Scintillation Properties of Non-doped and Pr-doped BaO–B₂O₃–SiO₂ Glasses and Glass-ceramics

Noriaki Kawaguchi,¹* Hirokazu Masai,² Masaki Akatsuka,¹ Daisuke Nakauchi,¹ Takumi Kato,¹ and Takayuki Yanagida¹

¹Nara Institute of Science and Technology, 8916-5 Takayama-cho, Ikoma, Nara 630-0192, Japan
²National Institute of Advanced Industrial Science and Technology, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

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We have studied the scintillation properties of non-doped and Pr-doped BaO–B₂O₃–SiO₂ glasses and glass-ceramics. The glass transition temperature (T_g), the temperature of crystallization onset (T_x), and the crystallization peak (T_p) were determined by differential thermal analysis. The glass-ceramics were obtained by heating at three different temperatures (T_g + 50 °C, T_x, and T_p). We confirmed that the X-ray diffraction peaks can be ascribed to the BaSiO₃ crystalline phase in the glass-ceramic samples. In the X-ray-induced scintillation spectra, we observed the intrinsic luminescence of the host glass and luminescence due to the 4f–4f transition of Pr³⁺ ions. In addition, the 1% Pr-doped BaO–B₂O₃–SiO₂ glass-ceramic with heating at T_g + 50 °C clearly showed luminescence in the wavelength range from 250 to 350 nm under X-ray excitation. Its photoluminescence (PL) decay time was estimated to be 26.28 ns and its luminescence is considered to be due to the 5f–4f transition of Pr³⁺ ions.

1. Introduction

Radiation detectors and dosimeters are widely utilized for medical, industrial, and scientific applications. Whereas radiation detectors can immediately detect ionizing radiation, dosimeters can record the information of radiation doses over a certain period of time. Some radiation detectors and dosimeters use phosphor materials such as scintillators and dosimetric materials. Scintillators¹–⁶ are materials that emit light in response to incident ionizing radiation and are widely used for non-destructive inspection,⁷,⁸ medical imaging,⁹ and well logging¹⁰,¹¹ applications using ionizing radiation. The properties required for scintillators are a high light yield, a fast decay time, and a high effective atomic number. Dosimetric materials¹² can be classified into three types: thermoluminescence (TL),¹³ optically stimulated luminescence (OSL),¹⁴,¹⁵ and radio-photoluminescence (RPL)¹⁶–¹⁸ materials. The main properties required for dosimetric materials are a wide measurable range and human tissue equivalency.

There have been many studies on the properties of scintillators and dosimetric materials in the last several decades,²–⁶,¹² and research on both types of phosphor materials is still an
attractive topic. As recent studies on scintillators and dosimetric materials, single crystals,\(^{(19–31)}\) sintered ceramics,\(^{(32–37)}\) glasses,\(^{(38–43)}\) eutectics,\(^{(44,45)}\) plastics,\(^{(46)}\) and organic-inorganic hybrid materials\(^{(47)}\) have been reported. Among them, glass materials have the advantages of high transparency, formability, and chemical stability. The disadvantage of glass materials is their lower luminescence efficiency than those of single-crystalline materials. A possible method to improve the luminescence properties of glass materials is the crystallization of glasses.

Crystallized glasses can have high translucency and contain crystallites in their glass matrix, which are called glass-ceramics. They have optical, medical, electronic, and military applications and are also used in kitchenware. Although no glass-ceramics are widely used as scintillators and dosimetric materials, a few interesting studies have been performed. For example, the germanate glass-ceramic containing Bi\(_4\)Ge\(_3\)O\(_{12}\) crystallites,\(^{(48)}\) the fluorophosphate glass-ceramic containing CeF\(_3\) crystallites,\(^{(49)}\) oxyfluoride glass-ceramics containing CaF\(_2\):Eu crystallites,\(^{(50,51)}\) and oxyfluoride glass-ceramics containing CeBr\(_3\) crystallites\(^{(52)}\) have been studied. Our group is also focusing on glass-ceramics as scintillators and dosimetric materials, and we have already shown an increase in the scintillation and TL intensities of 20SrO-20BaO-40Nb\(_2\)O\(_5\)-20P\(_2\)O\(_5\) glass upon its crystallization.\(^{(53)}\) However, there have been relatively few studies on glass-ceramic scintillators and dosimetric materials compared with those on single-crystalline materials, and further studies on glass-ceramic materials are desirable.

