

# Photo- and Radioluminescence of ZnO-Precipitated Glass-Ceramics

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The photoluminescence (PL) and radioluminescence (RL) of ZnO-precipitated CaO-B<sub>2</sub>O<sub>3</sub>-ZnO-Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O-SiO<sub>2</sub> (CaBZAKS) glass-ceramics were examined. Surface crystallization with a certain crystal orientation was observed after heat treatment. A broad emission was observed in both the CaBZAKS glass and the glass-ceramics. The PL decay curves of the glass-ceramics indicate that decay constants are increased by the crystallization of ZnO. Because the scintillation and scintillation decay spectra obtained by X-ray irradiation are independent of the heat treatment conditions, scintillation mainly depends on the host matrix, whose emission decays consist of at least three components. On the other hand, an optically stimulated luminescence (OSL) with a stimulation of 1.97 eV shows that the OSL intensity, whose emission energy is the same as that of scintillation, increases with heat treatment temperature.

## 1. Introduction

Emissions of materials are generally classified into two categories: photoluminescence (PL: by UV-IR excitation) and radioluminescence (RL: by X-ray or  $\gamma$ -ray excitation).<sup>(1)</sup> In contrast to a conventional PL process in which one photon activates the emission center, higher energy excitation to far exceed the bandgap involves the generation of multi-photoelectrons in the RL process. Although the mechanism of the entire energy relaxation process in RL is not yet clarified, RL materials have actually been used as practical components in, for example, medical, security, and environmental monitoring applications.

In the RL process, in which visible photons are generated after an energy relaxation process, there are several types of luminescence, such as scintillation,<sup>(2,3)</sup> optically stimulated luminescence (OSL),<sup>(4,5)</sup> and thermally stimulated luminescence (TSL).<sup>(6)</sup> These

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luminescences are classified by the timescale of the emission or stimulation source, and their required characteristics are different. Therefore, it is important to examine various materials exhibiting emission properties.<sup>(7–12)</sup>

In the present study, we focus on the glass-ceramics as a bulk emitting material. Glass-ceramics, which are obtained by a suitable heat treatment of a mother glass, consist of amorphous and crystalline regions.<sup>(13)</sup> Because the precipitated crystallites can exhibit a unique property in the matrix, the glass-ceramics may show unique physical properties that originate from the precipitated crystallites. In the case of glass crystallization, the precipitated crystallites sometimes take a preferable orientation at the surface. Such a crystallization behavior is generally called surface crystallization,<sup>(14,15)</sup> which is the opposite of bulk crystallization of the glass.<sup>(16,17)</sup> It is suggested that both the precipitated crystallites and the residual amorphous region affect the RL behavior in which energy transfer from the host matrix is inherently included. Because there are few reports on the RL of glass-ceramics,<sup>(18)</sup> it is worthwhile to examine the RL properties of glass-ceramics.

As a precipitated crystal, we selected an oxide semiconductor, ZnO. Because of its unique properties, ZnO has been used in a number of applications,<sup>(19)</sup> including emission materials,<sup>(20)</sup> transparent conductive devices,<sup>(21)</sup> and so on. In the case of photo induced emission, both the sharp emission due to free excitons and the broad emission attributable to the oxygen vacancies of ZnO<sup>(22)</sup> are observed. Because ZnO belongs to the so-called “intermediate oxide group” that can form a glass network, the number of reports on ZnO crystallization in glass-ceramics is not very large. In 2006, transparent glass-ceramics, in which 5–20 nm ZnO nanocrystallites were selectively precipitated, were first reported.<sup>(23)</sup> Recently, we have succeeded in preparing ZnO glass-ceramics by the heat treatment of CaO-K<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-ZnO-Al<sub>2</sub>O<sub>3</sub> glass.<sup>(24,25)</sup> The obtained glass-ceramics showed transparency despite the selective crystallization of ZnO exhibiting a high refractive index. Since we have found the PL of ZnO-precipitated glass-ceramics, it is expected that the glass-ceramics will be good candidates for RL applications. Here, we have investigated the PL and RL properties including the scintillation and OSL of ZnO crystallite-precipitated glass-ceramics and discussed their potential.

