The Gd$_2$O$_3$ effect study on properties of CaGdSiB: Tb$^{3+}$ glass for photonics applications

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Abstract. Tb$^{3+}$ doped calcium gadolinium silica borate glasses (CaGdSiB: Tb$^{3+}$) were prepared to study the influence of Gd$_2$O$_3$ concentration on physical, glass network, optical and luminescence properties. Glass density and molar volume increased with increment of Gd$_2$O$_3$ concentration. The enlargement of molar volume and evolution of FTIR spectra confirmed the non-bridging oxygen more occurring in glass network with increment of Gd$_2$O$_3$. Tb$^{3+}$ in glass absorbed photons in visible light and near-infrared region. Glass exhibited the strongest luminescence intensity of Tb$^{3+}$ at 542 nm under 275 nm excitation, passing through the Gd$^{3+}$ - Tb$^{3+}$ energy transfer. The overall color of emission is green in CIE 1931 chromaticity. The emission intensity did not show clear relation with Gd$_2$O$_3$ concentration. However, glass with 22.5 mol% of Gd$_2$O$_3$ possessed the highest emission intensity. The luminescence decay times of Tb$^{3+}$ was about 2 ms which decreased via increasing of Gd$_2$O$_3$ content. CaGdSiB: Tb$^{3+}$ glass performs the potential for using as a scintillator for detector with integration mode and a green light source medium.

1. Introduction

Recently, luminescence materials have been wildly used to applied in human life. They have been integrated or contained in the modern optic/photonic devices such as light bulb, LED, laser, display - screen, sensor, detector, etc. These materials can be in form of solid, liquid and gas. The luminescence bulks in crystal form often used commercially in laser device [1] and scintillation detector [2,3]. However, crystal materials possess high cost due to the complicated and long-time duration process. The chemical stoichiometry in crystal is in tight range which is so difficult to adapt. The material existing on the opposite side of crystal is glass. Easy, short time duration and wide range of chemicals for preparation are the advantage of glass beyond crystal. But amorphous nature of glass degrades its luminescence properties, therefore, it has been a challenge to study and develop the high-quality luminescence glass.

The lanthanide ions (Ln$^{3+}$) is quite suitable for doping as luminescence center in glass materials. The intra 4f-4f transition of this ions can release the sharp emission pattern when it is excited by proper energy. Terbium ion (Tb$^{3+}$) is one of Ln$^{3+}$ which can emit the strong green-light signal in millisecond decay time under 4f-4f transition from $^5$D$_4$ luminescence level. Then it was doped in
Various glasses to study and develop for laser, display, other green emitting devices [4-8], also in electromagnetic wave converter and scintillation detector [6,9-11]. Silica borate glass is a versatile glass former because it possesses the advantages from B2O3, such as low temperature preparation, high transparency, strong bonding, high chemical durability, good solubility for Ln3+ [12,13], and from SiO2, such as high chemical durability, high thermal expansion coefficient, good optical and mechanical property [14]. Some alkaline-earth oxide such as CaO can create the interstitial space for Ln3+ doping site in glass network [15], enhance the hygroscopic resistance [16] and improve the luminescence ability of Ln3+ [17]. Gd3+ from Gd2O3 have a sensitizer property which can transfer energy to Ln3+ for luminescence [18,19]. Moreover, Gd owns high radiation capture cross-section [20] and effective atomic number [16] those make Gd contained glass suitable for neutron, gamma and x-ray radiation detector. From these reasons, Tb3+ doped calcium gadolinium silica borate glasses were prepared to study the Tb2O3 concentration effect on luminescence property in our previous work [21]. 1.00 mol% of Tb2O3 was the optimum concentration resulting to the strongest emission of Tb3+ in that glass. However, influence of Gd2O3 concentration on Tb3+ luminescence also need to be fulfilled if we would like to apply this glass for using as electromagnetic wave converter and scintillator. Therefore, Tb3+ doped calcium gadolinium silica borate glass (CaGdSiB:Tb3+) with different concentration of Gd2O3 were prepared in this work, to investigate the Gd2O3 concentration effect on physical, glass network, optical and luminescence properties.

2. Experiment

2.1. Glass preparation

Glass samples with system, 10CaO - xGd2O3 - 10SiO2 - (79-x)B2O3 - 1Tb2O3 (where x = 20.0, 22.5, 25.0, 27.5, 30.0 mol%), were prepared by melt quenching technique. The abbreviation of each glass is Gd20.0, Gd22.5, Gd25.0, Gd27.5 and Gd30.0, respectively. High chemical raw materials such as CaCO3, Gd2O3, SiO2 and Tb2O3 were weighted with proper stoichiometry for total mass as 15 g. All powders were mixed together and crushed in the agate mortar before contained in the alumina crucible. All samples were melted in the electrical furnace at 1,400 °C for 3 hr. Melts were pour in to 500 °C graphite mould for quenching and shape arrangement. Then, glasses were annealed in furnace at 500 °C for 3 hr to reduce the thermal strain and sequentially left to cool down to room temperature. Obtained glass samples were cut and polished to be 1 x 1.5 x 0.3 cm3 dimension for good transparency and comfortable measurement.

