Proceedings of International Conference on Technology and Social Science 2017
Invited Paper

Comparison study of Dy^{3+} and Eu^{3+} of Gd_2O_3- CaO- SiO_2- B_2O_3 Glasses with BGO Crystal

Siriprapa Kaewjaeng[1, a], Suchart Kothan[1,b] , HongJoo Kim[2,c]
and Jakrapong Kaewkhao[3,d]

[1] Department of Radiologic Technology, Faculty of Associated Medical Science, Chiang Mai University, Chiang Mai, Thailand, 50200

[2]Department of Physics, Faculty of Natural Science, Kyungpook National University, Daegu, South of Korea, 706-784

[3]Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University, Nakhon Pathom, Thailand, 73000

[a]<bulli99@windowslive.com>, [b]<Suchartcmu@gmail.com>, [c]<Hongjooknu@gmail.com>, <mink110@gmail.com>

Keywords: Comparison, Dy^{3+}, Eu^{3+} Gd_2O_3, BGO

Abstract. In this studies, glass were prepared from the composition of (55-x) B_2O_3: 25Gd_2O_3: 10SiO_2: 10CaO: xA_2O_3, where A_2O_3 are Eu_2O_3 and Dy_2O_3 and x = 0.05 ,0.15 ,0.25, 0.35, 0.45 and 0.50 mol% by melt-quenching technique and were characterized through physical, optical and radioluminescence properties. The results show that the density of glass samples increased with increasing of dopant concentration. The optical spectra of glass shows two discrete absorption bands of Eu_2O_3 and nine absorption bands of Dy_2O_3. The integral scintillation efficiency of 0.35 mol% of Eu_2O_3 and 0.45 mol% of Dy_2O_3 doped glass were determined at 25% and 27% of commercial BGO scintillation crystal.

1. Introduction

Glass scintillators can be easily and economically fabricated in a variety of sizes and custom shapes. Production cost of the melt-quenching is cheaper than those of other techniques [1]. Applications of glass scintillators; each of techniques the fields of nuclear physics, high energy physics, astrophysics, medical imaging and homeland security [2].

Silica (SiO_2) and borate (B_2O_3) are the candidates for a glass former and a flux material significant role in various applications [2, 3]. The effect adding calcium oxide (CaO) helps improving hygroscopic property of the glass [4]. For heavy rare-earth metal oxide, intensive Gd_2O_3 are most popular based glass scintillator due to the efficient energy transfer from Gd^{3+} ions to the luminescence activators, high thermal neutron capture cross-section and increase the light yield of emission [5-7].

In recent years, rare-earth ions are used in a wide variety of applications [6-11]. The active Dy^{3+} ion provides two typical emission transitions that correspond to ${}^4F_{9/2}\rightarrow{}^6H_{15/2}$ transition in blue bands (~480 nm) and ${}^4F_{9/2}\rightarrow{}^6H_{13/2}$ (electric dipole) transition in yellow bands (~570 nm) regions, which are also necessary for full primary color displays. The relative intensities of the ${}^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition to the ${}^4F_{9/2}\rightarrow{}^6H_{15/2}$ transition known as a yellow-to-blue luminescence intensity ratio Y/B can be modulated by varying the glass host and its chemical composition as well as the excitation wavelengths [12–15].

The trivalent Eu_2O_3, with its unsplit ${}^7F_0$ ground state and relatively simple energy level scheme is a very convenient spectroscopic probe of the crystal field and can provide information related to the structure and bonding characteristics of different host matrices [16 -22].

In this work, we fabricated the Dy^{3+} and Eu^{3+} ion doped in B_2O_3-SiO_2-Gd_2O_3-CaO glass system and study on physical, optical and radioluminescence properties, the radioluminescence of the glass samples were compared with that of a commercial BGO scintillation crystal.

2. Materials and Method

Glass Preparation

Glasses with the chemical compositions $25Gd_2O_3$-10CaO-$10SiO_2$-(55-x) B_2O_3-xEu_2O_3 and Dy_2O_3 (where x is 0.05 ,0.15 ,0.25, 0.35, 0.45 and 0.50 mol %) were prepared by melt quenching technique. High purity chemicals, gadolinium oxide (Gd_2O_3), calcium oxide (CaO), silicon oxide (SiO_2), boric acid (H_3BO_3), europium oxide (Eu_2O_3) and dysprosium Oxide (Dy_2O_3) were mixed thoroughly. Each batch of formulas was weighted to 30 g and melted at 1673 K in alumina crucible by an electrical furnace. Dry oxygen was bubbled thoroughly for 1 hour. The quenched glasses were annealed at 823 K for 3 hours for reduces thermal stress before cool down to the room temperature.