## 2. Experimental Methods

CaO-B<sub>2</sub>O<sub>3</sub>-ZnO-Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O-SiO<sub>2</sub> (CaBZAKS) glass samples were prepared by a conventional melt quenching method using a 50 mL platinum crucible. Nominal chemical compositions of the 5CaO-23B<sub>2</sub>O<sub>3</sub>-41ZnO-8Al<sub>2</sub>O<sub>3</sub>-9K<sub>2</sub>O-14SiO<sub>2</sub> glass samples are reported in units of mol%. The preparation scheme in ambient air is shown in a previous paper.<sup>(24)</sup> After annealing at the glass transition temperature  $T_g$ , the glass samples were cut to dimensions of  $10 \times 10 \times 1$  mm<sup>3</sup> and mechanically polished to obtain a mirror surface. Each glass sample was then heat-treated on an alumina plate in an ambient atmosphere to obtain the corresponding glass-ceramics. Since the crystalline phase was observed at both the front side (air side) and the backside (alumina side) of a heat-treated sample, the backside was mechanically polished to remove the crystalline phase completely and to obtain a mirror surface.

$T_g$  was measured by differential thermal analysis (DTA, Thermo Plus 8120, Rigaku) at a heating rate of 10 °C/min. X-ray diffraction (XRD) analyses were performed at 40 kV and 40 mA using a RINT2000 (Rigaku) diffractometer. Optical absorption spectra were measured using a U-3500 spectrophotometer (Hitachi). PL and PL excitation (PLE) spectra were measured using an F-7000 fluorescence spectrophotometer (Hitachi) whose band pass filter for excitation and emission was 2.5 nm. PL decay curves were measured using Quantaurs-Tau (Hamamatsu Photonics). The RL spectra obtained by X-ray radiation at room temperature were measured using a monochromator equipped with a charge-coupled device (CCD, Andor DU-420-BU2).<sup>(26)</sup> The supplied bias voltage and tube current were 40 kV and 5.2 mA, respectively. The irradiation dose was calibrated using an ionization chamber. A pulse X-ray tube (Hamamatsu N5084) and a photomultiplier tube (Hamamatsu R7400) employed as a photodetector were used for the measurement of RL decay curves.<sup>(27)</sup> The basic concept of the system was the same as that of a pulse X-ray streak camera system,<sup>(28)</sup> only the photodetector was changed. OSL spectra were measured after X-ray exposure with 10 Gy using Quantaurs-Tau (Hamamatsu Photonics). The stimulation light source was chosen to be a 630 nm LED from the optimal stimulation wavelength.

### 3. Results and Discussion

The obtained CaBZAKS glass, whose optical absorption edge was about 5 eV, was transparent. Figure 1 shows the optical absorption spectra of the CaBZAKS glass and glass-ceramics heat-treated at different temperatures for 3 h, along with the photograph of these glasses. With increasing heat treatment temperature, the glass-ceramics became translucent owing to the light scattering of the precipitated crystallites.

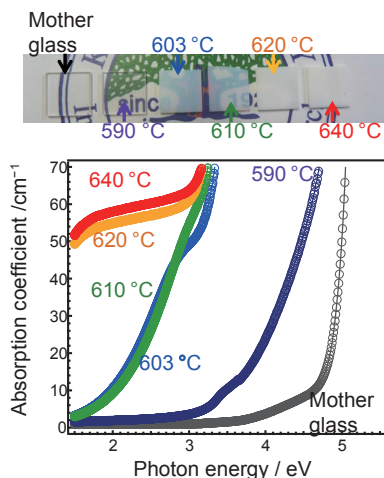


Fig. 1. (Color online) Optical absorption spectra of the CaBZAKS glass-ceramics heat-treated at different temperatures for 3 h. The spectrum of the mother glass is also shown for comparison.

Figure 2 shows the XRD patterns of the CaBZAKS glass-ceramics heat-treated at different heat treatment temperatures, along with the Joint Committee on Powder Diffraction Standards (JCPDS) card pattern of ZnO. The samples were heat-treated in air for 3 h. Although no diffraction was observed in the mother glass, the XRD patterns of the samples with increased heat treatment temperature showed clear diffraction peaks corresponding to a ZnO phase, with varying relative peak intensity. From the observed diffractions, we found that a small amount of  $\alpha$ -Zn<sub>3</sub>B<sub>2</sub>O<sub>6</sub> precipitated as a secondary phase. Because the measurement was performed using the bulk shape, some characteristic diffraction patterns due to surface crystallization were observed. It is often observed that the surface crystallized phase in glass-ceramics shows a preferential crystal growth direction.<sup>(14,15)</sup> Crystalline morphology of the CaBZAKS glass-ceramics, in which ZnO crystallites with several micrometer sizes at the surface grew with the *a*-axis,<sup>(24)</sup> was reported in the previous paper.