2.2. Glass characterization

All CaGdSiB:Tb3+ glasses were study the physical property by measuring density (ρ) and molar volume (Vm). The density was obtained using Archimedes principle [22] which glass mass were weighted in air and water by 4-digit sensitive microbalance (A&D, HR-200). Then, Vm can be evaluated from M1/ρ, where M1 is the total macular weight of glass components. Glass network was investigated the vibration of bonding and molecule via Fourier transform infrared (FTIR) spectrometer (Agilent Technologies, Carry 630 FTIR). Glasses were studied the optical property form absorption spectra using UV-VIS-NIR spectrophotometer (Shimadzu, UV-3600). The emission spectra and luminescence decay curve from spectrofluorophotometer (Shimadzu, RF-5301PC) were used to perform the luminescence property of Tb3+ in glass. Then, the emission spectra were taken to evaluate the color of emitted light which can be sensed by human eyes using CIE 1931 chromaticity [22]. While the decay curves were brought to fitted with exponential decay for decay time calculation.

3. Results and Discussion

3.1. Density and molar volume

The density and molar volume of CaGdSiB:Tb3+ glasses are shown in figure 1, with 3.82 - 4.41 g/cm3 and 33.76 - 35.84 cm3/mol values, respectively. Since Gd2O3 (362 g/mol) is heavier than B2O3 (70 g/mol), the substitution of B2O3 by Gd2O3 result to a rising of glass total molecular mass and density
with increment of Gd$_2$O$_3$ concentration. The molar volume of glass also increases with increasing of Gd$_2$O$_3$ content. It can be said that Gd$^{3+}$ act as glass modifier which generates the non-bridging oxygen (NBO) in glass sample. NBO annihilates the bonding of oxygen and cation leading to more interstitial spaces in glass network. This discussion will be supported by FTIR result mentioned in subsection.

![Figure 1](image1.png)

**Figure 1.** Density and molar volume of CaGdSiB:Tb$^{3+}$ glasses as a function of Gd$_2$O$_3$ concentration

### 3.2. FTIR spectra

![Figure 2](image2.png)

**Figure 2.** FTIR spectra of CaGdSiB:Tb$^{3+}$ glasses

The FTIR spectra of CaGdSiB:Tb$^{3+}$ glasses with vibration band are shown in figure 2. Gd20.0 glass absorbed the infrared with wave number around 833, 951, 1161 and 1342 cm$^{-1}$ those represent the vibration of molecule and bonding in glass network. The infrared absorption at 833 cm$^{-1}$ indicates the stretching vibrations of B-O bond in BO$_3$ tetrahedral units [23]. The absorption at 951 cm$^{-1}$ also represents the stretching B-O vibration of BO$_3$ units and associates with the stretching of Si-O-B [24,25]. The tri-, tetra-, penta- borate and di- borate belonging to BO$_3$ and BO$_4$ groups and asymmetric stretching of Si-O-Si bonds can be proved by the absorption at 1161 cm$^{-1}$ [25]. Finally, the absorption at 1342 cm$^{-1}$ can identify the asymmetric stretching of B-O bonds in trigonal BO$_3$ units [26-27] and stretching vibration of Si–O–Si [28]. From FTIR spectra, CaGdSiB:Tb$^{3+}$ glass network consist of...
borate units as BO$_3$ and BO$_4$, silicate unit as Si-O-Si and mixed silicate - borate unit as Si-O-B. These chemicals units were degraded with increasing of Gd$_2$O$_3$ concentration proved by the weakness of infrared absorption. It is a confirmation about glass modifier nature of Gd$^{3+}$ that annihilates some chemical bonds in glass network.

3.3. Absorption spectra
The transparency and colorless of CaGdSiB:Tb$^{3+}$ glasses can be confirmed by very weak absorption of visible light (VIS) in the absorption spectra in figure 3. On the other hand, these glasses strongly absorbed the photon of near-infrared radiation (NIR). The absorption band centered at 485, 1879 and 2204 nm corresponds to the direct transition of Tb$^{3+}$ from $^7F_6$ ground level to upper level comprising of $^7F_6 \rightarrow ^5D_4$, $^7F_6 \rightarrow ^7F_{0,1,2}$ and $^7F_6 \rightarrow ^7F_3$, respectively. Since so close energy level of $^7F_0$, $^7F_1$, and $^7F_3$ state and the amorphous nature of glass, the band of $^7F_6 \rightarrow ^7F_0$, $^7F_6 \rightarrow ^7F_1$ and $^7F_6 \rightarrow ^7F_3$ are integrated as one board band. Furthermore, the obvious relation between glass absorbance and Gd$_2$O$_3$ concentration cannot be identified.

