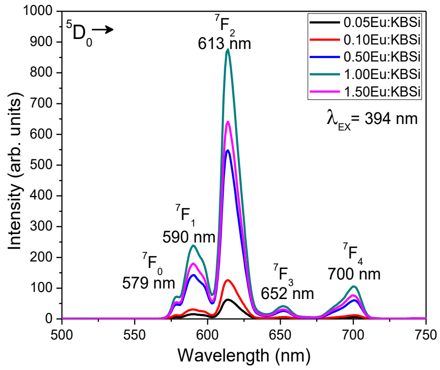

Figure 5. Emission spectra of KBSi:Eu^{3+} glasses in the range of 500 to 750 nm.

These spectra show five emission bands at 579, 590, 613, 652 and 700 nm representing the energy transitions from $^5D_0$ to $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$ and $^7F_4$, respectively.(1-4) Furthermore, the strongest band center at 613 nm and the intensity of emission spectra increase up to 1.00 mol% Eu_2O_3 concentration and then decrease (Figure 6). This result due to the concentration quenching effect of Eu_2O_3 in KBSi glass, the neighbor Eu^{3+} ion reabsorbed the emitting photon if the amount of Eu^{3+} were high over the optimum doped concentration. The energy level diagram for excitation and emission spectra of Eu^{3+} ion in KBSi glasses is shown in Figure 7. The experimental lifetime of KBSi:Eu^{3+} glasses were recorded at room temperature under excitation and emission wavelength 394 and 613 nm, respectively as shown in Figure 8. The lifetime increase from 2.077 to 2.258 ms with increasing concentration of Eu_2O_3 due to the decrease in symmetry around Eu^{3+} ion.(7)

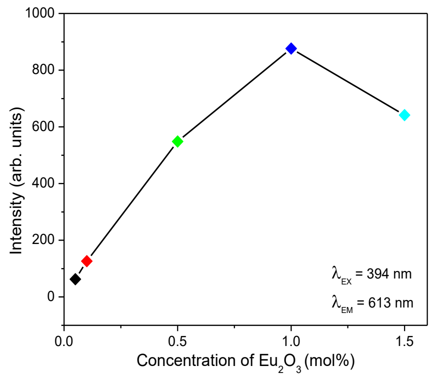

Figure 6. Relationship between the intensity of emission at 613 nm wavelength by excited 394 nm with the concentration of Eu_2O_3.

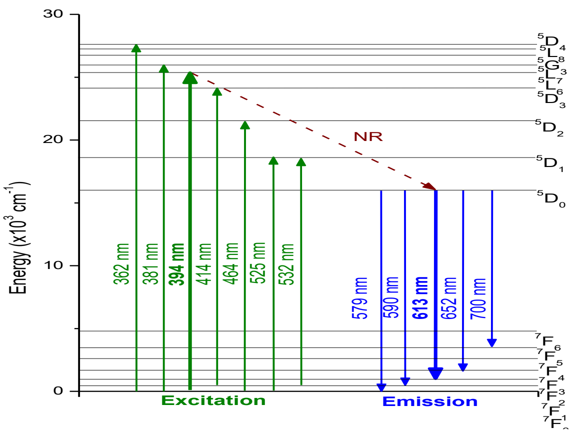

Figure 7. Energy level diagrams of Eu^{3+} doped KBSi glasses.

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The CIE 1931 chromaticity, which indicate the chromaticity visible to the human eye, was used to analyze color of glass emission. The emission spectra with 394 nm excitation wavelength of Eu^{3+} doped glasses were selected to monitor the color. The CIE color coordinates (x, y) of glasses with all Eu_2O_3 concentration are shows similarly at (0.64, 0.35). It was plotted at the edge of reddish orange region in color diagram as show in Figure 9. Therefore, it can be said that KBSi:Eu^{3+} glass can emit the light with reddish orange region color via 394 nm excitation

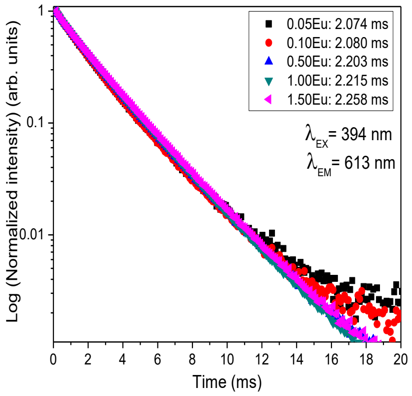

Figure 8. Lifetime of the KBSi:Eu^{3+} glasses.