Figure 3 shows the PL spectra of the CaBZAKS glass and glass-ceramics. These spectra were recorded at room temperature using a photon energy of 5.64 eV as an excitation source. The broad emission in the range of 2–4 eV was observed in the mother glass and glass-ceramics treated at 590 °C. Compared with the XRD patterns of the mother glass, the broad emission is due to the defect emission of the glass samples. On the other hand, the emission at 2–3.4 eV for other glass-ceramics consists of a broad band and several emission bands. In contrast to the previous report,<sup>(24)</sup> a clear emission at 3.3 eV, which is assigned to the free exciton emission of ZnO, was not observed.

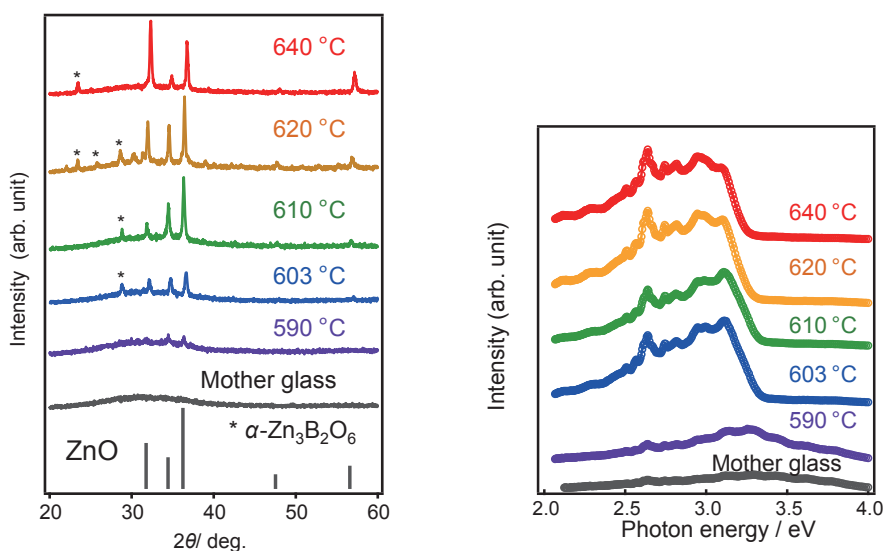


Fig. 2 (left). (Color online) XRD patterns of the CaBZAKS glass-ceramics heat-treated at different temperatures. The heat treatment duration in air was 3 h. The diffraction pattern of ZnO (JCPDS No. 00-021-1272) is also shown.

Fig. 3 (right). (Color online) PL-PL spectra of the CaBZAKS glass-ceramics heat-treated at different temperatures. Excitation energy is 5.64 eV (220 nm).

Since the observed emissions of the glass-ceramics as shown in Fig. 3 were not observed by surface polishing for removing the precipitated ZnO crystallites, it can be concluded that the observed emission originates from the ZnO-precipitated region at the surface. Although the origin of these emissions has not been clarified yet, it is expected that the emission from the glass-ceramics will depend on the state of the precipitated ZnO crystallites at the surface and the interface, which is attractive from the viewpoint of the self-organized structure.

Figure 4 shows the PL decay curves of the CaBZAKS glass-ceramics heat-treated at different temperatures. The PL decays at the PL peak energy (around 3 eV) were measured by excitation of 4.43 eV (280 nm) LED. For comparison, the decay curve of the mother glass is also shown. Because the decay curves are expected to consist of at least three components, the longest decay constants  $\tau_{1/e}$  are estimated by fitting each decay curve as shown in Fig. 4. By this fitting, the longest  $\tau_{1/e}$  of the mother glass is estimated as 400 ns, which is slightly shorter than those of the glass-ceramics (420–480 ns). Using these longest values, other decay constants can be estimated. The fastest decay is about 1.7–1.8 ns independent of the crystallization, whereas the middle decay is about 8–10 ns, whose constants decrease with increasing heat treatment temperature.