3.4. Emission spectra
This work focuses on the effect of Gd$_2$O$_3$ concentration on Tb$^{3+}$ luminescence properties. Therefore, the Gd$^{3+}$ excitation with 275 nm was done to study the emission spectra of Tb$^{3+}$ as shown in figure 4. This excitation with ultraviolet (UV) made Gd$^{3+}$ state rise up with $^8S_{7/2} \rightarrow ^6I_{5/2}$ transition. Then, the energy were transferred from Gd$^{3+}$ donor to Tb$^{3+}$ acceptor. After Tb$^{3+}$ acceptor non-radiate relaxed (NR) by phonon releasing, it decayed down to populate at the $^5D_4$ luminescence level. The de-excitation process sequentially occurred under 4 transitions comprising of $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$, those emitted the light with 488, 542, 585 and 621 nm wavelength, respectively. The strongest emission belonged to photon with 542 nm ($^5D_4 \rightarrow ^7F_5$). The emission intensity of Tb$^{3+}$ did not show clear relation with Gd$_2$O$_3$ concentration. However, Gd22.5 glass possessed the highest emission intensity. Due to sharp emission signal of Tb$^{3+}$ after receiving the energy transfer from Gd$^{3+}$, this glass can sense the ultraviolet and possibly use to detect the other radiations with high efficiency.
3.5. CIE 1931 chromaticity

The emission spectra of CaGdSiB:Tb$^{3+}$ glasses under 275 nm excitation were used to evaluate the color coordinate (x, y) and plotted in to the CIE 1931 chromaticity diagram as shown in figure 5. The obtained color coordinate of Gd20.0, Gd22.5, Gd25.0, Gd27.5 and Gd30.0 glass is so close together as (0.3056, 0.5946), (0.3061, 0.5939), (0.3067, 0.5930), (0.3072, 0.5918) and (0.3080, 0.5909), respectively. Therefore, they were plotted at the same site as red star in diagram which represents the green light emitting. The x value slightly increases, while y value slightly decreases with increment of Gd$_2$O$_3$ concentration. Chromaticity result exhibits the possibility for using our glass as a green light medium in visible light sources and display.

Figure 4. Emission spectra of CaGdSiB:Tb$^{3+}$ glasses

Figure 5. CIE 1931 chromaticity diagram [29] of CaGdSiB:Tb$^{3+}$ glasses under 275 nm excitation
3.6. Decay curves
The decay curves of Tb$^{3+}$ luminescence level, $^5\text{D}_4$, were investigated under 542 nm emission and 275 nm excitation wavelength as shown in figure 6. All curves perform the single-exponential decay which were fitted to gain the decay time in the order of millisecond. The decay value is $2.250 - 2.085$ ms decreased with increment of Gd$_2$O$_3$ concentration. With larger number of Gd$^{3+}$ in glass network, Tb$^{3+}$ were induced to de-excite from $^5\text{D}_4$ level in shorter time. The possible explanation for this phenomenon is the back energy transfer from Tb$^{3+}$ to Gd$^{3+}$ induced by the two photon excitation of Gd$^{3+}$. The emitted photon with 542 nm from 2 Tb$^{3+}$ ions can be back transferred together to Gd$^{3+}$ for $^8\text{S}_7/2 \rightarrow ^6\text{I}_1$ excitation. The decay time of CaGdSiB:Tb$^{3+}$ glass is suitable for display and detector with integration mode.

![Figure 6. Luminescence decay curves and decay time of CaGdSiB:Tb glasses](image)

4. Conclusion
The addition of more Gd$_2$O$_3$ amount in to CaGdSiB:Tb$^{3+}$ glasses make glass to be heavier. The chemical units in glass network consist of BO$_3$, BO$_4$, Si-O-Si, and Si-O-B which were degraded under increment of Gd$_2$O$_3$ concentration due to glass modifier role of Gd$^{3+}$. Glass absorbs photon in visible light and near-infrared region. The 275 nm excitation of Gd$^{3+}$ can transfer to Tb$^{3+}$ for the strongest emission with 542 nm as green light. The absorbance and emission intensity of glasses did not show an observed relation with Gd$_2$O$_3$ content. However, glass with 22.5 mol% of Gd$_2$O$_3$ performs the highest emission intensity. The luminescence decay time of Tb$^{3+}$ was reduced with increasing of Gd$_2$O$_3$ concentration, possibly due to the back transfer from Tb$^{3+}$ to Gd$^{3+}$ induced by the two photon excitation of Gd$^{3+}$. Since strong green emission signal and millisecond decay time under Gd$^{3+}$ energy transfer, CaGdSiB:Tb$^{3+}$ glass with 22.5 mol% of Gd$_2$O$_3$ perform the potential for using as a scintillator for radiation detector with integration mode and a green light source medium.

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