Visible luminescence properties of Sm\(^{3+}\)-dope barium gadolinium glasses

K Kirdsiri \(^1\)\(^2\) and J Kaewkhao \(^1\)\(^2\)

\(^1\) Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand
\(^2\) Physics Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand

E-mail: nanonymous@webmail.npru.ac.th

Abstract. A series of barium gadolinium borate glasses doped with Sm\(^{3+}\) ions in chemical composition of 20BaO:10Gd\(_2\)O\(_3\):(70-x)B\(_2\)O\(_3\):xSm\(_2\)O\(_3\) were synthesized by melt quenching technique, at different Sm\(_2\)O\(_3\) concentration varying from 0.0 to 1.5 mol\%. The prepared glasses were systematically characterized their properties through density, molar volume, absorption, excitation and emission spectra. The density and molar volume of glasses increased with increasing of Sm\(_2\)O\(_3\) in higher concentration. The absorption spectra show characteristic peaks of Sm\(^{3+}\) in visible and infrared regions. The emission spectra show the strongest reddish-orange emission at 598 nm under excitation at 403 nm. The CIE1931 chromaticity coordinate shows that all glasses emitted the orange color, which could be used as orange emitting material applications.

1. Introduction
Over the last few decades, the emerge of research topic on rare earth based crystalline and non-crystalline materials draw a great deal of interest from scientists. When compare to crystalline, glasses are potentiated materials for rare earth ions due to the variety of advantages such as low cost of preparation, no advanced manufacturing technology is needed, easy fabricate to various sizes and shapes, large amount of dopant capability [1-4]. Among different glassy materials, borate glasses stand out as possessing broad range of applications due to their low melting temperature and has a wide range of glass formation region with good transparency, non-hygroscopic nature [5-7]. Among rare earth ions, Gd\(_2\)O\(_3\) is a favorable material due to the efficient energy transfer from Gd\(^{3+}\) ions to the luminescence activators and increase the light yield of emission [8-12]. The Sm\(^{3+}\) ion is one of the important candidate activators for various host lattice producing orange-reddish light emitting with high efficiency due to the \(^{4}G_{5/2} \rightarrow ^{6}H_{J}\) (J = 5/2, 7/2, 9/2, 11/2) transitions. It is also well known that the intensities of emission bands of Sm\(^{3+}\) ion in glass matrices depend on its concentration and glass composition [8, 13-15].

In this research work, a glass systems of barium gadolinium borate glass were synthesized with Sm\(^{3+}\) ions at different concentration to study physical, optical and luminescence properties. Furthermore, this glass matrix has never been studied in any details. Thus, the objective of this research work is understanding the effect of Sm\(_2\)O\(_3\) on glass properties.
2. Experimental details
The Sm\textsuperscript{3+} ions doped barium gadolinium borate glasses were synthesized with molar composition of 20BaO: (70-x)Gd\textsubscript{2}O\textsubscript{3}: xSm\textsubscript{2}O\textsubscript{3} (where x are composition of Sm\textsubscript{2}O\textsubscript{3} oxide, varying from 0.0 to 1.5 mol\%) by ordinary melt quenching technique. The desired quantity of chemical powder such as BaCO\textsubscript{3}, Gd\textsubscript{2}O\textsubscript{3}, H\textsubscript{3}BO\textsubscript{3} and Sm\textsubscript{2}O\textsubscript{3} were carefully weighted and grounded in an agate mortar. The well-mixed powder was taken into an alumina crucible and heated at 1200 °C for 3 hours in an electric furnace in order to obtain completely molten mixture. The homogeneous mixture was quenched in preheated stainless steel mold. The glass samples were further annealed at 500 °C for 3 hours to diminish their thermal and mechanical strains. After annealing, the glasses were fine cut and polished to rectangular shape with 1.0 cm × 1.5 cm × 0.3 cm for scientific investigation. The Archimedes’s principle was applied for density measurement, using water as immersion liquid. The optical absorption spectra were recorded with a UV-VIS-NIR spectrophotometer (Shimadzu UV-3600) in the spectral wavelength range from 300 to 1800 nm. The emission and excitation spectra were recorded using a spectrofluorophotometer (Cary-Eclipse) with xenon lamp as a light source. All these characterization processes were operated at room temperature.

3. Results and discussion
The appearance of Sm\textsuperscript{3+} doped barium gadolinium borate glasses are transparent and soft yellow color as shown in figure 1.