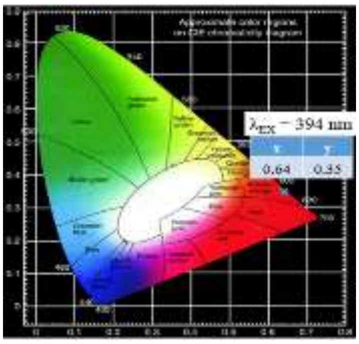

Figure 9. The CIE chromaticity diagram with 394 nm excitation of KBSi:Eu^{3+} glasses.

Conclusion

The Eu^{3+} doped potassium borosilicate (KBSi:Eu^{3+}) glasses were prepared by the melt quenching technique. The Density and molar volume of glasses tend to increase with increasing of Eu_2O_3 concentrations. Glass samples absorbed photon in visible light and near infrared region. Glass show the strongest emission with 613 nm wavelength ($^5D_0 \rightarrow {}^7F_2$ of Eu^{3+}) via 394 nm excitation. The optimum doped concentration of Eu_2O_3 in this glass is 1.0 mol% which results to the highest intensity of emission. The color of emission is reddish-orange. Luminescence decay time of glasses increases from 2.074 to 2.254 ms with more amount of Eu^{3+} in glass. Therefore, the KBSi:Eu^{3+} glasses performs the interesting property for using in the photonic devices.

Acknowledgements

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References

1. Guojun, G., Jingxue, W., Yang S., Mingying, P. and Lothar, W. (2014). Heavily Eu_2O_3-doped yttria-aluminoborate glasses for red photo conversion with a high quantum yield: luminescence quenching and statistics of cluster formation *Journal of Materials Chemistry C*. **2:** 8678-8682.

2. Saraf, R., Shivakumara, C., Behera, S., Nagabhushana, H. and Dhananjaya, N. (2015). Photoluminescence, photocatalysis and Judd-Ofelt analysis of Eu^{3+}-activated layered BiOCl phosphors. *RSC Advances*. **5:** 4109-4120.

3. Vijaya K., Jamalaiah M.V., Rama, B.C., Gopal, K. and Reddy, R.R. (2011). Novel Eu^{3+}-doped lead telluroborate glasses for red laser source applications. *Journal of Solid State Chemistry*. **184:** 2145-2149.

4. Ivankov, A., Seekamp, J., Bauhofer, W. (2006). Optical properties of Eu^{3+}-doped zinc borate glasses. *Journal of Luminescence*. **121:** 123-131.

5. Wantana, N., Kaewjaeng, S., Kothan, S., Kim, H.J. and Kaewkhao, J.. (2017). Energy transfer from Gd^{3+} to Sm^{3+} and luminescence characteristics of $CaO–Gd_2O_3–SiO_2–B_2O_3$ scintillating glasses. *Journal of Luminescence*. **181:** 382-386.

6. Hugo R.F., Dilshat U.T., Maria J.P., Vladislav V. K., Aleksey A. Y. and José M.F.F. 2012. The role of K_2O on sintering and crystallization of glass powder compacts in the Li_2O-K_2O-Al_2O_3-SiO_2 system. *Journal of the European Ceramic Society*. **32:** 2283-2292.

7. Kesavulu C.R., Kiran Kumar, K., Vijaya, N., Lim, K.S and Jayasankar, C.K. 2013. Thermal, vibrational and optical properties of Eu^{3+}-doped lead fluorophosphate glasses for red laser applications. *Materials Chemistry and Physics*. **141:** 903-911.