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X-ray/proton and photoluminescence behaviors of Sm³⁺ doped highdensity tungsten gadolinium borate scintillating glass



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ABSTRACT

Sm-activated scintillating glasses with high WO₃ concentration up to 42.5 mol% were studied in this work. The effects of Sm₂O₃ concentration on the density, absorption and various (photo-, X-ray induced-, proton- and temperature dependent-) luminescence properties have been monitored. The glasses possess a high density with maximum value around 6.18 g/cm³. The glass samples show the several absorption peaks of visible light and near-infrared wavelength those confirm the Sm³⁺ ion existence in glass matrices. The Gd³⁺ \rightarrow Sm³⁺ energy transfer took place in glasses which resulted to the strongest emission around 600 nm ($^4G_{5/2} \rightarrow ^{6}H_{7/2}$) of Sm³⁺ in the photo-, X-ray induced- and proton luminescence spectra. The optimal doping concentration of Sm₂O₃ in WO₃-Gd₂O₃-B₂O₃ glass is 1.0 mol% that performed the highest emission intensity in these three types of luminescence spectra. In 1.0 mol% doped glass, the decay time under pulse X-ray excitation was analyzed and found to be 0.27 ms. The temperature dependent luminescence in a range of 10 K–300 K of 1.0 mol% doped glass was measured via UV-laser excitation. The emission intensity of glass increased 3.76 times with the temperature decrease. In this work, the fabricated WO₃-Gd₂O₃-B₂O₃ glasses doped with Sm₂O₃ show the strong visible luminescence under visible light, X-ray and proton excitation. The developed glass performs the potential for X-ray scintillator applications with integration mode using in the medical, industrial and security imaging inspection system.

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1. Introduction

The scintillating glass has been developed for several applications such as high energy physics, medical imaging, homeland security, astrophysics and radiochemistry in recent years [1,2]. Many researchers have tried to replace the single-crystal scintillator with a glass scintillator because the production cost of glass is lower than single-crystal. In a radiation detection system, the essential properties of a glass scintillator are good transparency, high density, high interaction cross-section, high efficiency to convert radiation energy into scintillation light, strong emission in the UV-visible region and high light yield [3,4]. The interesting glass that possesses most of these properties is tungsten gadolinium borated glass doped with lanthanide ion (Ln:WGB) [5]. The high transparency, good physical and chemical properties of this glass come from borate (B_2O_3) host component [4–7]. Furthermore, ¹⁰B can interact to thermal neutron with high capture cross-section [8,9] which is advantage for neutron scintillator. The high density/heavy weight of WGB glass are the results of tungsten oxide (WO_3) [10] assembled in glass. This property can cause the high interaction of glass component - radiation and the low magnitude of phonon vibration in glass structure. The gadolinium (Gd) compound also enhances the glass density and improves the glass-radiation interaction due to its high atomic number [3]. The ¹⁵⁵Gd and ¹⁵⁷Gd isotopes also possess the high capture cross-section for thermal neutron [4-6,10]. Furthermore, the Gd³⁺ ion can transfer the radiation energy to luminescence center such as lanthanide

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ions (Ln^{3+}) [1,4–6]. Due to these advantages, WGB glass is very suitable for using as a host of glass scintillator. Then, it was doped with one of Ln^{3+} , terbium ion (Tb^{3+}) , in our previous work [5]. Tb:WGB glass gave us the very impressive luminescence signal under the excitation by ultraviolet (UV), visible light, X-ray and electron. This is an evident that Tb:WGB glass can be used as a scintillation material. Therefore, it is very attractive to dope the other Ln^{3+} into WGB glass and researches its potential for using as a glass scintillator. Samarium ion (Sm^{3+}) is another one of Ln^{3+} that performs the orange emission around 600 nm with millisecond decay time [11–13]. This characteristic luminescence is suitable for a lamp, LED, laser device and even for a scintillation detector with integration mode used in the radiation imaging system.