![Figure 1. The appearance of Sm\textsuperscript{3+} doped barium gadolinium borate glasses.](image_url)

3.1. Physical properties
The values of density and molar volume were obtained by using the expressions that are available in literature [16] and tabulated in Table 1.

| Sample No. | Concentration of Sm\textsubscript{2}O\textsubscript{3} (mol\%) | Density (g/cm\textsuperscript{3}) | Molar volume (cm\textsuperscript{3}/mol) |
|-----------|-----------------|-----------------|-----------------|
| 1         | 0.0             | 3.3287          | 34.7435         |
| 2         | 0.1             | 3.3326          | 34.8075         |
| 3         | 0.3             | 3.3391          | 34.9486         |
| 4         | 0.5             | 3.3454          | 35.0913         |
| 5         | 1.0             | 3.3608          | 35.4493         |
| 6         | 1.5             | 3.3712          | 35.8571         |

Glass density tends to increase with increasing of Sm\textsubscript{2}O\textsubscript{3} concentration due to increasing number of Sm\textsuperscript{3+} ions with higher molecular mass and density. The molar volume also increases along with density as the dopant concentration increase (as seen in figure 3). It can be implied that the structural arrangement of glass network change because Sm\textsubscript{2}O\textsubscript{3} breaks bonds on glass network, generates NBOs amount, thus resulting in loosely packed structure.
3.2. Optical property

The absorption spectra of Sm$^{3+}$ doped barium gadolinium borate glasses as shown in figure 3. It revealed eight transitions originating from the Sm$^{3+}$ ground state $^6H_{5/2}$ level to different excited states $^6P_{3/2}$, $^4I_{11/2}$, $^6F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$ and $^4H_{15/2}$ located at different wavelength such as 402, 475, 944, 1080, 1228, 1375, 1472 and 1531 nm, respectively [16]. Furthermore, the $^6H_{5/2} \rightarrow ^6H_{j}$ and $^6H_{5/2} \rightarrow ^6F_j$ transitions are spin allowed ($\Delta S = 0$), thus the transition in NIR region show more intense than that in UV-VIS region.

Figure 2. The density and molar volume of Sm$^{3+}$ doped barium gadolinium borate glasses.

Figure 3. The absorption spectra of barium gadolinium borate glass system doped with Sm$^{3+}$. 
3.3. Luminescence excitation and emission spectra

![Image of PL excitation spectra](image1)

*Figure 4.* The PL excitation spectra of glasses with different Sm$_2$O$_3$ concentration.

The photoluminescence excitation spectra for glasses were obtained by monitoring an emission at wavelength 598 nm. The PL excitation spectra as shown in figure 4 have both the Sm$^{3+}$ and Gd$^{3+}$ excitation peaks. The excitation spectra reveals two peaks at 275 ($^6$S$_{7/2} \rightarrow ^6$I$_{9/2}$) and 313 nm ($^6$S$_{7/2} \rightarrow ^6$P$_{7/2}$) belong to Gd$^{3+}$ ions, and nine peaks at 333 ($^6$H$_{5/2} \rightarrow ^4$H$_{9/2}$), 361 ($^6$H$_{5/2} \rightarrow ^4$D$_{3/2}$), 375 ($^6$H$_{5/2} \rightarrow ^6$P$_{7/2}$), 403 ($^6$H$_{5/2} \rightarrow ^6$P$_{5/2}$), 416 ($^6$H$_{5/2} \rightarrow ^6$P$_{3/2}$), 437 ($^6$H$_{5/2} \rightarrow ^4$G$_{7/2}$), 472 ($^6$H$_{5/2} \rightarrow ^4$M$_{15/2}$), 500 ($^6$H$_{5/2} \rightarrow ^4$G$_{7/2}$) and 526 nm ($^6$H$_{5/2} \rightarrow ^4$F$_{3/2}$) belong to Sm$^{3+}$ ions. From excitation spectra in figure 4, the two intense peaks locate at 275 and 403 nm belong to Gd$^{3+}$ and Sm$^{3+}$ ions, respectively were used for studying in the emission spectra.

![Image of PL emission spectra](image2)

*Figure 5.* The PL emission spectra of barium gadolinium borate glasses with different Sm$_2$O$_3$ concentration by monitoring excitation at 403 nm.

![Image of PL emission spectra](image3)

*Figure 6.* The PL emission spectra of barium gadolinium borate glasses with different Sm$_2$O$_3$ concentration by monitoring excitation at 275 nm.
Figure 5. shows the PL emission spectra with four Sm$^{3+}$ characteristic emission bands by monitored excitation wavelength at 403 nm, correspond to transition from $^4G_{7/2}$ to $^6H_{52}$ (563 nm, yellow color), $^6H_{32}$ (598 nm, orange color), $^6H_{42}$ (645 nm, orange-redish color) and $^6H_{112}$ (708 nm, reddish color), respectively. Among all transition level, the transition with wavelength 598 nm has the highest intensity. Similarly, the figure 6 shows the emission spectra of glasses recorded at 275 nm, the emission peaks at 311 nm corresponds to the Gd$^{3+}$ transition of $^6P_{7/2} \rightarrow ^8S_{7/2}$ and one at 624 nm (2$^\text{nd}$ harmonics of UV-luminescence) corresponds to the Gd$^{3+}$ transition of $^6G_{7/2} \rightarrow ^8P_{7/2}$. For Sm$^{3+}$ ions, the emission peaks observed in this figure have same position as observed in figure 5. Moreover, when Gd$^{3+}$ ions are excited by wavelength at 275 nm, the excitation energy may migrate to the lower levels of $^6G_{52}$ of Sm$^{3+}$ ions by energy transfer phenomenon as seen in energy level scheme for Gd$^{3+}$ and Sm$^{3+}$ ions in figure 7. The emission band of Gd$^{3+}$ ions at 311 nm decreases with increasing of Sm$_2$O$_3$ concentration, whereas the emission bands of Sm$^{3+}$ increase until 0.3 mol%. The decreasing of Gd$^{3+}$ emission intensity, while increasing in Sm$^{3+}$ emission also depicts the energy transfer phenomenon from Gd$^{3+}$ to Sm$^{3+}$ ions.

