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Photoluminescence and scintillation of TlBr crystals at low temperatures

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The photoluminescence and X-ray-induced radioluminescence properties of TlBr crystals were analyzed. We compared the samples cut from two parts of the crystal that are empirically known to be appropriate and inappropriate for semiconductor detectors. In the X-ray-induced radioluminescence spectra, two bands were observed at 490 and 650 nm for both the samples. We observed an additional band at 560 nm only for the inappropriate part of the crystal. We observed an emission band at 520 nm in the photoluminescence spectra of both the samples and attributed this to some defects near the surface on which photoexcitation occurs. Interestingly, an emission band at 560 nm appeared after thermal cycle from room temperature to 5 K and back to room temperature. Assuming that the thermal cycle introduced some distortions in the sample, the emission band at 560 nm could be related to lattice defects, such as dislocation, that are relevant to distortion.

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1. Introduction

TlBr is an indirect-gap semiconductor having a wide band-gap energy and attracting considerable attention of researchers with expertise on radiation detection using semiconductors. Due to the high atomic numbers of the constituent elements (Tl: 81, Br: 35) and high density of (7.56 g cm^{-3}), semiconductor detectors based on TlBr are expected to have high detection efficiency for high energy photons such as gamma-rays and X-rays. For the last two decades, the crystalline quality and energy resolution of TlBr semiconductor detectors have been continuously improved.¹⁾ In particular, the purification of raw materials for crystal growth has been extensively studied to improve these properties.^{2–14)} Many semiconductor detectors based on high-purity TlBr crystals have been developed.

In this study, we focused on the emission properties, such as photoluminescence and scintillation, of high-purity TlBr crystals at low temperatures because of their certain useful features. First, the optical response of high-purity TlBr crystals with good crystallinity is of interest from the viewpoint of basic optical physics of semiconductors. Second, the crystalline quality could be assessed based on the emission properties. For the development of TlBr based semiconductor detectors, it is difficult to judge whether a given crystal is appropriate for it. Detection of lattice defects from the emission properties would significantly facilitate improving the poor performance of TlBr based semiconductor detectors that have defects. This exercise is similar to the detection of stacking faults in SiC based power semiconductor devices through photoluminescence measurements.¹⁵⁾ The third reason is that fast scintillation in TlBr crystals for semiconductor detectors can be used for the timing signal of the arrival of ionizing radiation. Although this technique has already been developed using Cherenkov radiation from the photoelectrons,¹⁶⁾ fast timing based on the scintillation would be favorable from the viewpoint of detecting signal intensity.

Thus far, several research groups have reported the photoluminescence or cathodoluminescence properties of TlBr crystals. The photoluminescence properties of I-doped TlBr crystals have been reported, and the emission bands

were attributed to excitons bound to I^- and self-trapped excitons perturbed by I^- .^{17–19)} Sharp lines from bound excitons at the liquid helium temperature have been reported.²⁰⁾ Relaxation of hot excitons via phonon emission was clearly demonstrated in the photoluminescence excitation spectra.²¹⁾ Influence of direct gap in the relaxation process of excitons was elucidated based on electro-modulated excitation spectroscopy.²²⁾ At high excitation density, luminescence from the electron-hole plasma at the direct gap was also observed.^{23,24)} Some researchers have also reported the emission properties induced by X-ray or electron beam irradiations.^{25–27)} Various luminescence bands have been observed and are tentatively attributed to free or bound excitons or electronic transitions at localized centers such as defects or impurities.

In this study, we analyzed the photoluminescence and scintillation properties of TlBr crystals. We compared the properties of the samples cut from two parts of the crystal that are empirically known to be appropriate and inappropriate for semiconductor detectors. We also analyzed the change in the photoluminescence spectra after the thermal cycle from room temperature to 5 K and back to room temperature. The thermal cycle is expected to cause distortion in the crystals and introduce lattice defects such as dislocations.

2. Experimental

The raw TlBr powder (99.999%, Sigma Aldrich) was purified and the crystals were grown using traveling molten zone method. The samples were cut from two parts of the crystal that are empirically known to be appropriate and inappropriate for semiconductor detectors. For the sample appropriate and inappropriate for semiconductor detectors, the purification was performed using the traveling molten zone method for 322 and 228 times, respectively. The details of the crystal growth are given elsewhere.¹⁾

X-ray-induced radioluminescence spectra were recorded using an X-ray tube operating at 80 kV and 2.5 mA as the excitation source. The sample crystals were placed on a Cu sample holder in a closed-cycle-type cryostat and irradiated with the X-rays through a Kapton window. The photons emitted from the samples were delivered via an optical fiber