In this work, we developed the Sm³⁺ doped tungsten gadolinium borate (Sm:WGB) glass scintillators to investigate their physics, structures, optics and several types of luminescence properties. These glasses were monitored the luminescence signal that responded to UV, X-ray and proton for analyzing the scintillation potential. The luminescence spectra of glasses also were studied in different temperature condition to study the thermal effect on this glass.

2. Experimental

The Sm:WGB glasses were synthesized by melt-quenching technique. The composition system of glasses are 42.5WO₃- $27.5Gd_2O_3-(30-x)B_2O_3-xSm_2O_3$ (where x = 0.0, 0.1, 0.5, 1.0 and 2.0 mol% referred as 0.0Sm:WGB. 0.1Sm:WGB. 0.5Sm:WGB. 1.0Sm:WGB and 2.0Sm:WGB) and 27.5Gd₂O₃-71.5B₂O₃-1Sm₂O₃ (Sm:GB). The high-purity raw compounds such as WO₃, Gd₂O₃, H₃BO₃ and Sm₂O₃ were mixed totally 10 g and contained in the alumina crucible. The batches were taken into the electrical furnace using 1200 °C temperature for 3 h to melt chemicals. Then, vitreous liquids were poured onto a 500 °C graphite mold. The quenched glasses were taken into the furnace for annealing at 500 °C for 3 h to reduce the thermal strain. After that, they were left in a furnace to cool down to the room temperature. All obtained glasses were cut and polished in 1.0 x 1.5×0.3 cm³ dimension for good transparency and suitability in the experiment. The structure of glasses were identified by X-ray diffraction (XRD) using a Shimadzu XRD-6100 diffractometer with Cu-K α radiation. The density (ρ) of the glasses were investigated by using the 4-digits microbalance (AND, HR-200) under Archimedes' principle with water as immersion liquid. The glasses molar volume (V_M) were evaluated by $V_M = M_T/\rho$ relation, where M_T is the total molecular mass of chemical composition in glass. The absorption spectra of glasses were monitored by UV-3600 Shimadzu spectrophotometer. The photoluminescence spectra and decay time were measured by Cary Eclipse fluorescence spectrophotometer with xenon lamp light source. The color of emission was determined by CIE 1931 chromaticity principle [14]. The temperature-dependent luminescence spectra, in the temperature range of 10-300 K, were monitored under excitation by a 266 nm laser from an UV solid state laser system (Changchun New Industries (CNI) Co, MPL-F 266). A copper cold finger was used to mount the glass samples and the fiber optic spectrometer (Ocean Optics, QE65000) was used to detect the spectra signal. The X-ray induced optical luminescence or radioluminescence spectra of glasses were measured by the instrumental setup designed by our research lab. The X-ray was generated with 50 kV and 30 mA power from Cu target X-ray generator (Inel, XRG3D-E) while the optical fiber and spectrometer (Ocean Optics, QE65 Pro) observed the emission signal. The radioluminescence decay curves were investigated under excitation of 20 ns X-ray pulsing source (Golden engineering, Inc, XR200). This X-ray energy was operated by high voltage power supply (QRTEC, models 566). Glass samples were attached on the PbWO₄ single crystal connected to PMT in the lead box. The PbWO₄ single crystal was used to protect the PMT from degradations by X-rays. This PbWO₄ possess low light yield (few hundreds photon/MeV) and very fast decay time (few ns), which is different from Sm³⁺ decay time (ms). Therefore, it is clear to separate the signal between our glass sample and PbWO₄ which displayed on the 1 GHz oscilloscope (LeCROY, models 610 zi). The proton luminescence (PTL) spectrum was studied at the Korea Institute of Radiological & Medical Sciences by the 50-MeV proton beam test facility.

3. Results and discussion

The Sm:WGB glasses were successfully obtained by a meltquenching preparation as shown in Fig. 1. From the visual observation, all glasses are yellow color and highly transparent.