The CIE1931 diagram is a standard technique to validate the emission color for any visible light, by considering the sensitivity of human eyes to various color. The values of x and y were calculated coordinates corresponding to the position of light emission, with white light region locates at the center of chromaticity diagram [7, 13]. In this work, the x, y coordinates were obtained by converting the emission spectra of glass samples with different concentration of Sm$_2$O$_3$ onto the CIE1931 diagram. From figure 8, it reveals that the color coordinate (x, y) are found to be (0.59, 0.40), (0.59, 0.40), (0.59, 0.40), (0.59, 0.41) and (0.59, 0.41) corresponding to 0.1, 0.3, 0.5, 1.0 and 1.5 mol% of Sm$_2$O$_3$ concentration, lie in the range of orange region in the CIE1931 diagram. It confirms that the prepared Sm$^{3+}$ doped barium gadolinium borate glasses are suitable for the applications in the orange light-emitting diodes.

![Figure 7. The simplified energy level diagram for Gd$^{3+}$ and Sm$^{3+}$ doped glass.](image1)

![Figure 8. The CIE1931 Chromaticity diagram for glass doped with 0.3 mol% of Sm$_2$O$_3$ concentration.](image2)

4. Conclusion

The soft yellow color Sm$^{3+}$ doped barium gadolinium borate glasses were prepared by melt quenching technique and were investigated their physical, optical and photoluminescence properties. The glass density show increasing with increase Sm$_2$O$_3$ content. The optical absorption spectra exhibited the characteristic Sm$^{3+}$ absorption bands, assigned to the transitions from $^6H_{52}$ ground state to another states. Exciting glasses by ultraviolet range of 275 nm, the photon was absorbed by Gd$^{3+}$ ions resulting in the
strongest excitation of Gd$^{3+}$ which transfer and generate the emission of Sm$^{3+}$ through energy transfer phenomenon. The emitted light was confirmed by the CIE1931 chromaticity diagram, the color coordinates locate the orange light region. The above results indicate that the prepared glass is a potential candidate for the lighting applications in the orange light emission.

5. Acknowledgement
The authors would like to thanks Nakhon Pathom Rajabat University (NPRU) and the National Research Council of Thailand (NRCT) to support this work.

References
[1] Kaushal J and Jayasimhadri 2016 J. Alloys Compd. 688 833
[2] Thomas S, Rasool Sk N, Rathiaiah M, Venkatramu V, Joseph C and Unnikrishnan NV 2013 J. Non-Cryst. Solid 376 106
[3] Mahamuda Sk, Swapna K, Packiyaraj P, Rao A S and Prakash G V 2014 J. Lumin. 153 382
[4] Kaewkhao J, Wantana N, Kaewjaeng S, Kothan S and Kim H J 2016 J. Rare Earth. 34(6) 583
[5] Swapna K, Mahamuda Sk, Rao A S, Sasikala T and Moorthy L R 2014 J. Lumin. 146 288
[6] Kindrat I I, Padyak B V and Drzewiecki A 2015 J. Lumin. 166 264
[7] Ullah I, Shah S K, Khan A, Shoaib M, Kaewkhao J, Ahmad T, Ahmed E and Rooh G 2021 J. Lumin. 230 117700
[8] Wantana N, Kaewjaeng S, Kothan S, Kim H J and Kaewkhao J 2017 J. Lumin. 181 382
[9] Pawlik N, Szpikowska-Sroka B, Soltys M and PIsarski W A 2016 J. Rare Earth. 34(8) 786
[10] Reisfeld R, Greenberg E and Biron E 1974 J. Solid Stare Chem. 9 244
[11] Padyak B V, Drzewiecki A, Padyak T B, Adamiv V T and Teslyuk I M 2018 Opt. Mater. 79 302
[12] Kesavulu C R, Kim H J, Lee S W, Kaewkhao J, Kaewnuam E and Wantana N 2017 J. Alloys Compd. 704 557
[13] Klimesz B, Lisiecki R and Ryba-Romanowski W 2019 J. Alloys Compd. 788 658
[14] Babu K V and Cole S 2018 Materials Today. 5 26440
[15] Kolavekar S B, Ayachit N H, Rajaramakrishna R and Kaewkhao J 2020 J. Lumin. 226 117498
[16] Khan I, Rooh G, Rajaramakrishna R, Srisittipokakun N, Kim H J, Kirdsiri K and Kaewkhao J 2019 Spectrochim. Acta A Mol. Part A. 214 14