Physical Property

The density measurements by applying Archimedes principle, the weights of the prepared glass samples were measured in air and in xylene using a 4-digit sensitive microbalance (AND, HR 200). Then, the density, ρ, was determined from the relation [23-24]:

$$\rho = \frac{W_a}{W_a - W_b} \times \rho_b \tag{1}$$

where W_a is the weight in air, W_b is the weight in xylene and ρ_b is the density of xylene ($\rho_b = 0.863$ g/cm^3).

Optical Property

The optical spectra in UV-VIS-NIR range were measured by UV-VIS-NIR spectrophotometer (UV-3600, Shimadzu) in the wavelength range 200-2200 nm.

Radioluminescence property

The X-ray luminescence spectra of glasses were measured with a Cu target X-ray generator (Inel, XRG3D-E), whose X-ray source was operated at 50kV and 30mA, and the spectrometer (QE65Pro, Ocean Optics) with an optical fiber to detect the emission spectra

3. Results

Physical Property

The glass samples in this work are colorless. After cut and polished, the good optical qualities were obtained. The density of Dy^{3+} and Eu^{3+} glass samples in this research are in the range of 4.00-4.18 g/cm^3 and 4.06 – 4.22 g/cm^3.

Optical Property

The absorption bands increases with the increase of Eu_2O_3 concentration. Two absorption bands were observed and assigned to transitions from the $^7F_0$ ground state to 2100 nm ($^7F_1$) and 2203 nm ($^7F_6$) [25-27] shown in Fig 1. Fig.2. shows the absorption bands increases with the increase of Dy_2O_3 concentration. Nine absorption bands were observed and assigned to transitions from the $^6H_{15/2}$ ground state to 387 nm $^4I_{13/2}$ + $^4F_{7/2}$ + $^4M_{21/2}$ + $^4K_{17/2}$), 426 nm ($^4G_{11/2}$), 455 nm ($^4I_{15/2}$), 751 nm ($^6F_{3/2}$), 805 nm ($^6F_{5/2}$), 898 nm ($^6F_{7/2}$), 1085 nm ($^6H_{7/2}$+ $^6F_{9/2}$), 1261 nm ($^6F_{11/2}$ + $^6H_{9/2}$) and 1672 nm ($^6H_{11/2}$) [28-35].

