

Tb³⁺ CONCENTRATION EFFECT ON THE PHOTO - AND RADIOLUMINESCENCE RESULT OF LANTHANUM BORATE GLASS FOR YELLOWISH GREEN LASER APPLICATION

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Abstract

The melt-quenching technique was used to prepare lanthanum borate glass doping with Tb³⁺ (LBTb) to investigate physical and luminescent characteristics. The result more a concentration of doped terbium increases the glass density, molar volume, and refractive index. The higher Tb₂O₃ concentrations in glasses led to an increase of absorbance in the VIS and NIR range. The emission spectra of glasses were recorded at excitation wavelengths of 228 and 377 nm, and it was found that these glasses emit yellowish-green light. Tb³⁺ doped glass exhibited the highest intensity at 544 nm. The optimal concentration of terbium with the most significant emission in LBTb glass is 7 mol%, whereas decay time decreases as Tb₂O₃ content increases. The PL measurement showed a similar pattern with the spectrum of RL emissions. Moreover, this glass performs an integral scintillation efficiency of 36.32% compared with BGO crystal. According to the CIE 1931 chromaticity, the LBTb emitted a yellowish-green color. Terbium-doped glasses have attractive potential to be used in yellowish-green lasers.

Keywords: Borate glasses, photoluminescence, radioluminescence, terbium

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Introduction

Glass is a very interesting material because it can be doped with trivalent lanthanide (Ln^{3+}), and they have contributed to the development of light-emitting devices, optical amplifiers, optical waveguides, optical fibers, and lasers. Owing shielding effect of the outer 5s and 5p shell electrons of Ln ion, the observed 4f-4f transition in them has low sensitivity to ion surroundings and optical amplification in the infrared range, it promotes laser action (Kesavulu and Jayasankar, 2011; Lira *et al.*, 2014). Since the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of terbium-doped materials. This makes the low-power laser system have 4 levels. To achieve the operation of a strong green laser at 543 nm, oxide-based glasses activated with terbium ions would illustrate to be a delightful candidate. In addition, the experimental branching ratio of $^5\text{D}_4$ to $^7\text{F}_5$ transition (543 nm) is often greater than 50%, making terbium an appealing ion for green laser application. To select a suitable new host for Ln^{3+} ions. Borate glass is a good host glass for considerable benefits and improvements due to its advantages such as chemical stability, in addition to physical, good Ln^{3+} ion solubility, low non-linear refractive index, high thermal stability, excellent transparency, and low melting point. In order to obtain the enhanced quantum photoluminescence (PL) yield of RE ions, the RE should be placed in a low phonon energy which reduces the possibility of non-radiative transitions and resulting in high PL efficiency (Ramesh *et al.*, 2021). Moreover, Adding the lanthanum oxide into the glass compositions, the phonon energy of the parent glass host can be minimized and thereby increase the optical and spectroscopic properties of activated RE glasses. A glass system with low phonon energy is widely recognized to be ideal for high-efficiency laser and fiber (Kirdsiri *et al.*, 2016; Yasaka *et al.*, 2016). In addition, lanthanum can increase the hardness, chemical endurance, and refractive index of glass (Singh *et al.*, 2009; Bahari *et al.*, 2011; Kaur *et al.*, 2012). Huang *et al.* (2022) Tb^{3+} doped borosilicate aluminate glasses were studied for radioluminescence and compared with BGO crystal. The result is the integrated intensity of X-ray excited luminescence is 66.6% of that of a commercial $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) single crystal scintillator. Teng *et al.* (2020) have studied $\text{Sr}_2\text{GdF}_7\text{Tb}$ results its X-ray excited luminescence (XEL) intensity is 194% of that of a commercial BGO scintillator.

Thus, this work has investigated the photoluminescence and radioluminescence results on the doping Tb^{3+} concentration in lanthanum borate glass. Including the emission color of glasses

has been studied by CIE 1931 chromaticity for laser application.