The XRD result of the 1.0Sm:WGB glass is presented in Fig. 2 (a). The XRD pattern of ideal crystalline material is characterized by the well-defined Bragg peaks, while the ideal amorphous material is identified by the absence of Bragg peak. For 1.0Sm:WGB glass, its XRD pattern consists of two very board peaks with high noise. This result indicates that the dominant structure in Sm:WGB glass is an amorphous nature but it also shows the weak character of crvstalline structure in glass. Both broad diffraction peaks roughly correspond to the diffraction database (ICPDS 00-023-1076) of $Gd_2(WO_4)_3$ composition as also shown in Fig. 2 (a). It is probably an evident of the very short-range atomic ordering of crystalline $Gd_2(WO_4)_3$ structure which inserts in the glass network. Taki et al. explained the simultaneous existence of both [WO₄]²⁻ and [WO₆]⁶⁻ group in WGdB glass [10,15]. Tetrahedral [WO₄]²⁻ unit belongs to the inserted crystalline α -Gd₂(WO₄)₃ structure while the octahedral [WO₆]⁶⁻ unit is a part of glass network in WGdB glass. The freetungsten glass (Sm:GB) was also measured the XRD and its result is shown in Fig. 2 (a). In contrast to the glass with tungsten, the XRD pattern of Sm:GB glass is obviously absent of any Bragg peak which represents the complete amorphous structure. Therefore, it can be stated that the tungsten oxide is an important factor which cause the existence of weak crystalline structure in Sm:WGdB glass network.

In Fig. 2 (b), it exhibits the glass density and molar volume as a function of Sm₂O₃ concentrations. As the increment of Sm₂O₃ concentration (x) in 42.5WO₃-27.5Gd₂O₃-(30-x)B₂O₃-xSm₂O₃ glass system, the lightweight B₂O₃ component (69.62 g/mol) were more substituted by the heavy Sm₂O₃ dopant (348.72 g/mol) that results to an addition of glass total mass (m). From $\rho = m/V$ relation, the density then increases via increment of Sm₂O₃ concentration. For glass molar volume, it decreases with increment of Sm₂O₃ amount that exhibits more atomic compactness in glass network. This corresponds to the density increment of glass. The density of Sm:WGB glass is around 5.986–6.180 g/cm³ which is high compared to the other glass scintillators as exhibited in Table 1. High density of Sm:WGB glass performs the potential of good interaction with incoming radiation [3].

The absorption spectra of all Sm:WGB glasses are exhibited in Fig. 3 (a). There are obvious absorptions in the region of UV, visible



Fig. 1. The Sm:WGB glasses.



Fig. 2. (a) XRD result of Sm:GB and 1.0Sm:WGB glass and (b) density and molar volume of Sm:WGB glasses.

Table 1

The density of various glass scintillators.

Glass scintillator	Density (g/cm ³)
Sm:WGB [This work]	6.18
Tb:WGB [5]	6.15
Gd ₂ O ₃ -WO ₃ -H ₃ BO ₃ -Eu ₂ O ₃ [16]	5.84
La ₂ O ₃ -Gd ₂ O ₃ -ZrO ₂ -WO ₃ -H ₃ BO ₃ -SiO ₂ -Al ₂ O ₃ -Eu ₂ O ₃ [16]	5.68
B ₂ O ₃ -SiO ₂ -SiC-Al ₂ O ₃ -Gd ₂ O ₃ -CeF ₃ [17]	4.97
SiO ₂ -B ₂ O ₃ -BaO-Al ₂ O ₃ -Gd ₂ O ₃ -P ₂ O ₅ -Tb ₂ O ₃ -Sb ₂ O ₃ [18]	4.90
Gd ₂ O ₃ -SiO ₂ -H ₃ BO ₃ -Al ₂ O ₃ -CeCl ₃ [16]	4.74