Figure 5 shows the X-ray induced scintillation spectra of the CaBZAKS glass and glass-ceramics heat-treated at different temperatures. The X-ray irradiation dose was 1 Gy. The broad emissions from 2 to 3 eV, which can be fit to Gaussian curves, are observed. Similar to PL spectra shown in Fig. 3, sharp emissions around 3.3 eV due to free excitons<sup>(29,30)</sup> are not observed. Because the present center energy of the glass-ceramics (~2.9 eV) is higher than that of ZnO single crystal (~2.3 eV) owing to oxygen

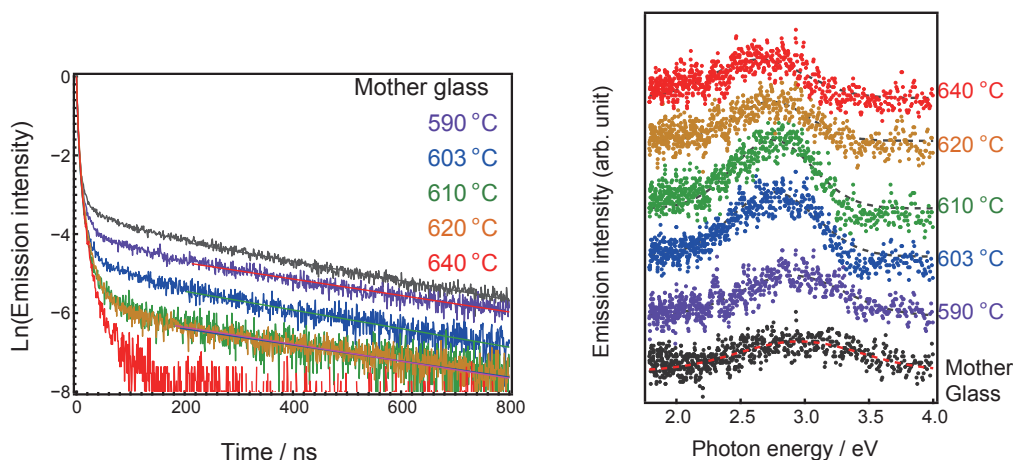


Fig. 4 (left). (Color online) PL decay curves of the CaBZAKS glass-ceramics heat-treated at different temperatures. The decay curve of the mother glass is also shown for comparison.

Fig. 5 (right). (Color online) RL spectra of the CaBZAKS glass and glass-ceramics heat-treated at different temperatures. The excitation light source is X-ray and the irradiation dose is 1 Gy. Dashed lines show the curves fit using a Gaussian function.

vacancies,<sup>(29,30)</sup> the observed emission is thought to mainly originate from the defect in the host glass. Compared with the host glass, peak centers slightly red shift, whereas the emission intensities roughly (independent of the heat treatment temperature) increase. However, degree of the spectral change of RL by the crystallization is not large compared with that of PL. We assume that the penetration depth of X-rays is much deeper compared with that of UV light, and that the RL spectra, which reflect the presence of both the precipitated ZnO phase and the amorphous region, are less sensitive to the crystallization. On the other hand, it has been recently reported that there are stress and strain at the interface of the precipitated ZnO crystallites in the glass-ceramics.<sup>(31)</sup> A complicated morphology is one of the origins of the observed X-ray-induced scintillation spectra.

Figure 6 shows the RL decay curves of the CaBZAKS glass-ceramics heat-treated at different temperatures along with that of the mother glass. The decay curves also consist of three components, the same as PL decay. By fitting with exponential functions, the decay constants are calculated as 0.6, 10, and 190 ns. In contrast to the PL decay (Fig. 4), all samples including the mother glass show similar decay curves. Comparing the decay constants of RL with that of PL, we have found that the decays in the middle range, which differentiate PL decay curves, show similar values. If the origin of the decays is the excitation of the host matrix, the crystallized region with small volume fraction has a very small contribution to the decay profile. The obtained result in which an apparent difference was not observed supports this assumption.