Materials and Methods

The melt quenching technique was used to create terbium-doped lanthanum borate glasses with the chemical formula $27.5\text{La}_2\text{O}_3-(72.5-x)\text{B}_2\text{O}_3-x\text{Tb}_2\text{O}_3$ (LBTb) ($x = 0, 1, 2, 3, 4, 5, 6, 7, 8$, and 9 mol%). All glass was cut and polished after melting at $1,400^\circ\text{C}$ for 3 h in an electric furnace. The glass was annealed at 500°C for 3 h, and cool to room temperature. Figure 1 displays a Photograph of LBTb glasses for different concentrations.

The physical parameters, such as density (ρ), were obtained use Archimedes's technique implements distilled water as an immersion liquid. Then, molar volume (V_M) can be evaluated from M_T/ρ , where M_T is the total molecular weight of glass components. A UV-Vis-NIR spectrophotometer was used to measure the absorption spectra in the wavelength, range of 400-2,500 nm. The photoluminescence excitation spectra, emission spectra, and luminescence decay time measurements were measured by a fluorescence spectrophotometer (Agilent Technologies, Cary Eclipse) with a xenon lamp as a light source. All measurements were carried out at room temperature.



Figure 1. Photograph of LBTb glasses for different concentrations

Results and Discussion

Figure 2 shows the density, molar volume and refractive index of LBTb glass tend to rise as the terbium content increases. Since Tb_2O_3 is heavier than B_2O_3 , replacing B_2O_3 with Tb_2O_3 results in an increase in the total molecular weight of LBTb glass. Besides, data demonstrates that the terbium ions in glass destroyed boron-oxygen bonds in its network, resulting in non-bridging oxygen (NBOs)

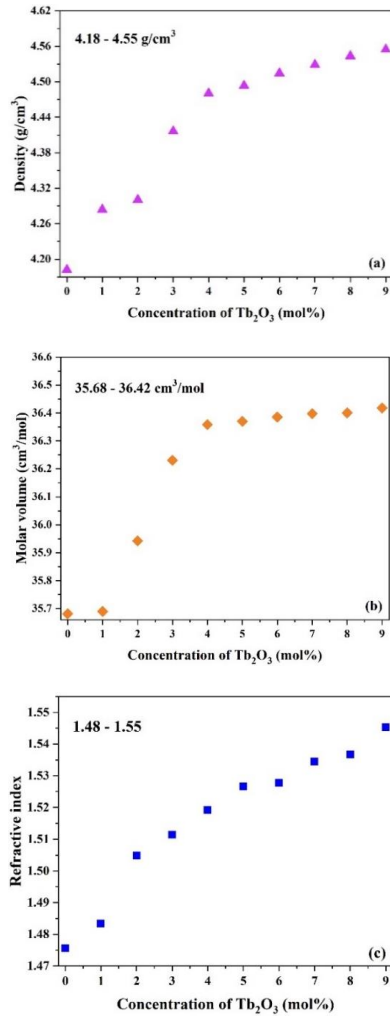


Figure 2. (a) Density, (b) molar volume and (c) refractive index of LBTb glasses for different concentrations

(Jarucha *et al.*, 2020). From dielectric theory, the refractive index of a transparent material such as glass is proportional to its density (Luewarasirikul *et al.*, 2017).

The samples absorption spectra show just 1 peak visible range and 2 peak NIR region. The absorbance increases dramatically as the concentration of Tb_2O_3 increases when the Tb_2O_3 concentration was raised to 9 mol%, a mild absorption developed in Figure 3 at 485 nm in VIS and at 1,888 and 2,213 nm in the NIR range (Kesavulu *et al.*, 2017). Referring to the equation Beer-Lambert law (1) (Antele and Deniz, 2017), the results reveal that the peak of absorption spectra increases with increasing terbium concentration since the absorbed number of photons as Tb^{3+} concentration increased.