light (VIS) and near infrared (NIR). The absorption shoulder in UV range, around 200–370 nm, belongs to the absorbing of host component confirmed by the spectrum of 0.0Sm:WGB glass. Sm³⁺ dopant possess the sharp absorption bands in VIS and NIR range with 403, 438, 475, 526, 562, 945, 1080, 1229, 1374, 1476, 1529, 1588 and 1974 nm wavelength corresponding to the energy transition from $^{6}H_{5/2}$ ground state to $^{6}P_{3/2}$, $^{4}G_{9/2}$, $^{4}I_{11/2}$, $^{4}F_{3/2}$, $^{4}G_{5/2}$, $^{6}F_{11/2}$, $^{6}F_{9/2}$, $^{6}F_{7/2}$, $^{6}F_{5/2}$, $^{6}F_{3/2}$, $^{6}H_{15/2}$ and $^{6}H_{13/2}$ upper state, respectively [11–13,19–21]. The blue light (403 nm and 475 nm) absorption of Sm³⁺ left the other visible-light to reflect from the glass. The mixing of reflected light, especially red and green light, results in the yellow color of Sm:WGB glass. It was found that the absorbance of those bands increases with addition of Sm₂O₃ concentration. It is

well known that the signature emission of Sm³⁺ is around 600 nm wavelength. Therefore, this wavelength was used to monitor the photoluminescence (PL) excitation spectra of Sm:WGB glass as represented in Fig. 3 (b). There are many excitation peaks in the spectra. The broad peak in a range of 250–335 nm represents the $O^{2-}-W^{6+}$ charge transfer (CT) that the electron in 2p shell of O^{2-} ion was excited and transferred to 5d shell of W^{6+} ion [5,6,22,23]. This broad peak of O²⁻-W⁶⁺ CT overlaps on the Gd³⁺ excitation peaks at 275 and 311 nm which correspond to the ${}^8S_{7/2} \rightarrow {}^6I_{7/2}$ and ${}^8S_{7/1}$ $_2 \rightarrow {}^{6}P_{7/2}$ transition, respectively [5,6]. To confirm the overlap between $O^{2^{-}}-W^{6+}$ CT peak and Gd^{3+} excitation peaks, the freetungsten Sm:GB glass was also investigated the excitation spectra as shown as pink line in Fig. 3 (b). Considering the excitation spectra, the broad peak of $O^{2^{-}}-W^{6^{+}}$ CT in free-tungsten glass disappears which lets the sharp excitation peaks of Gd^{3+} at 275 and 311 nm to be obvious. For Sm:WGB glass, the Gd³⁺ excitation peaks are also possibly exist but they are hidden under the board peak of $O^{2-}W^{6+}$ CT. This phenomena was similarly found in Tb:WGB glass of our previous work [5]. The presences of $O^{2-}-W^{6+}$ CT and Gd^{3+} excitation peaks are an evidence of energy transfer process from the host component to the Sm³⁺ luminescence center. The other strong excitation peaks at 345, 362, 376, 403, 417, 438, 465, 476, 501, 526 and 562 nm wavelength correspond to the 4f - 4f Sm^{3+} transition of ${}^{6}H_{5/2} \rightarrow {}^{4}K_{15/2}$, ${}^{4}L_{17/2}$, ${}^{6}P_{5/2}$, ${}^{6}P_{3/2}$, ${}^{4}P_{5/2}$, ${}^{4}G_{9/2}$, ${}^{4}I_{13/2}$, ${}^{4}I_{11/2}$, ${}^{4}G_{7/2}$, ${}^{4}F_{3/2}$ and ${}^{4}G_{5/2}$, respectively [11–13,19–21].The strongest



Fig. 3. (a) Absorption spectra and (b) excitation spectra of the Sm:WGB and Sm:GB glasses.

excitation peak centers at 403 nm (${}^{6}H_{5/2} \rightarrow {}^{6}P_{3/2}$ of Sm³⁺) and the highest luminescence intensity belongs to 1.0Sm:WGB glass.