In this study, we focus on glass-ceramics containing Pr-doped BaSiO\(_3\) crystallites for scintillator applications. Since Ba is a heavy element, it is expected that Ba-rich glasses can exhibit a high effective atomic number. Furthermore, luminescence due to the 5d–4f transitions of Pr\(^{3+}\) ions can show a fast decay time. Because it is difficult to obtain transparent 50BaO-50SiO\(_2\) glass with the stoichiometric chemical composition of BaSiO\(_3\), we added a small amount of B\(_2\)O\(_3\). Therefore, the compositions of non-doped and Pr-doped 47.5BaO-5B\(_2\)O\(_3\)-47.5SiO\(_2\) glasses and glass-ceramics were investigated.

2. Materials and Methods

Non-doped and Pr-doped 47.5BaO-5B\(_2\)O\(_3\)-47.5SiO\(_2\) glasses (hereinafter referred to as BaO–B\(_2\)O\(_3\)–SiO\(_2\) glasses) were prepared using a conventional melt-quenching method. The Pr ions were doped with 0.1, 0.5, and 1 mol% of the total amount of cations. High-purity Pr\(_6\)O\(_{11}\) (99.9%), BaCO\(_3\) (99.95%), B\(_2\)O\(_3\) (99.9%), and SiO\(_2\) (99.999%) powders were used as starting materials. The powders were mixed and loaded into a platinum crucible, then melted at 1600 °C for 30 min using an electric furnace under ambient atmosphere. The melt was quenched on a stainless steel plate maintained at 200 °C.

Small pieces were taken from the obtained glasses and used for differential thermal analysis (DTA) measurements. The DTA curves of the non-doped and Pr-doped BaO–B\(_2\)O\(_3\)–SiO\(_2\) glasses were measured at a heating rate of 10 °C/min using a DTA measurement system (Thermo plus EVO2/TG-DTA8120; Rigaku, Akishima, Japan). The glass transition temperature (\(T_g\)), the temperature of crystallization onset (\(T_x\)), and the crystallization peak (\(T_p\)) of each glass were determined from the obtained DTA curves using the data analysis software for Thermo plus EVO2/TG-DTA8120.
The glass pieces that were not used for DTA measurements were annealed at $T_g$ under ambient atmosphere for stress relaxation. The annealed glasses were cut into pieces of approximately $10 \times 10 \times 1 \text{ mm}^3$ and mechanically polished. The obtained glass pieces were individually heated at three different temperatures ($T_g + 50 \degree C$, $T_x$, and $T_p$) in ambient atmosphere with a holding time of 3 h to induce the nucleation and growth of crystallites using the electric furnace.

The crystalline phases of the samples were identified by X-ray diffraction (XRD). The XRD patterns of the samples were measured using an X-ray diffractometer equipped with a Cu-Kα X-ray source (MiniFlex600; Rigaku). Crystal phases were identified using the Powder Diffraction File (PDF) from the International Centre for Diffraction Data (ICDD). To investigate the optical properties, diffuse transmittance spectra of the samples were measured using a UV-VIS-NIR spectrophotometer (SolidSpec-3700; SHIMADZU, Kyoto, Japan) across the spectral range from 200 to 800 nm. Backscattered electron images were obtained using a desktop scanning electron microscope (JCM-6000Plus; JEOL, Akishima, Japan) to observe the microstructures of the samples.

To investigate the scintillation properties, X-ray-induced scintillation spectra of the samples were measured using our customized setup comprising an X-ray generator, an optical fiber, and a spectrometer, as described in detail elsewhere. X-rays were irradiated to the samples from the X-ray generator (XRB80P&N200X4550; Spellman High Voltage Electronics, New York, United States), and then emissions from the samples were guided to the monochromator (Shamrock 163; Andor Technology, Belfast, UK) with a CCD-based spectrometer (DU920-BU2NC; Andor Technology). The X-ray generator was operated with a tube voltage of 80 kV and a tube current of 1.2 mA. In addition, we measured the photoluminescence (PL) decay curve of the 1% Pr-doped sample heated at $T_g + 50 \degree C$ using a fluorescence lifetime spectrometer (Quantaurus-Tau C11367; Hamamatsu Photonics, Hamamatsu, Japan) to consider the origin of scintillation in the UV range.

3. Results and Discussion

Figure 1 shows the DTA curves of the non-doped and Pr-doped BaO–B$_2$O$_3$–SiO$_2$ glasses. Exothermic peaks due to glass crystallization were clearly observed. The DTA curves are shown with two different scales because the exothermic peaks were high. The crystallization peak was strong because these compositions were easily crystallized. This is consistent with the fact that the transparent 50BaO-50SiO$_2$ glass was difficult to obtain. Although we added a small amount of B$_2$O$_3$ to obtain the transparent glasses, the samples still showed strong peaks due to glass crystallization.