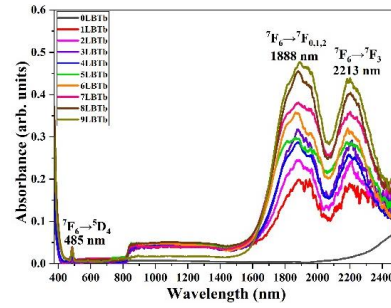


Figure 3. Absorption spectra of LBTb glasses for different concentrations

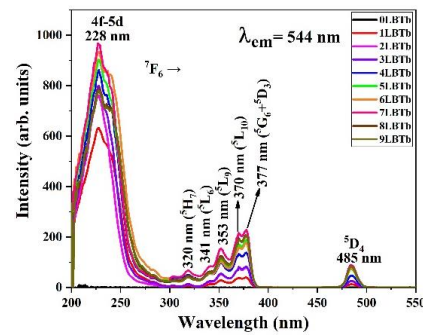


Figure 4. Excitation spectra of LBTb glasses for different concentrations

$$A = -\log T = \log \frac{I_0}{I} = \varepsilon \cdot c \cdot d \quad (1)$$

A is absorbance, I_0/I is the measuring beam's intensity before and after passing through the sample, T is transmittance, c is concentration, ε is molar absorption coefficient, d is the path length of the measuring beam in the sample.

To measure photoluminescence spectra (PL), excitation spectra of terbium-doped LB glasses are shown in Figure 4 by verification of the green emission (λ_{em}) at 544 nm. All the LB sample glasses excitation spectra shows 7 luminescence band transitions at 228, 321, 341, 353, 370, 377, and 485 nm, caused by the activation of Tb^{3+} ions. Since excitation at 228 nm cause by a transition in the 7F_6 energy level to higher spin-allowed 4f-5d level of terbium ions in the ultraviolet range, and excitation peak at 377 nm cause by a transition in the 7F_6 energy level to $^5G_6 + ^5D_3$ level of Tb^{3+} ions in the visible range (Zuo *et al.*, 2015), thus they are used to explore the emission spectra features of the LBTb glass (Kesavulu *et al.*, 2015).

The emission spectra of LBTb glasses doped with 0 to 9 mol% Tb were measured by excitation at 228 and 377 nm, as shown in Figure 5. It was

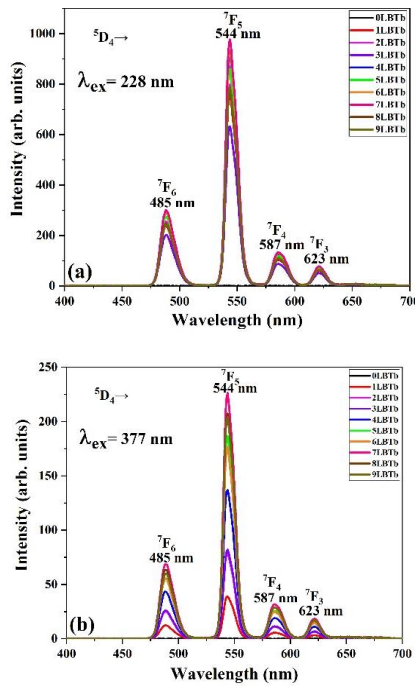


Figure 5. (a) Emission spectra from $\lambda_{\text{ex}} = 228$ and (b) emission spectra from $\lambda_{\text{ex}} = 377$ of LBTb glasses for different concentrations

noticed that glass emitted 4 peaks at 485, 544, 587, and 623 nm, with the light intensity at 544 nm being the highest. Besides, as show in Figure 5, the connection between the intensity of the produced light and the quantity of terbium doped in the glass (for emitting the wavelength 544 nm) is highest at 7 mol% terbium doped glass. When this doping level is exceeded by up to 7 mol%, the intensity of the emission decreases. It might be caused by the concentration quenching effect, which occurs when more than 7 mol% terbium as shown in Figure 6. It may cause terbium ions in the glass network to be too near to one another. The drop in released intensity may be explained by the reabsorption effect, which is responsible for a considerable fluctuation in the emission spectra energy due to the absorption of the light emitted by terbium. When pumped with UV light, the investigated materials produce yellowish-green light at an optimal concentration of 7 mol% terbium in present glass. The effect of doped on the intenseness of emission spectra is similar to that of excitation spectra (Wantana *et al.*, 2019; Rittisut *et al.*, 2021).