Sm:WGB glasses were excited by photons with 275, 311 and 403 nm wavelength to measure the PL emission spectra. The excitation wavelength at 275 and 311 nm was intently used to study the energy transfer, $Gd^{3+} \rightarrow Sm^{3+}$ and $O^{2-}W^{6+} \rightarrow Sm^{3+}$, respectively which result in the Sm^{3+} luminescence. These energy transfer phenomena are the important process in the radiation detection applications. For the excitation wavelength at 403 nm, it was intently used to study the luminescence under direct excitation (down-conversion) of Sm^{3+} . The emission spectra under these three excitations perform the similar pattern of four sharp emission peaks as presented in Fig. 4 (a), (b) and (c). The band at 564 nm, 600 nm, 646 nm and 707 nm assigns to the Sm^{3+} transition, ${}^4G_{5/2}$, ${}^{6}H_{7/2}$, ${}^{6}H_{9/2}$ and ${}^{6}H_{11/2}$, respectively [11–13,19–21]. Moreover, the emission spectra under 275 nm excitation in Fig. 4 (a) exhibit the small additional emission peak around 311 nm

that represents the ${}^{6}P_{7/2} \rightarrow {}^{8}S_{7/2}$ transition of Gd³⁺. The emission intensity of this Gd³⁺ peak decreases while ones of Sm³⁺ peaks increase, with increment of Sm₂O₃ concentration from 0.0 to 1.0 mol%. This is an evidence to confirm that energy more transfer from Gd³⁺ to Sm³⁺ with increasing Sm₂O₃ amount in glass. The emission intensity of Sm³⁺ peaks decrease if the Sm₂O₃ concentration is higher than 1.0 mol% as exhibited in Fig. 4 (d). It is the concentration quenching effect that was found in the emission spectra under all three excitations. The mechanism of energy transitions in photoluminescence emission spectra are explained in Fig. 5. The excitation by UV with 275 nm rose the Gd³⁺ energy state from ${}^{8}S_{7/2}$ to ${}^{6}I_{7/2}$. Then, Gd³⁺ dropped from ${}^{6}I_{7/2}$ to ${}^{6}P_{7/2}$ tate by non-radiative relaxation (NR). The next process of Gd³⁺ can be separated in 2 routes. Some Gd³⁺ ions decayed from ${}^{6}P_{7/2}$ to ${}^{8}S_{7/2}$ ground state by releasing the photon with 311 nm, while the other ones transferred the energy to Sm³⁺. The Sm³⁺ acceptor then reduced its state by NR to ${}^{4}G_{5/2}$ luminescence level. Later, Sm³⁺



Fig. 4. Emission spectra of the Sm:WGB glasses (a) with 275 nm excitation wavelength (Gd^{3+} excitation), (b) with 311 nm excitation wavelength ($O^{2-}W^{6+}$ CT), (c) with 403 nm excitation wavelength (direct Sm³⁺ excitation) and (d) the intensity of 600 nm emission as a function of Sm₂O₃ concentration.



Fig. 5. Energy level diagram of Gd^{3+} and Sm^{3+} in the Sm:WGB glasses for photoluminescence emission spectra.

took the transition from ${}^{4}G_{5/2}$ level to ${}^{6}H_{5/2}$, ${}^{6}H_{7/2}$, ${}^{6}H_{9/2}$ and ${}^{6}H_{11/2}$ level by emitting the visible light with 564, 600, 646 and 707 nm, respectively. For the excitation by UV with 311 nm, it possibly made the process of Gd^{3+} excitation and $O^{2-}W^{6+}$ charge transfer. If this photon excited Gd^{3+} , it lifted the Gd^{3+} state up from ${}^{8}S_{7/2}$ to ${}^{6}P_{7/2}$ and the energy then transferred to Sm^{3+} . After that, the 4 emissions of Sm³⁺ occurred similarly with emissions under 275 nm excitation. If UV with 311 nm excited the 2p electron of O²⁻ to transfer to 5d shell of W^{6+} [5,22], the energy produced from this CT process then migrated to Sm³⁺. Those 4 emissions subsequently occurred under Sm³⁺ radiative transitions. For the excitation by light with 403 nm, it lifted the Sm³⁺ from ground ${}^{6}H_{5/2}$ to ${}^{6}P_{3/2}$ state and Sm³⁺ then changed the state down to ${}^{4}G_{5/2}$ by NR. The Sm^{3+} ion emitted the light with 4 wavelengths from ${}^{4}G_{5/2}$ level similarly to the emissions under 275 and 311 nm excitation. Compare the emission spectra between these three excitations, the emission under 403 nm excitation wavelength perform the highest intensity because Sm³⁺ were directly excited.

