Luminescence properties of Sm^{3+} -doped borosilicate glasses

N. Srisittipokakun^{a,b*}, J. Kaewkhao^{a,b}

^aCenter of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand

^bPhysics Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, Nakhon Pathom, 73000, Thailand

*Corresponding Author: nattapon2004@gmail.com

Abstract

The spectroscopic characterization of borosilicate glasses doped with Sm^{3+} have been developed by melt quenching technique and investigated by using absorption spectra, excitation spectra, emission spectra and CIE chromaticity diagram analysis. From absorption spectra the most intense and hyper sensitive transition is $^6\text{H}_{5/2} \rightarrow ^6\text{P}_{3/2}$ at 403 nm. From photoluminescence emission spectra at excitation wavelength 403 nm, four prominent emission peaks were observed at 563, 600, 647 and 709 nm. For Sm^{3+} ion the quenching point were observed at 0.5 mol% of borosilicate glasses. The measured color coordinates for the prepared glass matrix fall in the orange region of the CIE diagram.

Keywords: Luminescence, borosilicate glasses, Sm^{3+}

1. Introduction

The luminescence properties of the lanthanide ion-doped materials have been hot research topic for decades. The color of the emitted light depends on the lanthanide ion. For instance, Sm^{3+} , Dy^{3+} and Tb^{3+} emit orange, blue and green light, while Pr^{3+} ion can emit different colored light depending on the concentration of RE ions as well as surrounding environment [1,2]. This characteristic of lanthanide ions makes it very attractive for synthesizing various kinds of functional materials for application in outdoor devices, fabrication of light emitting diodes, scintillators, lasers, telecommunications, optical fiber cables, solar concentrators, optical detectors such as and the production of wide variety of optical components (as windows, prisms, beam splitters, etc.) [1,3]. Moreover, it has $4f_5$ electronic configuration which exhibits orange-red

fluorescence in the visible region with strong fluorescence intensity, large emission cross-section and high quantum efficiency. Further, the Sm^{3+} ion is well suited to analyze the energy transfer processes, since its emitting $^4\text{G}_{5/2}$ level has comparatively high quantum efficiency and shows different quenching channels. The luminescence intensity of Sm^{3+} ion depends on the concentration of RE ions as well as surrounding environment [4-8].

The aim of the present work is to develop borosilicate glasses doped with Sm^{3+} and investigate their luminescence properties through absorption, photoluminescence (PL) and CIE chromaticity diagram for different application in the solid state lighting field.

2. Experimental procedure

2.1 Glass composition

Glass with composition of $(40-x)\text{SiO}_2 : 10\text{B}_2\text{O}_3 : 25\text{Na}_2\text{O} : 8\text{CaO} : 5\text{ZrO} : 1\text{Bi}_2\text{O}_3 : 0.5\text{TiO}_2 : 0.5\text{Al}_2\text{O}_3 : 10\text{BaO} : x\text{Sm}_2\text{O}_3$ mol% (where $x = 0.0, 0.5, 1.0, 1.5, 2.0$ and 2.5 mol% labeled as Sm0.0, Sm0.5, Sm1.0, Sm1.5, Sm2.0 and Sm2.5, respectively) were prepared by melt-quenching method. The starting raw materials were obtained from Sigma Aldrich and Fluka having purity of 99.99%. B_2O_3 and Na_2O were introduced from H_3BO_3 and Na_2CO_3 while SiO_2 , CaO , ZrO , Bi_2O_3 , TiO_2 , Al_2O_3 , BaO and Sm_2O_3 powders were used as starting materials. All the raw materials were analytical purity. The batches of 30 g were mixed homogeneously then melted in a furnace at $1,200^\circ\text{C}$ for 3 hr in a covered alumina crucible. The melts were poured on to a steel plate and annealed in a muffle furnace at 600°C for 3 hr to release the inner stress and then cooled to room temperature slowly. Finally, samples were surface polished for luminescent measurements. The photographs

of the cut and polished prepared glass samples were shown

in Figure. 1.