Figure 7 shows a partial energy level diagram of the emission with UV $\lambda_{\text{ex}} = 228$ nm which excited the Tb^{3+} ion from the ground state of $^7\text{F}_6$ to the excited state of 4f-5d . Then the non-radiative of the terbium ion relaxes to the luminescence level at $^5\text{D}_4$. The transition of $^5\text{D}_4$ to $^7\text{F}_{6-3}$ causes 4

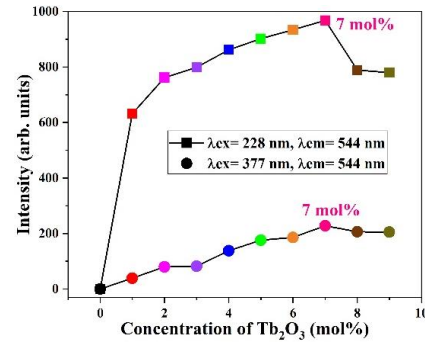


Figure 6. Intensity emission ($\lambda_{\text{ex}} = 228$ and 377) spectra of LBTb glasses for different concentrations

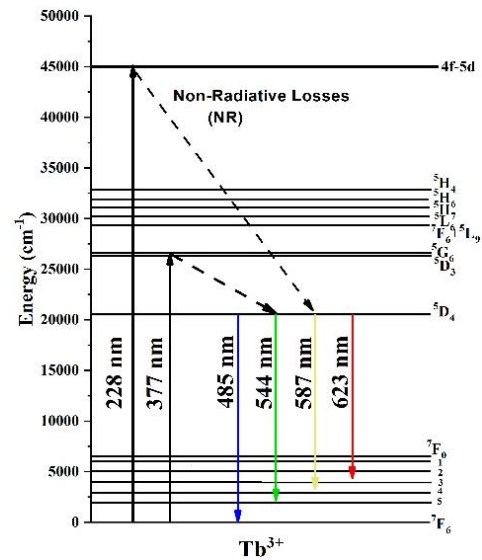


Figure 7. Energy level diagram for emission spectra of LBTb glass

emissions and $\lambda_{\text{ex}} = 377$ nm from $^5\text{D}_4$ to $^7\text{F}_{6-3}$ of LBTb glass, similar to the emission under 228 nm (Rittisut *et al.*, 2021).

The emission color of glass, in general, contains color pairs to evaluate and is a useful certification for luminescence applications. CIE created a universal quantitative model of color spaces in 1931. The CIE 1931 chromaticity standard can be confirmed emission color of 7 mol% terbium doped glass by examining the color coordinates (x, y) depicted on the CIE 1931. The coordinates of glass are coordinated at (0.31, 0.60) for both emission lines under excitation wavelengths of 228 and 377 nm, which were drawn in the yellowish-green area of the CIE color diagram. Under UV light stimulation, the naked eye noticed yellowish green emission from all of the glasses, as seen on the right side of Figure 8. It follows that LBTb glasses are

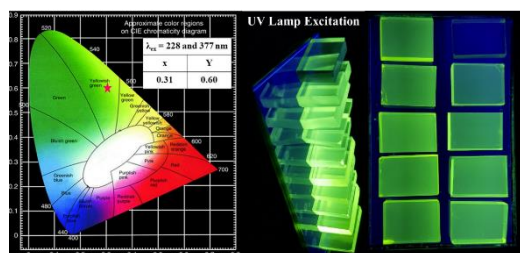


Figure 8. 1931 CIE of 7LBTb glass under 228 and 377 nm excitation

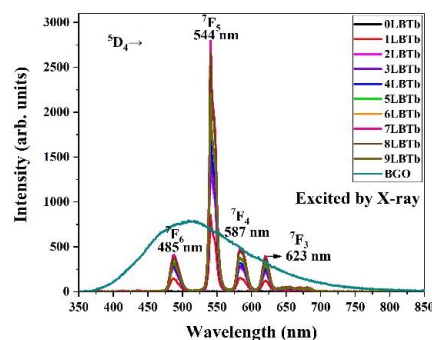


Figure 10. Radioluminescence spectra of LBTb glasses for different concentrations, compared with BGO crystal