The PL emission spectra of 1.0Sm:WGB glass were chosen to analyze the color of emitted light by using CIE 1931 chromaticity. The color coordinates (x, y) were calculated from the spectra data and plotted into the CIE 1931 chromaticity diagram as exhibited in Fig. 6 (a). The coordinate of emission under 275, 311 and 403 nm excitation wavelength is same as (0.59, 0.40) which locate on the orange color region. To proof the color of emission by real human vision, all Sm:WGB glasses were excite by UV lamp and taken a photograph of emitted light as shown in Fig. 6 (a). All glasses perform the obvious orange emission.

The PL decay curves of Sm³⁺ were measured with 600 nm emission and 275 nm excitation wavelength. These curves are presented in Fig. 6 (b) and were fitted with the general exponential decay equation to evaluate the luminescence decay time (τ). The obtained τ values are 1.244, 0.957, 0.695 and 0.414 ms for 0.1Sm:WGB, 0.5Sm:WGB, 1.0Sm:WGB and 2.0Sm:WGB glass, respectively. The non-single exponential decay behavior and the decay time reduction via Sm₂O₃ increment are the results of Sm³⁺- Sm³⁺ energy transfer called "cross relaxation (CR)". This CR phenomena is often identified by The Inokuti Hirayama (IH) model [14] with relation

$$I(t) = I_0 \exp\left\{-\frac{t}{\tau_0} - Q\left(\frac{t}{\tau_0}\right)^{3/S}\right\}$$
(1)

where τ_0 is the decay time of glass with the lowest concentration of luminescence dopant (in this work, $\tau_0 = 1.244$ ms), Q is the energy transfer parameter and S is IH parameter. The S value can be 6, 8 and 10 depending on the type of CR process, which consists of dipole - dipole, dipole - quadrupole and quadrupole - quadrupole interaction, respectively [14.24]. The exponential decay curves of 0.5Sm:WGB. 1.0Sm:WGB and 2.0Sm:WGB glasses were fitted with an equation (1) by using different S value as 6, 8 and 10. It was found that S = 6 condition resulted to the best fit with the highest R² value as 0.992, 0.994 and 0.987 for 0.5Sm:WGB, 1.0Sm:WGB and 2.0Sm:WGB glass, respectively. The fitted lines are shown as black solid line in Fig. 6 (b). Therefore, the CR between Sm³⁺ donor and Sm^{3+} acceptor in glass is a dipole – dipole interaction. Additionally, the result of IH fitting performs the Q value that relates to the energy-transfer probability between Sm³⁺ ions. The Q value is 0.350, 0.718 and 1.370 for 0.5Sm:WGB, 1.0Sm:WGB and 2.0Sm:WGB glass, respectively. This means the probability of CR between Sm³⁺ ions increase with the addition of Sm₂O₃ concentration in glass. Since Sm:WGB glass performs the strong orange emission in millisecond decay time, it can be used for the light source applications such as laser, LED and display. Moreover, this glass also exhibits the Gd³⁺-Sm³⁺ energy transfer which is a potential for using as the radiation detection material operated with integration mode.