Fig. 1. Photograph of Sm³⁺-doped borosilicate glasses

2.2 Instrumentation and parameters

In the present work, the X-ray diffraction were used to determine amorphous nature of our prepared samples. For the best result the samples were prepared in powder forms and analyzed based on the scattering diffraction of the incident X-ray. A Shimadzu Diffractometer XRD-6100 equipped with diffraction software analysis and provides with Cu radiation was operated at 40kV, 30mA at room temperature. The diffractograms were calibrated to measure in the range of 2 θ from 10° to 80°, in steps of 0.02° and 1 s counting time per step and speed of 5°/min. The density of our sample were determined by using Archimedes method Eq. (1). Water was selected as an immersive fluid. For all samples, the measurement was done at room temperature and repeated three times to reduce the error.

$$\rho = \frac{W_a}{W_a - W_b} \times \rho_b \quad (1)$$

where W_a and W_b is the weight of glass in air and water, respectively, and ρ_b is the density of water at room temperature (27°C), which is 1g/cm³. All weight measurements were used a sensitive microbalance. Consequently, the molar volumes of the glass samples were calculated based on the density values according to the following equation:

$$V_m = \frac{M_T}{\rho} \quad (2)$$

where, V_m is the molar volume, M_T is the total molecular weight and ρ is the calculated density of the glass.

The refractive index were measured by using an Abbe refractometer (ATAGO) with a sodium vapor lamp as the light source emitting the light at a wavelength (λ) of 589.3 nm (D line) and having mono-bromonaphthalene as the contact layer between the sample and prism of the refractometer. The visible and near ultraviolet region were determine by using bulk form of the samples. Shimadzu 3600 UV-VIS-NIR spectrophotometer was used in the

range of 200–1800 nm to find the absorption spectra of each sample at room temperature. The spectrophotometer results were revealed at the range 200–1800 nm, double monochromatic diffraction grating system and photomultiplier detector with resolution about 0.1 nm. The absorption peaks and band assignments will be obtained from the absorption spectra of each sample. The photo luminescence spectra was determent by using Perkin Elmer LS55 Luminescence Spectrophotometer. The samples were excited with a xenon discharge lamp (200 < λ < 300 nm).

3. Results and discussion

The X-ray diffraction (XRD) pattern of (40-x)SiO₂ : 10B₂O₃: 25Na₂O: 8CaO: 5ZrO: 1Bi₂O₃: 0.5TiO₂: 0.5Al₂O₃: 10BaO: xSm₂O₃ mol% (where x = 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 mol% are shown in Figure. 2. The XRD spectra show no sharp peak appeared at two theta (2 θ), which confirmed the amorphous nature of our samples. Figure 3 shows the density values of Sm³⁺-doped borosilicate glasses. The densities decreased from 3.2250 to 3.1048 g/cm³ with concentration of Sm³⁺ ion. The molar volume, on the other hand, show an opposite trend in which increase with concentration of Sm³⁺ ion are show in Figure 4. From the results indicate that Sm³⁺ ion concentration increases and oxygen packing density decreases. The decreases in oxygen packing density may cause an increase of molar volume, which in turn decreases the mass density of glass samples. The increase in molar volume is due to the increasing of number of non-bridging oxygens (NBOs), which as a result breaks the bonds and loosely packed structure.

Figure 5 shows the variation of refractive index with concentration of Sm³⁺ ion in borosilicate glass samples. The refractive index values decrease linearly with concentration of Sm³⁺ ion, it is because of the decreasing density of the prepared glass samples. According to the classical dielectric theory, the refractive index depends on density and on polarizability of the atom in a given materials [7]. When the density of the developed glass samples decreases the

structure of the glass will be do not compact and velocity of refractive index decreases. light in this material are not changed which cause the

Fig. 2. XRD spectra of Sm^{3+} -doped borosilicate glasses.

Fig. 3. Variation of density of Sm^{3+} -doped borosilicate glasses.

Fig. 4. Variation of molar volume of Sm^{3+} -doped borosilicate glasses.

Fig. 5. Refractive index of borosilicate glasses doped with Sm³⁺.

Fig. 6. The optical absorption spectra of Sm³⁺-doped borosilicate glasses in the (a) ultraviolet–visible and (b) near infrared regions

The optical absorption spectra of Sm³⁺-doped borosilicate glass measured at room temperature in the ultraviolet–visible (UV–VIS) and near infrared (NIR) regions show in Figure 6. There are eight discrete absorption bands observed due to transitions from the ⁶H_{5/2} level to the various excited states of Sm³⁺ ion. The observed absorption bands in the present Sm³⁺-doped borosilicate glass are centered at 403, 479, 942, 1081, 1229, 1377, 1486 and 1534 nm which are assigned to ⁴L_{13/2} + ⁴F_{7/2} + ⁶P_{3/2}, ⁴I_{11/2} + ⁴M_{15/2} + ⁴I_{9/2}, ⁶F_{11/2}, ⁶F_{9/2}, ⁶F_{7/2}, ⁶F_{5/2}, ⁶F_{3/2} and ⁶H_{15/2}

energy levels, respectively. These absorption spectra were assigned by comparing the band positions in the absorption spectra with those reported in previous the literature [9]. The transition at ⁴L_{13/2} + ⁴F_{7/2} + ⁶P_{3/2} (403 nm) is the most intense and hyper sensitive absorption transition.