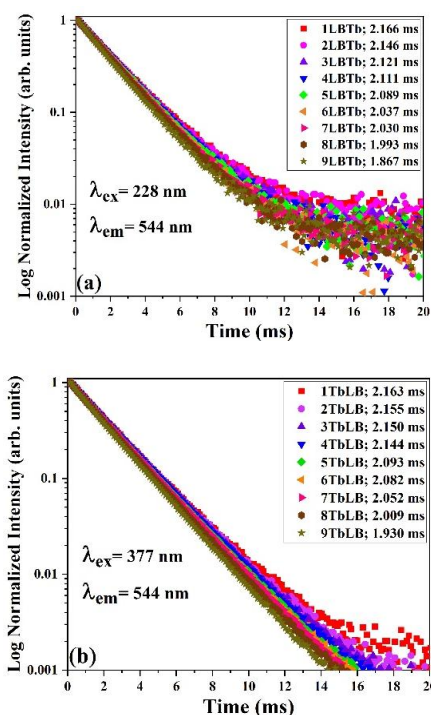


Figure 9. (a) Decay curves from $\lambda_{ex} = 228$ and (b) decay curves from $\lambda_{ex} = 377$ of LBTb glasses for different concentrations

appropriate for use as yellowish-green lasers (Kesavulu *et al.*, 2017; Kaewnuam *et al.*, 2018).

The decay curves (DC) of terbium for the 5D_4 level at various terbium concentrations are depicted in Figure 9. From the Figure 9, the DC of terbium illustrated single exponential nature for all the concentrations, which is equal to 2.166–1.867 ms ($\lambda_{ex} = 228$ nm), and 2.163–1.930 ms ($\lambda_{ex} = 377$ nm) for 1, 2, 3, 4, 5, 6, 7, 8, and 9 mol% of terbium doped glass sequentially (Rittisut *et al.*, 2021). It is noticed that the lifetime of the 5D_4 level decreases very slightly as the Tb^{3+} concentration increases. This indicates that energy migration does not affect the 5D_4 lifetime as observed in most Tb^{3+} -doped glasses. The multiphonon relaxation rate is also

expected to be negligible due to the large energy gap ($\sim 15,285$ cm^{-1}) between the 5D_4 emitting level and the next lower-lying 7F_0 level and as well as the absence of cross-relaxation (CR) channels for the 5D_4 level. The long fluorescence decay time of Tb^{3+} ions in these glasses can reduce the pump threshold to get the strong green laser emission from the 5D_4 level (Jamalaiah *et al.*, 2020).

Figure 10 presents the radioluminescence spectra (RL) of LBTb glasses. All samples shows a dominant green emission of Tb^{3+} at 544 nm. As displayed in Figure 10, the RL has the same quenching concentration (7 mol%), like the PL spectra. It is worth noting that the RL (Figure 10) and PL (Figure 5) spectra have a similar pattern. From that UV excitation, Tb^{3+} ions are directly stimulated into excite states during UV excitation by absorbing high-energy photons from the excitation source and subsequently emitting a low-energy photon. While X-ray excites electrons of both Ln ions and the host. X-ray excitation in host glass results in the hole-electron interaction, then a large number of secondary electrons are produced. Electrons finally indirectly and directly excite the Ln ions in the glass (Rittisut *et al.*, 2021). A comparison of the X-ray luminescence spectra between the glasses and the BGO crystal is displayed in Figure 10. From all areas under the peak of the spectra, the integrated scintillation efficiency of 1–9 mol % terbium doped glasses was determined and found to be 11.93, 20.78, 22.21, 24.42, 28.12, 35.92, 36.32, 34.40, and 28.64% respectively, of the BGO crystal (Huang *et al.*, 2022).