Figure 7(a) shows the OSL spectra of the CaBZAKS glass-ceramics after X-ray (10 Gy) irradiation. The stimulation wavelength was 630 nm. Although OSL is hardly observed in the mother glass, two OSL emissions are observed in the glass-ceramics. Figure 7(b) shows the correlation between the normalized OSL intensity and heat treatment temperature of the CaBZAKS glass-ceramics. The standard intensity (= 1) is that of the CaBZAKS glass-ceramic treated at 590 °C. The figure shows that

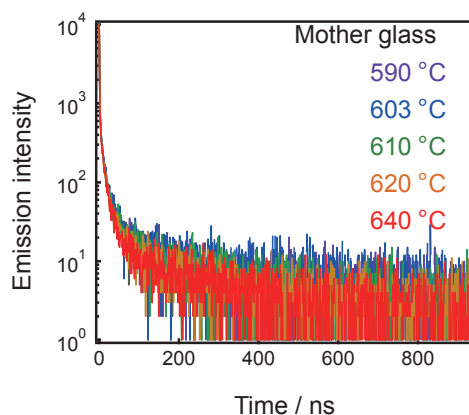


Fig. 6. (Color online) RL decay curves of the CaBZAKS glass-ceramics heat-treated at different temperatures. The decay curve of the mother glass is also shown for comparison.

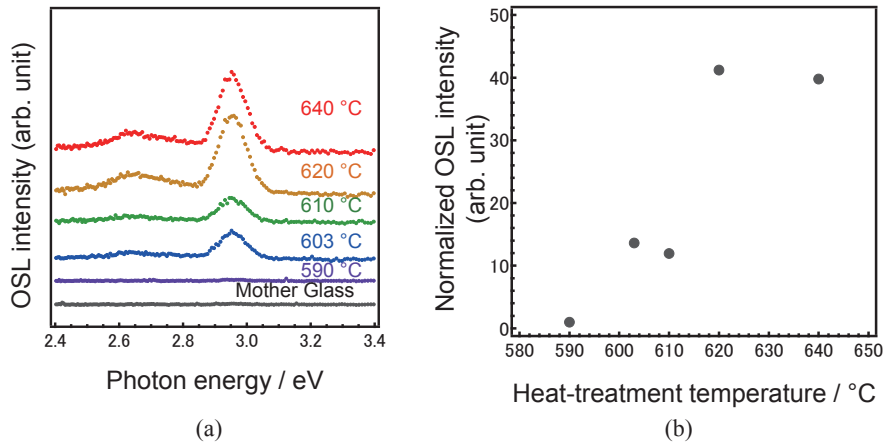


Fig. 7. (Color online) (a) OSL spectra of the CaBZAKS glass-ceramics after 10 Gy X-ray irradiation. The stimulation wavelength was 630 nm. (b) Correlation between normalized OSL intensity and heat treatment temperature of the CaBZAKS glass-ceramics. The standard intensity (= 1) is that of the CaBZAKS glass-ceramic treated at 590 °C.

the intensity increases with the heat treatment temperature, that is, the crystallization behavior affects the OSL intensity. The OSL spectra roughly consist of two regions: 2.95 eV with an HWHM of 0.06 eV, and 2.67 eV with an HWHM of 0.13 eV. Compared with the photon energies of the scintillation spectra shown in Fig. 5, a narrower emission is observed in the OSL spectra. Therefore, several emission (trap) sites were formed at the ZnO-precipitated region of the glass-ceramics and only the crystallization-related defect affects the OSL behavior, although the local structure has not yet been clarified. Throughout the present work, it is confirmed that glass-ceramic materials can be applied in radiation detectors, and such confirmation opens a new aspect of applications for these materials.

#### 4. Conclusions

We have examined the PL and RL of ZnO-precipitated CaO-B<sub>2</sub>O<sub>3</sub>-ZnO-Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O-SiO<sub>2</sub> glass-ceramics and the mother glass. The PL spectra of these glass-ceramics show a broad band emission with several sharp peaks, whose origin is not clarified in the present paper. Both PL and RL decays consist of several decay components whose decay constants mainly correlate with the defects of the host glass, not with the crystallization of ZnO. Because the volume fraction of ZnO crystallites precipitated near the surface of the sample is smaller than in the amorphous regions, RL spectra with broad band emission are almost independent of the heat treatment condition. OSL spectra suggest that the trap level generated by crystallization is strongly affected by the heat treatment temperature. The present results indicate that glass-ceramics can be possible candidate light-emitting glass-based materials.

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