For measurement of the luminescence spectra of prepared glass samples it will be important to know the excitation wavelength of the Sm³⁺ ions. Figure. 7 shows the excitation spectra from 300 to 550 nm for all borosilicate glass doped with Sm³⁺ at emission wavelength 600 nm.

From the excitation spectrum, three excitation peaks at wavelength 344, 362, 375, 389, 403, 416, 437, 449, 471, 487, 500 and 528 nm assigned to $^4D_{7/2}+^4H_{9/2}$, $^4D_{3/2}$, $^4D_{1/2}+^6P_{7/2}$, $^4L_{15/2}$, $^6P_{3/2}$, $^4M_{17/2}$, $^4G_{9/2}$, $^4F_{5/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4G_{7/2}$ and $^4F_{3/2}$ respectively [8]. From all these transitions,

transition at $^3H_4 \rightarrow ^3P_2$ at wavelength 403 nm has shown the more intensity and has been used as an excitation wavelength for measuring the emission spectra of Sm^{3+} -doped borosilicate glasses.

Fig. 7. Photoluminescence Excitation spectra of Sm_2O_3 glasses.

Fig. 8. Emission spectra of Sm^{3+} -doped borosilicate glasses excited at $\lambda_{ex} = 403$ nm.

The emission spectrum of Sm^{3+} -doped borosilicate glass measured at room temperature is shown in Fig. 8. The emission spectra was recorded in the range 500–800 nm, after excitation at wavelength 403 nm. The glass showed orange emission when illuminated by near UV light/black light. The orange emission in the present work results from a mixture of four emissions lines located at 563, 600, 647 and 709 nm, instead of a monochromatic color having a single peak in the spectrum. The emission spectra are contributed from the intra 4f orbitals transition from $^4G_{5/2}$

level to the $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$ levels of Sm^{3+} ion, respectively as shown in Fig. 9 [10-13]. Out of these emissions, the emission line located at 600 nm ($^4G_{5/2} \rightarrow ^6H_{7/2}$) is the most intense. Particularly, the emission lines located at 600, 647 and 709 nm are the most important emissions because these are located at the longer wavelength region of the spectrum. From Fig. 8. it is also observed that emission quenching has been occurred at 0.5 mol% for all the observed bands.

Fig. 9. Partial energy levels diagram of Sm^{3+} -doped borosilicate glasses showing excitation, emission and cross relaxation channels

Fig. 10. 1931 CIE chromaticity diagram (adopted relaxation from Gage et al. 1977)

The chromaticity diagram of the Commission International de l'Eclairage (CIE) indicates that coordinates are highly useful in determining the exact emission color and color purity of a sample. Thus, the CIE chromaticity coordinates for Sm^{3+} -doped borosilicate glass were calculated from the PL spectra under 403 nm excitation and marked with a white circle in the CIE 1931 chromaticity diagram in Fig. 10. The chromaticity coordinates (x, y) of these glass samples are located in the orange region. The quality of light emitted is represented by the color correlated temperature (CCT), which is calculated by using McCamy empirical formula and is given by ^[14].

$$\text{CCT} = -437n^3 + 3601n^2 - 6861n + 5514.31 \quad (1)$$

Where, $n = (x - x_e)/(y - y_e)$ and the chromaticity epicenter is at $x_e = 0.5952$ and $y_e = 0.4034$.

4. Conclusions

In summary, the Sm^{3+} -doped borosilicate glasses have been prepared for different applications in solid state lighting by melt quenching technique and characterized by using absorption, photoluminescence and CIE chromaticity

diagram were analyzed. The absorption spectra showed eight absorption band with hypersensitive transition corresponding to $^6P_{3/2}$ at 403 nm. The excitation spectra showed that the developed glasses could be effectively excited by UV-light. The emission spectra showed four emission peaks at 563, 600, 647 and 709 nm for borosilicate glasses. From CIE chromaticity diagram the color coordinates of Sm^{3+} -doped borosilicate glasses fall in the orange light region.

Acknowledgment

The authors would like to thank Center of Excellence in Glass Technology and Material Science, Nakhon Pathom Rajabhat University, for instrumentation and facilities.