Conclusions

LBTb glasses physical, optical, and luminescent properties have been investigated. Density, molar

volume and refractive index increase as terbium concentration increases. Absorption spectra at visible and near-infrared wavelengths exhibited the absorbed photon of terbium. The excitation wavelengths at 228 and 377 nm, it was noticed that these glasses emit yellowish green light. According to emission spectra, terbium-doped glass emits the most strongly at 544 nm. The terbium concentration in LBTb glass shoed the highest emission at 7 mol%. The decay time decreases as the concentration of Tb₂O₃ increases. The greatest peak of RL occurs at 544 nm. Furthermore, it was found that the intensity of glasses increases with increasing terbium concentration until 7 mol%, after which it decreases due to the concentration quenching effect. The RL spectra have shape and position like the PL spectra. In a comparison of the scintillation property between 7 mol% doped glass and BGO crystal, the integral scintillation efficiency of glass was 36.32% of BGO crystal. According to CIE 1931 chromaticity measurements, terbium-doped glass produces light that is yellowish green. As a result, the current findings suggest that these LBTb glasses might be used in yellowish-green lasers.

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References

- Antele, W.M. and Deniz, E. (2017). UV-VIS Absorption spectroscopy: Lambert-Beer reloaded. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 173:965-968. <https://doi.org/10.1016/j.saa.2016.09.037>
- Bahari, A., Anasari, A., and Rahmani, Z. (2011). Low temperature synthesis of La₂O₃ and CrO₂ by Sol-gel process. *Journal of Engineering and Technology Research*, 3(7):203-208.
- Huang, W.J., Wen, Z.X., Li, L.J., Ashraf, G.A., Chen, L.P., Lei, L., Guo, H., and Li, X.M. (2022). Photoluminescence and X-ray excited scintillating properties of Tb³⁺-doped borosilicate aluminate glass scintillators. *Ceramics International*, 48(12):17178-17184. <https://doi.org/10.1016/j.ceramint.2022.02.274>
- Jamalaiah, B.C., Madhu, N., Rao, K.V., Viswanadha, G., and Ram, D.V.R. (2020). Enhanced red luminescent PBTNAEu glasses for solid state lasers. *Journal of Luminescence*, 223:117200. <https://doi.org/10.1016/j.jlumin.2020.117200>
- Jarucha, N., Wantana, N., Sareein, T., and Kaewkhao, J. (2020). Studying the properties of Gd₂O₃-WO₃-CaO-SiO₂-B₂O₃ glasses doped with Tb³⁺. *Semiconductor Physics, Quantum Electronics & Optoelectronics*, 23(3):276-281. <https://doi.org/10.15407/spqeo23.03.276>
- Kaewnuam, E., Wantana, N., Rajagukguk, J., and Kaewkhao, J. (2018). The Gd₂O₃ effect study on properties of CaGdSiB:Tb³⁺ glass for photonics applications. *Journal of Physics: Conference Series*, 1120:012013. <https://doi.org/10.1088/1742-6596/1120/1/012013>
- Kaur, G., Pandey, O.P., and Singh, K. (2012). Effect of modifiers field strength on optical, structural and mechanical properties of lanthanum borosilicate glasses. *Journal of Non-Crystalline Solids*, 358(18-19):2589-2596. <https://doi.org/10.1016/j.jnoncrysol.2012.06.006>
- Kesavulu, C.R., Silva, A.C.A., Dousti, M.R., Dantas, N.O., de Camargo, A.S.S., and Catunda, T. (2015). Concentration effect on the spectroscopic behavior of Tb³⁺ ions in zinc phosphate glasses. *Journal of Luminescence*, 165: 77-84. <https://doi.org/10.1016/j.jlumin.2015.04.012>