The $T_g$, $T_x$, and $T_p$ values were determined from the DTA curves. $T_g$ and $T_x$ are shown in Fig. 1(a) and $T_p$ is shown in Fig. 1(b). The $T_g$ value was determined as the temperature of the intersection between the tangent line to the initial baseline and that to the first slope. Similarly, the $T_x$ value was determined as the temperature of the intersection between the tangent line to the gentle slope before the exothermic peak due to glass crystallization and that to the rising slope of this exothermic peak. The $T_p$ value was determined as the temperature of this exothermic peak. Table 1 shows the thermal properties of the non-doped and Pr-doped BaO–B$_2$O$_3$–SiO$_2$
glasses. $T_g$, $T_x$, and $T_p$ of the non-doped BaO–B$_2$O$_3$–SiO$_2$ glass were 623, 710, and 726 °C, respectively. The glass with the highest Pr-doping concentration (the 1% Pr-doped BaO–B$_2$O$_3$–SiO$_2$ glass) showed $T_g$, $T_x$, and $T_p$ of 622, 715, and 738 °C, respectively. It was revealed that $T_g$ of the samples did not depend on the Pr-doping concentration. In contrast, $T_x$ and $T_p$ increased with increasing Pr-doping concentration. Since $\Delta T (= T_x - T_g)$ increased with increasing Pr-doping concentration, Pr doping seemed to slightly contribute to the increased thermal stability of the BaO–B$_2$O$_3$–SiO$_2$ glass upon crystallization.

Figure 2 shows the appearance of the non-doped and Pr-doped BaO–B$_2$O$_3$–SiO$_2$ glasses and glass-ceramics. All the samples were transparent or translucent. Since all the samples were successfully cut and polished to a size of approximately $10 \times 10 \times 1$ mm$^3$ with no visible large cracks, the annealing temperatures were considered to be suitable. The non-heated samples showed high transparency and a green color due to Pr doping. In addition, the heated samples were opaque, possibly due to scattering centers. The samples heated at higher temperatures became more opaque. The samples obtained with heating at $T_x$ and $T_p$ were more opaque than those heated at $T_g + 50$ °C; however, no difference between the opacities of the samples heated to $T_x$ and $T_p$ was visually observed.

The crystalline phases of the samples were determined by XRD. Figure 3 shows XRD patterns of the non-doped and 1% Pr-doped BaO–B$_2$O$_3$–SiO$_2$ glasses and glass-ceramics.
Fig. 2. (Color online) Non-doped and Pr-doped BaO–B₂O₃–SiO₂ glasses and glass-ceramics.

Fig. 3. (Color online) XRD patterns of (a) non-doped and (b) 1% Pr-doped BaO–B₂O₃–SiO₂ glasses and glass-ceramics.

Whereas the XRD patterns of the non-heated glass samples only showed halo patterns, the heated glass-ceramic samples showed XRD peaks ascribed to the BaSiO₃ phase (ICDD, PDF No. 26-1402) as shown in the figure. No significant differences in the crystalline phases were observed between the non-doped and 1% Pr-doped samples, and no Pr-related crystalline phases were observed. It is possible that the Pr element was contained in both the glass matrix and the BaSiO₃ crystallites. None of the XRD patterns of the heated samples showed clear halo peaks. However, it is possible that the XRD patterns of the weak halo peaks overlapped because the intensities of the halo patterns produced by the BaO–B₂O₃–SiO₂ glasses were significantly lower than those produced by the BaSiO₃ crystalline phases.
Figure 4 shows the diffuse transmittance spectra of the samples. The Pr-doped samples showed absorption bands of Pr$^{3+}$ ions at around 450 and 600 nm. Furthermore, the samples heated at higher temperatures showed lower transmittance due to the scattering by BaSiO$_3$ crystallites. Here, Rayleigh scattering, which is scattering by particles with a small size compared with the wavelength of visible light, should be considered. Assuming independent spherical particles, the scattering cross section $\sigma_s$ given by Rayleigh can be written as