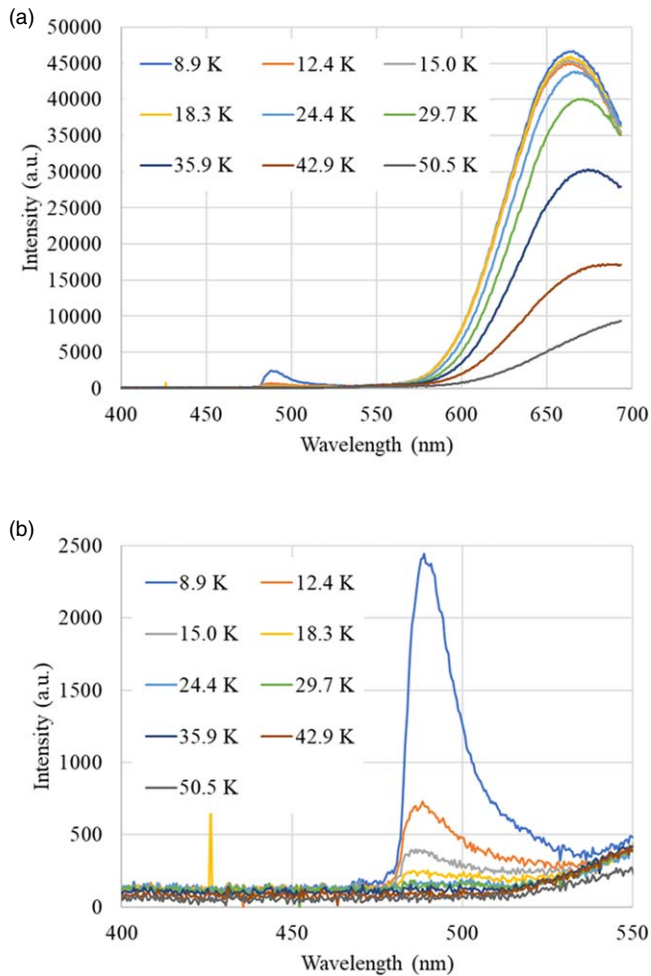


Fig. 1. (Color online) X-ray-induced radioluminescence spectra (a) in the entire visible region and (b) between 400 and 550 nm of the appropriate crystal at low temperatures.

to a spectrometer equipped with a CCD detector (DU-420-BU2, Andor) and a monochromator (Shamrock SR163, Andor). The details of the measurement system are given elsewhere.²⁸⁾

The photoluminescence spectra at low temperatures were recorded using a He–Cd laser (wavelength: 325 nm) as the excitation source. Since the excitation photon energy is much higher than both the indirect band gap energy (2.67–2.69 eV)^{29–31)} and direct band gap energy (3.00–3.05 eV),^{31–33)} only the near-surface region of the sample crystals was excited. The samples in a closed-cycle-type cryostat were illuminated with the laser. The emitted photons from the samples were delivered to a monochromator (MicroHR, Horiba) using a couple of convex lenses. The monochromatic light was detected with a photomultiplier tube. The excitation light was modulated at 140 Hz using a chopper. The detection signal synchronized to the modulated excitation light was recorded with a lock-in amplifier (5610B, NF Corporation). The temporal profiles of photoluminescence were obtained using a time-correlated single photon counting technique (DeltaFlex TMK2, Horiba). The samples were excited using a pulsed LED (NanoLED-320, Horiba) at 326 nm for 100 μ s, and another pulsed LED (SpectraLED-320, Horiba) at 315 nm was used to monitor the luminescence at longer time scales in the phosphorescence measurement mode. As the excitation photon energy is much higher than the