- Kesavulu, C.R. and Jayasankar, C.K. (2011). White light emission in Dy³⁺-doped lead fluorophosphate glasses. *Mater. Materials Chemistry and Physics*, 130(3):1078-1085. <https://doi.org/10.1016/j.matchemphys.2011.08.037>
- Kesavulu, C.R., Kim, H.J., Lee, S.W., Kaewkhao, J., Kaewnuam, E., and Wantana, N. (2017). Luminescence properties and energy transfer from Gd³⁺ to Tb³⁺ ions in gadolinium calcium silicoborate glasses for green laser application. *Journal of Alloys and Compounds*, 704:557-564. <https://doi.org/10.1016/j.jallcom.2017.02.056>
- Kirdsiri, K., Damdee, B., and Kaewkhao, J. (2016). Photoluminescence and optical properties study of dy³⁺-doped lithium calcium borate glasses. *Suranaree Journal of Science Technology*, 23(1):53-58.
- Lira, A., Speghini, A., Camarillo, E., Bettinelli, M., and Caldino, U. (2014). Spectroscopic evaluation of Zn (PO₃)₂:Dy³⁺ glass as an active medium for solid state yellow laser. *Optical Materials*, 38:188-192. <https://doi.org/10.1016/j.optmat.2014.10.024>
- Luewarasirikul, N., Kim, H.J., Meejitpaisan, P., and Kaewkhao, J. (2017). White light emission of dysprosium doped lanthanum calcium phosphate oxide and oxyfluoride glasses. *Optical Materials*, 66:559-566. <https://doi.org/10.1016/j.optmat.2017.02.049>
- Ramesh, P., Gangareddy, J., Sathish, K.N., Pramod, A.G., Hegde, V., Pasha, U.M., Khan, S., Annapurna, K., Sayyed, M.I., Alhuthali, A.M.S., Agarkov, D.A., and Kokila, M.K. (2021). Effect of heavy metal oxides on photoluminescence and spectroscopic attributes of Eu³⁺ activated borate glasses. *Optical Materials*, 114:110933. <https://doi.org/10.1016/j.optmat.2021.110933>
- Rittisut, W., Wantana, N., Ruangtaweep, Y., Mool-am-kha, P., Rujirawat, S., Manyum, P., Yimnirun, R., Kidkhunthod, P., Prasathetragarn, A., Kothan, S., Kim, H.J., and Kaewkhao, J. (2021). The radioluminescence and photoluminescence behaviour of lithium alumino borate glasses doped with Tb₂O₃ and Gd₂O₃ for green luminescence applications. *Opt. Mater.*, 121:111437. <https://doi.org/10.1016/j.optmat.2021.111437>
- Singh, K., Bala, I., and Kumar, V. (2009). Structural, optical and bioactive properties of calcium borosilicate glasses. *Ceramics International*, 35(8):3401-3406. <https://doi.org/10.1016/j.ceramint.2009.06.006>
- Teng, L., Zhang, W., Chen, W., Cao, J., Sun, X.Y., and Guo, H. (2020). Highly efficient luminescence in bulk transparent Sr₂GdF₇:Tb³⁺ glass ceramic for potential X-ray detection. *Ceramics International*, 46(8)partA:10718-10722. <https://doi.org/10.1016/j.ceramint.2020.01.079>
- Wantana, N., Kaewnuam, E., Ruangtaweep, Y., Valiev, D., Stepanov, S., Yamanoi, K., Kim, H.J., and Kaewkhao, J. (2019). Radio, cathodo and photoluminescence

- investigations of high density $\text{WO}_3\text{-Gd}_2\text{O}_3\text{-B}_2\text{O}_3$ glass doped with Tb^{3+} . *Radiation Physics and Chemistry*, 164:108350. <https://doi.org/10.1016/j.radphyschem.2019.108350>
- Yasaka, P., Boonin K., and Kaewkhao, J. (2016). Structural and photoluminescence properties of Dy^{3+} ion in zinc bismuth borate glasses. *Suranaree Journal of Science and Technology*, 23(1):69-75.
- Zuo, C., Zhou, Z., Zhu, L., Xiao, A., Chen, Y., Zhang, X., Zhuang, Y., Li, X., and Ge, Q. (2015). Luminescence properties of Tb^{3+} -doped borosilicate scintillating glass under UV excitation. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 147:324-327. <https://doi.org/10.1016/j.saa.2015.03.097>