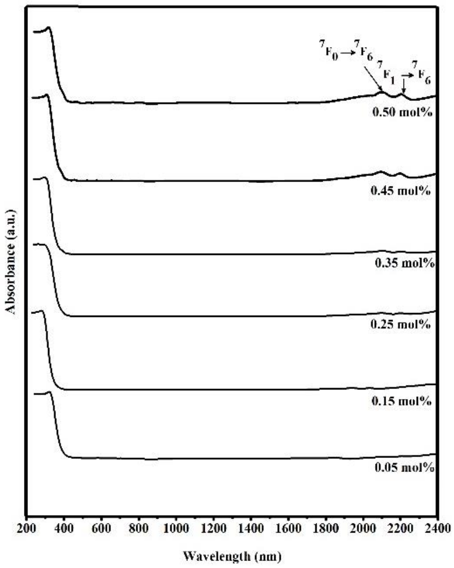

Fig. 1 The absorption spectra of Eu

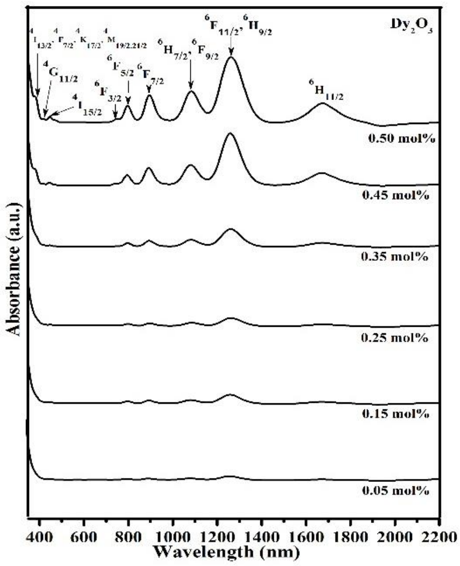

Fig. 2 The absorption spectra of Dy

Radioluminescence Property

The radioluminescence spectrum of 0.35 mol% of Eu_2O_3 show six peaks relatively strong emission peaks at occurring 578 ($^5D_0 \rightarrow ^7F_0$), 590 ($^5D_0 \rightarrow ^7F_1$), 616 ($^5D_0 \rightarrow ^7F_2$), 652($^5D_0 \rightarrow ^7F_3$) and 703 ($^5D_0 \rightarrow ^7F_5$) nm shown in Fig 3 [25-27]. In Fig. 4 was shown glass doped with 0.45 mol% of Dy_2O_3 have four relatively strong emission peaks at occurring 482 nm ($^4F9/2 \rightarrow ^6H_{15/2}$), 577 nm ($^4F_{9/2} \rightarrow ^6H_{13/2}$), 661 nm ($^4F_{9/2} \rightarrow ^6H_{11/2}$) and 751 nm ($^4F_{9/2} \rightarrow ^6H_{9/2} + ^6F_{11/2}$) [28-36]. The compared x-ray luminescence properties between glass samples with commercial BGO scintillator crystal was found that the integral scintillation efficiency of glass samples doped with Eu_2O_3 and Dy_2O_3 was determined as 25% and 27% of commercial BGO scintillator crystal.

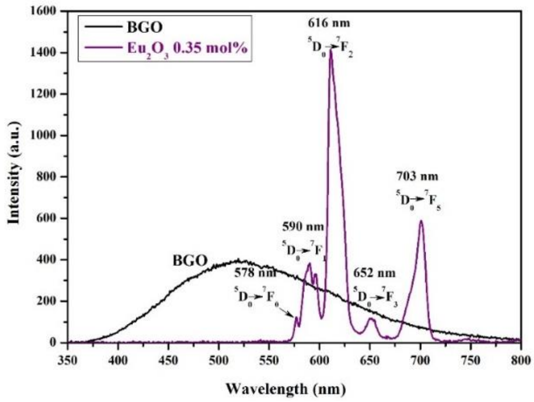

Fig 3. Eu_2O_3 0.35 mol% with BGO

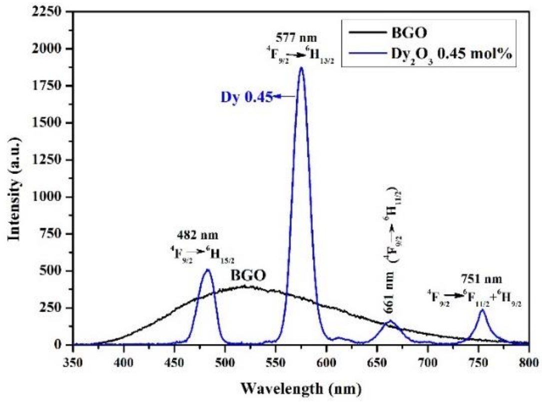

Fig 4. Dy_2O_3 0.45 mol% with BGO [36]

4. Conclusion

In conclusions, different concentrations of Eu^{3+} and Dy^{3+} doped in B_2O_3-SiO_2-Gd_2O_3-CaO glasses have been fabricated and the investigations on their physical, optical and radioluminescence properties. The conclusions from the studied results are as follows;

- The density of $25Gd_2O_3$: 10CaO: $10SiO_2$: (55-x) B_2O_3: xEu_2O_3 and xDy_2O_3 glasses were increased with increasing of Eu_2O_3 and Dy_2O_3 concentration.
- Two Eu^{3+} absorption bands corresponding to the $^7F_0 \rightarrow ^4F_6$, $^7F_1 \rightarrow ^7F_6$ transitions respectively absorption bands peaked at 2100 and 2203 nm.
- Nine Dy^{3+} absorption bands corresponding to the $^6H_{15/2}$ ground state to 387 nm ($^4I_{13/2} + ^4F_{7/2} + ^4M_{21/2} + ^4K_{17/2}$), 426 nm ($^4G_{11/2}$), 455 nm ($^4I_{15/2}$), 751 nm ($^6F_{3/2}$), 805 nm ($^6F_{5/2}$), 898 nm ($^6F_{7/2}$), 1085 nm ($^6H_{7/2} + ^6F_{9/2}$), 1261 nm ($^6F_{11/2} + ^6H_{9/2}$) and 1672 nm ($^6H_{11/2}$).

The compared x-ray luminescence properties between glass samples with commercial BGO scintillator crystal was found that the integral scintillation efficiency of glass samples doped with Eu_2O_3 and Dy_2O_3 was determined as 25% and 27% of commercial BGO scintillation crystal.

Acknowledgements

S. Kaewjeang and S. Kothan would like to thanks Department of Radiologic Technology, Faculty of Associated Medical Sciences, Chiang Mai University, Thailand for partially support. J. Kaewkhao would like to thanks National Research Council of Thailand (NRCT) for funding support.

References

[1] Neal JS, Boatner LA, Wisniewski D, Ramey JO, Spectroscopic refractive indices of monoclinic single crystal and ceramic lutetium oxyorthosilicate from 200 to 850 nm Proc. of SPIE. (2007) 6706.