$$\sigma_s \propto \frac{\alpha^6}{\lambda^4},$$

where $\lambda$ is the wavelength and $\alpha$ is the radius of the scattering material. In the case of glass-ceramics, the scattering material is the crystallites contained in the glass. If $\alpha$ is not sufficiently smaller than $\lambda$, then glass-ceramics are not transparent in the short-wavelength range. Here, we confirmed a significant decrease in the diffuse transmittance of the samples in the short-wavelength range, which was due to Rayleigh scattering by the crystallites.
Furthermore, the samples obtained with heating at \( T_g + 50 \, ^\circ\text{C} \) tended to show higher transmittance than the samples obtained with heating at \( T_x \) and \( T_p \). In particular, this tendency was clearly confirmed in the 1% Pr-doped BaO–B\(_2\)O\(_3\)–SiO\(_2\) glass-ceramics. Figure 5 shows backscattered electron images of the 1% Pr-doped BaO–B\(_2\)O\(_3\)–SiO\(_2\) glasses obtained with heating at \( T_g + 50 \), \( T_x \), and \( T_p \). It was observed that the 1% Pr-doped BaO–B\(_2\)O\(_3\)–SiO\(_2\) glass-ceramic obtained with heating at \( T_g + 50 \, ^\circ\text{C} \) had fewer grains than the other samples. This is the reason why the 1% Pr-doped BaO–B\(_2\)O\(_3\)–SiO\(_2\) glass-ceramic showed relatively high transmittance.

Figure 6 shows X-ray-induced scintillation spectra of the samples. All the non-doped samples showed a similar broad emission band from 300 to 600 nm, which is considered to have originated from the intrinsic luminescence of the host glass. In general, intrinsic luminescence can be observed in non-doped oxide glasses. As the origin of such intrinsic luminescence, for example, the luminescence related to radiative annihilation of the self-trapped excitons and the luminescence due to the recombination of electrons with O\(^-\) hole centers have been considered.\(^{(56)}\) The Pr-doped samples showed emission peaks at around 450, 500, and 600 nm, overlapping with the broad emission from 300 to 600 nm. These peaks are considered to originate from the 4f–4f transition of Pr\(^{3+}\) ions. The scintillation intensities of the samples obtained with heating at \( T_x \) and \( T_p \) tended to be lower than those of the non-heated samples. This is consistent with the decrease in the transmittances of the samples obtained with heating at \( T_x \) and \( T_p \). Although the scintillation intensities of glasses can be sometimes enhanced by crystallization,\(^{(53)}\) the effect of a decrease in transmittance seems to be dominant in this study. Furthermore, some of the heated Pr-doped samples showed a broad emission band from 250 to 350 nm, which was not observed in the non-doped and non-heated samples. This was particularly apparent in the 0.5 and 1% Pr-doped BaO–B\(_2\)O\(_3\)–SiO\(_2\) glass-ceramics obtained with heating at \( T_g + 50 \, ^\circ\text{C} \). These samples also showed relatively high transmittance in the short wavelength range as shown in Fig. 4. The clear observation of this emission band is considered to be due to their higher transparency in the short wavelength range compared with the other heated samples. Moreover, we propose that its origin was the emission from Pr-doped BaSiO\(_3\) because it was clearly observed only in the heated Pr-doped samples.

Figure 7 shows the PL emission and excitation spectra of the 1% Pr-doped BaO–B\(_2\)O\(_3\)–SiO\(_2\) glass-ceramic obtained with heating at \( T_g + 50 \, ^\circ\text{C} \), the 1% Pr-doped BaO–B\(_2\)O\(_3\)–SiO\(_2\) glass, and...
the non-doped BaO–B₂O₃–SiO₂ glass. The non-doped BaO–B₂O₃–SiO₂ glass clearly showed a shorter excitation wavelength and a longer emission wavelength than those of the other samples. Their origin was considered to be the excitation and emission bands of the intrinsic luminescence in the BaO–B₂O₃–SiO₂ glass.
The emission peaks of the 1% Pr-doped BaO–B₂O₃–SiO₂ glass and 1% Pr-doped BaO–B₂O₃–SiO₂ glass-ceramic obtained with heating at \( T_g + 50 \) °C were around 300 and 290 nm, respectively. Since their excitation spectra seem to have two components, we fitted the excitation spectra to the sum of two Gaussian functions. Whereas the excitation spectrum of the non-heated 1% Pr-doped BaO–B₂O₃–SiO₂ glass had components with peaks at 240.0 and 257.6 nm, that of the 1% Pr-doped BaO–B₂O₃–SiO₂ glass-ceramic obtained with heating at \( T_g + 50 \) °C had components with peaks at 226.3 and 248.7 nm. Therefore, the glass-ceramic sample showed shorter emission and excitation wavelengths. These components appear to be due to the luminescence associated with the 5d–4f transition of Pr³⁺ ions because their emission wavelengths were shorter than the other emission peaks and the Stokes shifts were small. The difference in the emission and excitation wavelengths between the samples can also be explained because the emission and excitation wavelengths associated with the 5d–4f transition of Pr³⁺ ions generally depend on the host material, in contrast to those associated with the 4f–4f transition of Pr³⁺ ions. We believe that the shorter emission and excitation wavelengths originated from the 5d–4f transition of Pr³⁺ ions in the BaSiO₃ crystalline phase. To the best of our knowledge, the emission spectrum of Pr-doped BaSiO₃ in the wavelength range from 250 to 350 nm has not been reported; however, there has been a study on the broad emission band around 300 nm of Pr-doped CaSiO₃.(57) This similar oxide compound shows luminescence due to the 5d–4f transition of Pr³⁺ ions. Therefore, it is a possible explanation for the origin of the luminescence.