Since 1.0Sm:WGB glass showed the highest PL emission intensity, it was selected to study the temperature dependent luminescence (TDL). The TDL results in 10-300 K temperature range of 1.0Sm:WGB glass under 266 nm laser excitation are exhibited in Fig. 7. There are 4 emissions at 565, 602, 650 and 710 nm wavelength those are attributed to the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$, ${}^{6}H_{7/2}$, ${}^{6}H_{9/2}$ and ${}^{6}H_{7/2}$ transition of Sm³⁺, respectively [11–13,19–21]. The pattern of these emission in TDL spectra are similar to PL emission spectra via excitation at 275, 311 and 403 nm. The intensity of 602 nm emission peak (${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$) with temperature dependence is presented in the inset figure of Fig. 7 (a). It indicates the luminescence thermalquenching, the emission intensity decreases with increment of temperature. The intensity at 10 K is around 3.76 times of one at 300 K. The explanation of this quenching is the increment of phonon number in glass network via temperature rising [25,26]. The phonon is a structure vibration that its strength and number increase with increment of temperature [27]. The Sm³⁺ ion can change the state from luminescence level ${}^{4}G_{5/2}$ to lower state by using one of the two process. Some Sm³⁺ ions used the radiative transition (emitted the light), while the other ones used NR process (didn't emitted the light). The existence of NR process such as the multi-phonon relaxation (MPR) reduces the total emission intensity. For Sm^{3+} , the energy gap between the ${}^{4}\text{G}_{5/2}$ level and its first lower state (${}^{6}F_{11/2}$) is around 7,212 cm⁻¹ (calculated from the absorption spectra). If the total phonon energy (E_t) is higher than or equal to 7,212 cm⁻¹, Sm³⁺ possibly change the state from ${}^{4}G_{5/2}$ down to ${}^{6}F_{11/2}$ level under the MPR process. The E_t can be defined from relation, $E_t = n_{ph} \, \times \, E_{ph}$, where n_{ph} is the average phonon number and E_{ph} is the phonon energy of host glass. In our previous work, the Eu^{3+} ion doped tungsten gadolinium borate glasses (Eu:WGB) was studied in the excitation spectra [6]. The E_{ph} of WGB glass, around 816 cm⁻¹, can be evaluated by the different energy between phonon side band (PSB) and pure electronic transition (PET) of Eu^{3+} in the adapted excitation spectra in Fig. 7 (b). At the absolute zero temperature with absence of the phonon $(n_{ph} = 0)$, the MPR process doesn't occur that results to the maximum total emission intensity from Sm³⁺. If the temperature increases until the average phonon number $n_{ph} \ge 8.84 \ (= 7,212 \ cm^{-1}/816 \ cm^{-1})$, some Sm^{3+} ions will relax down from ${}^{4}\text{G}_{5/2}$ level by the MPR process. It results to the reduction of total emission intensity called thermal-quenching. Then, the luminescence intensity decreases



Fig. 6. (a) 1931 CIE chromaticity diagram for emission of the 1.0Sm:WGB glass under 275, 311 and 403 nm excitation wavelength and photograph of orange emission for all glasses under UV lamp excitation, (b) PL decay curves of the Sm:WGB glasses for 600 nm emission with 275 nm excitation wavelength. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 7. (a) TDL spectra of 1.0Sm:WGB glass and (b) the adapted excitation spectrum of 2.0Eu:WGB glass from previous work [6].

with increment of temperature. This result is probably beneficial for some photonic applications of glass operated in the low temperature environment.

The Radioluminescence (RL) results of the Sm:WGB glasses are presented in Fig. 8 (a). All glasses were irradiated with X-ray from 50 kV to 30 mA power source. The Sm:WGB glasses exhibit 4 obvious emissions at 564, 602, 648 and 708 nm corresponding to the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$, ${}^{6}H_{7/2}$, ${}^{6}H_{9/2}$ and ${}^{6}H_{7/2}$ transition of Sm³⁺, respectively [12–14,20–22]. The peak positions and the intensity variation of these 4 emission peaks are close to PL and TDL spectra. However, the strongest emission wavelength of RL is around 647 nm (${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$) that is different from PL and TDL spectra due to the different excitation energy (wavelength). The RL intensity rises with increment of Sm₂O₃ concentration until 1.0 mol% and it quenches with higher than this concentration. The mechanism of RL process started when X-ray was incident to the component of glass. The X-ray energy then excited electrons which

generated the electron-hole pairs in glass sample. The electron hole pairs were bound in the exciton state. Some electron holepairs then could transported and recombined together at the self trap excitons (STE). This STE probably associated with the defect, rapture of the chemical bond and molecular energy state of the chemical group in glass network [28,29]. The electron-hole recombination at STE could release the energy in form of the lumimescence. However, this luminescence from STE (luminescence of host) didn't appeared in the RL luminescence spectra due to the 2 possible reasons. The first one is the low-intensity emission from STE or out of the range of detection, that the detector device couldn't measure. For the second reason, the emitted photon from STE was incident and absorbed by the Gd^{3+} and Sm^{3+} in glass. Some Gd³⁺ ions those absorbed photons transferred the energy to Sm³⁺ [30]. The Sm³⁺ ion acceptors, which recieved the energy from host component or from Gd³⁺, then relaxed by NR process to the ${}^{4}G_{5/2}$ luminescence level. Later, Sm $^{3+}$ emitted the photons with 4