[2] Park JK, Kim HJ, Limsuwan P, Kaewkhao J, Luminescence property of rare-earth-doped bismuth-borate glasses with different concentrations of bismuth and rare-earth materia, Journal of Korean Physical Society, Vol. 61(2), 2012, 248.

[3] Chanthima N, Kaewkhao J, Kedkaew C, Chewpraditkul W, Pokaipisit A, Limsuwan P, Study on Interaction of Bi2O3, PbO and BaO in Silicate Glass System at 662 keV for Development of Gamma-Rays Shielding Materials, Progress in nuclear Science and Technology 1 (2011) 106.

[4] Zhou Y, Li H, Lin K, Zhai K, Gu W, Chang J, Effect of heat treatment on the properties of SiO_2-CaO-MgO-P_2O_5 bioactive glasses Journal Materials Science: Materials in Medicine. 23 (2012) 2101.

[5] Wantana N, Kaewjaeng S, Kothan S, Kim HJ, Kaewkhao J, 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 (2017) 382.

[6] Dorenbos P, The $4f^n$-$4f^{n-1}$5d transitions of the trivalent lanthanides in halogenides and chalcogenides Journal of Luminescence, 91, (2000) 91.

[7] Kumar A, Rai DK, Rai SB , Luminescence of Gd^{3+} ions doped in oxyfluoroborate glass, Solid State Communications 117 (2001) 387.

[8] Park JK, Kim HJ, Kim S, Limsuwan P, Kaewkhao J, Luminescence Property of Rare-Earth Doped Bismuth-Borate Glasse, Procedia Enginerring 32 (2012) 855.

[9] Thiel CW, Sun Y, Cone RL, Progress in Relating Rare Earth Ion 4f and 5d Energy Levels to Host Bands in Optical Materials for Hole Burning, Quantum Information, and Phosphors, Journal of Modern Optics, 49 (2002) 2399.

[10] Park JK, Kim HJ, Kim S, Cheon J, Kaewkhao J, Limsuwan P, Iniripong S, X-ray and proton luminescence of bismuth-borate glasses, Journal of Korean Physical Society, Vol. 59(2), 657.

[11] Lakshminarayana G, Qiu J, Brik MG, Kityk IV, Spectral analysis of Er^{3+}-, Er^{3+}/Yb^{3+}- and $Er^{3+}/Tm^{3+}/Yb^{3+}$-doped TeO_2-ZnO- WO_3-TiO_2-Na_2O glasses, Journal of Physics Condensed Matter, 20, (2008) 335106

[12] Marzouk MA, Ouis MA, Hamdy YM, Spectroscopic Studies and Luminescence Spectra of Dy_2O_3 Doped Lead Phosphate Glasses, Silicon, 4 (2012) 221.

[13] Barkyoumb JH, Mathur VK, Lewandowski AC, Tookey A, Townsend PD, Giblin I, Low-temperature luminescence properties of $CaSO_4$:Dy, Journal of Luminescence, 72–74, (1997) 629.

[14] Tanabe S, Kang J, Hanada T, Soga N, Spectroscopic properties and Judd-Ofelt theory analysis of Dy^{3+} doped oxyfluoride silicate glass Journal of Non-Crystal Solids 239, (1998) 170.

[15] Yu M, Lin J, Wang J, Fu J, Wang S, Zhang HJ, Han YC, Fabrication, patterning, and optical properties of nanocrystalline YVO4 : A (A = Eu^{3+}, Dy^{3+}, Sm^{3+}, Er^{3+}) phosphor films via sol-gel soft lithography Chem. Mater. 14, (2002) 2224,.

[16] Pisarski WA, Pisarska J, Dominiak-Dzik G, Maczka M, Ryba-Romanowski W, Compositional-dependent lead borate based glasses doped with Eu^{3+}ions: Synthesis and spectroscopic properties, Journal of Physics and Chemistry of Solids 67 (2006) 2452.

[17] Meng F, Zhang X, Kim S., Yu Y., Seo HJ, Luminescence properties of Eu^{3+}in gadolinium molybdate β'-$Gd_2Mo_3O_{12}$ phosphors. Optik 125 (2014) 3578.

[18] Sigoli FA, Davolos MR, Jafelicci M, Red and blue emissions of europium doped gadolinium silicate from porous silica matrix and hydroxide carbonate with spherical shaped particles, Journal of Alloys and Compounds 344 (2002) 308.