To discuss the origin of the luminescence on the basis of the decay time, the PL decay curve was measured. Figure 8 shows the PL decay curve of the 1% Pr-doped BaO–B₂O₃–SiO₂ glass-ceramic obtained with heating at \( T_g + 50 \) °C. In this experiment, the excitation and observation wavelengths were 280 and 310 nm, respectively (the shortest excitation wavelength of our PL spectrometer was 280 nm). The obtained decay curve was well fit by a triple exponential function. The estimated decay times were 1.610, 6.772, and 26.28 ns. The faster decay components of 1.610 and 6.772 ns were considered to be due to the instrumental response function (IRF). The decay time of 26.28 ns is a typical value for the 5d–4f transition of Pr³⁺ ions.(58) Because no other slower components were observed, this result seems to be consistent with the discussion of the PL emission and excitation spectra.

![PL decay curve](image.png)

**Fig. 8.** (Color online) PL decay curve of the 1% Pr-doped BaO–B₂O₃–SiO₂ glass-ceramic obtained with heating at \( T_g + 50 \) °C under an excitation wavelength of 280 nm and an observation wavelength of 310 nm.
Although samples with fast decay times can be useful for scintillator applications, the scintillation intensities of the samples in the wavelength range from 250 to 350 nm were low. Further studies are needed to increase the scintillation intensity of the Pr-doped glass-ceramics while maintaining the fast decay time.

4. Conclusions

The scintillation properties of non-doped and Pr-doped BaO–B₂O₃–SiO₂ glasses and glass-ceramics were studied. In the DTA curves of the non-doped and Pr-doped BaO–B₂O₃–SiO₂ glasses, we observed exothermic peaks due to glass crystallization and estimated the \( T_g \), \( T_x \), and \( T_p \) values. \( \Delta T (= T_x - T_g) \) of the 1% Pr-doped BaO–B₂O₃–SiO₂ glass was higher than that of the other samples. This result indicates that Pr doping improves the thermal stability of BaO–B₂O₃–SiO₂ glasses against crystallization. In the diffuse transmittance spectra of the samples, we observed a decrease in transmittance due to crystallization. BaSiO₃ crystalline phases were confirmed in the heated non-doped and Pr-doped BaO–B₂O₃–SiO₂ glasses by XRD. Among the glass-ceramics samples, those obtained with heating at \( T_g + 50 ^\circ C \) (the lowest heating temperature in this study) showed the highest transmittance. This is because the crystallization at \( T_g + 50 ^\circ C \) proceeded less than that at \( T_x \) and \( T_p \). This was confirmed by backscattered electron images.

In the X-ray-induced scintillation spectra, the heated and non-heated BaO–B₂O₃–SiO₂ glasses showed intrinsic luminescence in the wavelength range from 300 to 600 nm. The Pr-doped BaO–B₂O₃–SiO₂ glasses and glass-ceramics showed luminescence due to the 4f–4f transition of Pr³⁺ ions. The luminescence due to the 5d–4f transition of Pr³⁺ ions was also observed, particularly in the 0.5 and 1% Pr-doped BaO–B₂O₃–SiO₂ glass-ceramics obtained with heating at \( T_g + 50 ^\circ C \) because of its relatively high transmittance in the wavelength range from 250 to 350 nm. From the PL excitation and emission spectra, it was confirmed that these emissions at short wavelengths have small Stokes shifts, in contrast to the intrinsic luminescence of the non-heated BaO–B₂O₃–SiO₂ glass. From the PL decay curve of the 1% Pr-doped BaO–B₂O₃–SiO₂ glass obtained with heating at \( T_g + 50 ^\circ C \), a fast decay component of 26.28 ns was estimated in the short wavelength range. These results indicate that the emissions in the short wavelength range were due to the 5d–4f transition of Pr³⁺ ions. The scintillation intensity of this fast emission was not high; however, the decay time is suitable for scintillator applications. The results of this study indicate that the crystallization of glasses can generate new luminescent centers that are suitable for scintillators.

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