Fig. 8. (a) RL spectra of Sm:WGB glasses and (b) RL decay curve of 1.0Sm:WGB glass.

wavelengths under 4 transitions from ${}^{4}G_{5/2}$ level similarly to the PL and TDL. The RL decay curve of the 1.0Sm:WGB glass is presented in Fig. 8 (b). The double-exponential decay relation, $I(t) = A_1 exp(-t/\tau_1) + A_2 exp(-t/\tau_2) + I_0$, was fitted with this decay curve. From fitting, the fast (τ_1) and slow (τ_2) luminescence decay time is 0.020 and 0.268 ms, respectively. The τ_1 value possibly belongs to the luminescence of PbWO₄ crystal which is in the range of nanosecond. It is faster than the decay time of Sm³⁺ doped glass (in the range of millisecond). The τ_2 value is in the millisecond order that is similar to the PL decay time of Sm³⁺. The strong luminescence spectra and short decay time under X-ray excitation shows the potential of Sm:WGB glass for X-ray detector applications with integration mode, such as in the radiation imaging system.

To confirm the proton scintillation property of the Sm:WGB glass, we irradiated 1.0Sm:WGB glass with proton beam to measure the PrL spectrum as shown in Fig. 9. The 4 emission wavelengths of Sm³⁺ in the PrL spectrum are 560 (${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$), 600 (${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$), 650 (${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$) and 750 (${}^{4}G_{5/2} \rightarrow {}^{6}H_{1/2}$) nm [11–13,19–21]. The overall patterns, peak position and intensity variation, of the PrL spectrum are close to the RL spectra. The strongest emission wavelength is 650 nm. The sharp emission bands in the PrL spectrum represent the interesting ability of Sm:WGB glass that can convert the energy of proton to be visible light.



Fig. 9. PrL spectrum of 1.0Sm:WGB glass.

4. Conclusion

The Sm:WGB glasses were synthesized by melt-quenching method. Glasses in this work are very heavy with density up to 6.18 g/cm³. They absorb photons in UV, VIS and NIR region. For photoluminescence, the Gd^{3+} - Sm^{3+} energy transfer, $O^{2-}W^{6+}$ charge transfer and Sm^{3+} 4f-4f transition resulted to the strongest emission around 600 nm of Sm³⁺ (${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$) under UV and VIS excitation. In the radioluminescence and proton luminescence, the emission patterns are nearly identical with ones of the photoluminescence, but the strongest emission is centered at 647 and 650 nm wavelength (${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$). The optimal concentration of Sm₂O₃ in WO₃-Gd₂O₃-B₂O₃ glass is 1.0 mol% that performs the highest emission intensity in photoluminescence and radioluminescence spectra. The photoluminescence decay time of Sm³⁺ is in millisecond which is close to the slow decay time component of radioluminescence. The emission intensity of glass decreases with temperature rising under the thermal quenching effect. Sm:WGB glass could be used as a X-ray detection material in imaging inspection system, medical diagnosis, industry defect inspection and security check.

CRediT authorship contribution statement

N. Wantana: Writing - original draft, Formal analysis, Visualization. **E. Kaewnuam:** Formal analysis, Investigation, Investigation. **H.J. Kim:** Supervision. **S.C. Kang:** Formal analysis. **Y. Ruangtaweep:** Conceptualization. **S. Kothan:** Funding acquisition, Investigation. **J. Kaewkhao:** Conceptualization, Investigation, Writing - review & editing, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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