References

- (1) Feng Tao, Congrong Hu, Zhijun Wang, Geng Zhu, Yufeng Sun and Da Shu: "Hydrothermal synthesis and luminescence properties of $\text{YF}_3:\text{Ln}$ (Ln=Sm, Dy, Tb and Pr) nano-/microcrystals", *Ceramics International*, Vol. 39, pp. 4089–4098, 2013
- (2) Abu Zayed Mohammad Saliur Rahman, Xingzhong Cao, Long Wei, Baoyi Wang and Haichen Wu: "Luminescence properties of samarium-doped $\text{SiO}_2\text{--Na}_2\text{SO}_4$ composite", *Materials Letters*, Vol. 99, pp. 142–145, 2013
- (3) G. Venkataiah, C.K. Jayasankar, K. Venkata Krishnaiah, P. Dharmiah and N. Vijaya: "Concentration dependent luminescence properties of Sm^{3+} -ions in tellurite–tungsten–zirconium glasses", *Optical Materials*, Vol. 40, pp. 26–35, 2015
- (4) K. Linganna, Ch. Basavapoornima and C.K. Jayasankar: "Luminescence properties of Sm^{3+} -doped fluorosilicate glasses", *Optics Communications*, Vol. 344, pp. 100–105, 2015
- (5) Yahong Jin, Yihua Hu, Li Chen, Xiaojuan Wang, Guifang Ju, Zhongfei Mou and Feng Liang: "Luminescence properties of a novel orange emission long persistent phosphor $\text{CaO}:\text{Sm}^{3+}$ ", *Optics Communications*, Vol. 311, pp. 266–269, 2013
- (6) Jin He, Su Zhang, Jianbang Zhou, Jiuping Zhong, Hongbin Liang, Shuaishuai Sun, Yan Huang and Ye Tao: "Luminescence properties of an orange-red phosphor $\text{GdAl}_3(\text{BO}_3)_4:\text{Sm}^{3+}$ under VUV excitation and energy transfer from Gd^{3+} to Sm^{3+} ", *Optical Materials*, Vol. 39, pp. 81–85, 2015
- (7) Panlai Li, Zhijun Wang, Qinglin Guo, Zhiping Yang, Xu Li and Feng Teng: "Luminescence, energy transfer and thermal stability of $\text{LiBaB}_9\text{O}_{15}:\text{Sm}^{3+}$, Eu^{3+} for white LEDs", *Materials Research Bulletin*, Vol. 70, pp. 789–794, 2015
- (8) I.I. Kindrat, B.V. Padlyak and A. Drzewiecki: "Luminescence properties of the Sm-doped borate glasses", *Journal of Luminescence*, Vol. 166, pp. 264–275, 2015
- (9) K. Selvaraju and K. Marimuthu: "Structural and spectroscopic studies on concentration dependent Sm^{3+} doped boro-tellurite glasses", *Journal of Alloys and Compounds*, Vol. 553, pp. 273–281, 2013
- (10) Marcin Sobczyk: "Optical spectroscopy of Sm^{3+} doped $\text{Na}_2\text{O--ZnO--La}_2\text{O}_3\text{--TeO}_2$ glasses", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, Vol. 149, pp. 965–970, 2015
- (11) Huajuan Deng, Ze Zhao, Jing Wang, Zhoufei Hei, Mengxue Li, Hyeon Mi Noh, Jung Hyun Jeong and Ruijin Yu: "Photoluminescence properties of a new orange–red emitting Sm^{3+} -doped $\text{Y}_2\text{Mo}_4\text{O}_{15}$ phosphor", *Journal of Solid State Chemistry*, Vol. 228, pp. 110–116, 2015
- (12) Hom Nath Luitel, Takanori Watari, Rumi Chand, Toshio Torikai and Mitsunori Yada: "Photoluminescence properties of a novel orange red emitting $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Sm}^{3+}$ phosphor and PL enhancement by Bi^{3+} co-doping", *Optical Materials*, Vol. 34, pp. 1375–1380, 2012
- (13) YANG Zhiping, DONG Hongyan, LIU Pengfei, HOU Chuncai, LIANG Xiaoshuang, WANG Can and LU Fachun: "Photoluminescence properties of Sm^{3+} -doped $\text{LiY}(\text{MoO}_4)_2$ red phosphors", *JOURNAL OF RARE EARTHS*, Vol. 32, No. 5, pp. 404, 2014
- (14) C.K. Jayasankar and P. Babu: "Optical properties of Sm^{3+} ions in lithium borate and lithium fluoroborate glasses", *Journal of Alloys and Compounds*, Vol. 307, pp. 82–95, 2000