[19] Rada S, Pascuta P, Bosca M, Culea M, Pop L, Culea E , Structural properties of the boro-bismuthate glasses containing gadolinium ions, Vibrational Spectroscopy 48 (2008) 255.

[20] Saif M, Luminescence based on energy transfer in silica doped with lanthanide titania ($Gd_2Ti_2O_7$:Ln^{3+}) [Ln3+ =Eu^{3+} or Dy^{3+}], Journal of Photochemistry and Photobiology A: Chemistry 205 (2009) 145.

[21] Liang H, Su Q, Tao Y, Hu T, Liu T, VUV excited luminescence of europium activated calcium borophosphate prepared in air, Journal of Alloys and Compounds 334 (2002) 293.

[22] Wang C, g Peng M, Jiang N, Jiang X, Zhao X, Qiu J, Tuning the Eu luminescence in glass materials synthesized in air by adjusting glass compositions, Materials Letters 61 (2007) 3608.

[23] Kaewjang S, Maghanemi U, Kothan S, Kim HJ, Limkitjaroenporn P, Kaewkhao J, New Gadolinium Based Glasses for Gamma-Rays Shielding Materials, Nuclear Engineering and Design, 280, 2014, 21.

[24] Kirdsiri K, J. Kaewkhao, A. Pokaipisit, W. Chewpraditkul, P. Limsuwan, Gamma-rays shielding properties of xPbO:(100-x)B_2O_3 glasses system at 662 keV", Annals of Nuclear energy, Vol. 36 (9), 2009, 1360.

[25] Annapurna K, Das M, Kundu P, Dwivedi RN, Buddhudu S., Spectral properties of Eu^{3+}: ZnO-B_2O_3–SiO_2 glasses. Journal of Molecular Structure. 741(1-3) 2005, 53.

[26] Lakshminarayana G, Buddhudu S., 2007. Spectral analysis of Eu^{3+} and Tb^{3+}:B_2O_3–ZnO–PbO glasses. Materials Chemistry and Physics. 102(2-3):181-6.

[27] Pisarski WA, Pisarska J, Dominiak-Dzik G, Mączka M, Ryba-Romanowski W., Compositional-dependent lead borate based glasses doped with Eu^{3+} ions: Synthesis and spectroscopic properties. Journal of Physics and Chemistry of Solids. 67(12) 2006, 2452.

[28] Hussin R. HD, Husin M., Hamdam S., Yusof M. Luminescence properties of 30SrO-30MgO-40P_2O_5 doped with Dy_2O_3. Solid State Science and Technology, 17(2) 2009, 123.

[29] Insitipong S, Kaewkhao J, Ratana T, Limsuwan P., Optical and Structural Investigation of Bismuth Borate Glasses Doped With Dy^{3+}. Procedia Engineering. 8 2011, 195.

[30] Lakshminarayana G, Qiu J., Photoluminescence of Pr^{3+}, Sm^{3+} and Dy^{3+}-doped SiO_2–Al_2O_3–BaF_2–GdF_3 glasses. Journal of Alloys and Compounds. 476(1-2) 2009, 70.

[31] Lakshminarayana G, Qiu J., Photoluminescence of Pr^{3+}, Sm^{3+} and Dy^{3+}: SiO_2–Al_2O_3–LiF–GdF_3 glass ceramics and Sm^{3+}, Dy^{3+}: GeO_2–B_2O_3–ZnO–LaF_3 glasses. Physica B: Condensed Matter. 404(8-11) 2009, 1169.

[32] Lakshminarayana G, Yang R, Mao M, Qiu J., Spectral analysis of RE^{3+} (RE=Sm, Dy, and Tm): P_2O_5–Al_2O_3–Na_2O glasses. Optical Materials. 31(10) 2009, 1506.

[33] Sreedhar VB, Ramachari D, Jayasankar CK., Optical properties of zincfluorophosphate glasses doped with Dy^{3+} ions. Physica B: Condensed Matter. 408 2013, 158.

[34] Zhang F, Xiao Z, Yan L, Zhu F, Huang A., Visible luminescence properties of Er^{3+}–Dy^{3+} codoped tellurite glasses. Applied Physics A. 2010;101(4) 2010, 777.

[35] Yan Z, Chunhua L, Yaru N, Qitu Z, Zhongzi X., Optical Properties of Dy^{3+} Doped in Boroaluminasilicate Glass. Journal of Rare Earths.25 2007, 99.

[36] Kaewkhao J, Wantana1 N, Kaewjaeng S, Kothan S, Kim HJ, Luminescence characteristics of Dy^{3+} doped Gd_2O_3-CaO-SiO_2-B_2O_3 scintillating glasses, JOURNAL OF RARE EARTHS, 34, 2016, 583.