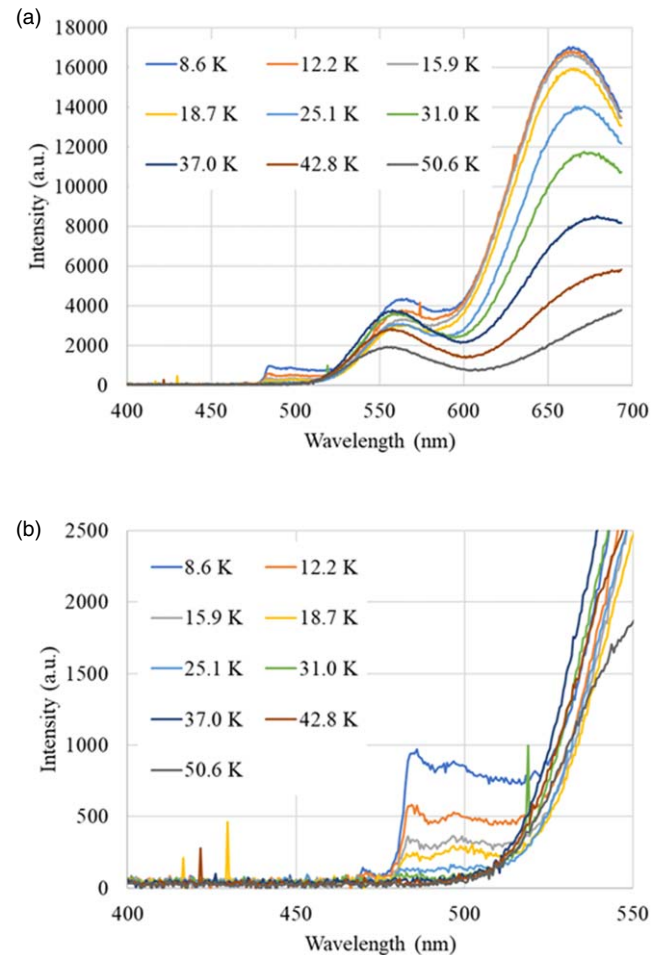


Fig. 2. (Color online) X-ray-induced radioluminescence spectra (a) in the entire visible region and (b) between 400 and 550 nm of the inappropriate crystal at low temperatures.

indirect and direct band gap energies, only the near-surface region of the sample crystals was excited while recording the temporal profiles of photoluminescence.

3. Results and discussion

Figure 1 shows the X-ray-induced radioluminescence spectra in the entire visible region and between 400 and 550 nm of the crystal appropriate for semiconductor detectors at low temperatures. A band at ca. 490 nm is observed at temperatures below 20 K. A similar band was observed at 100 K under electron beam irradiation and is thought to be related to TI vacancies and interstitials.²⁵⁾ In addition, a dominant band between 650 and 700 nm was observed. The wavelength maxima of this band shifted toward the longer wavelengths. This emission band is attributed to TI vacancies.²⁵⁾ Figure 2 shows the X-ray-induced radioluminescence spectra in the entire visible region and between 400 and 550 nm of the crystal inappropriate for semiconductor detectors at low temperatures. In addition to the emission band at 490 nm and that between 650 and 700 nm, which are observed for the appropriate crystal, a band at 560 nm is observed. This band could be observed at least up to 50 K. The nature of this band is discussed later.

Figure 3 shows the photoluminescence spectra of the appropriate and inappropriate crystals at 5 K upon excitation at 325 nm. During the measurements on the first day, the

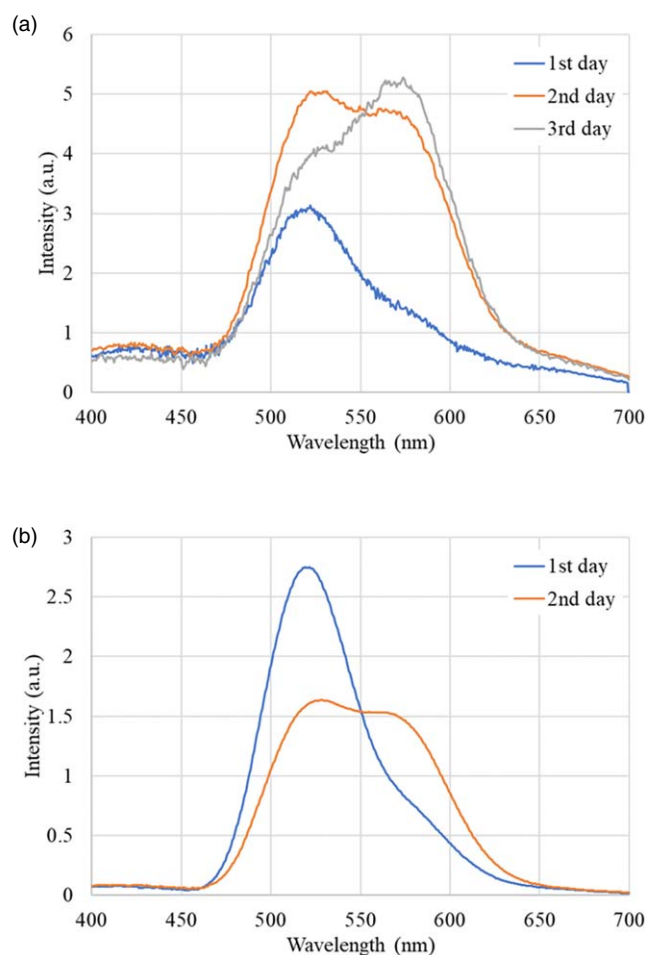


Fig. 3. (Color online) Photoluminescence spectra of the (a) appropriate and (b) inappropriate crystals at 5 K upon excitation at 325 nm. During the measurements on the first day, the samples were cooled down to 5 K and subsequently warmed gradually to room temperature in vacuum.

samples were cooled to 5 K and subsequently warmed gradually to room temperature in vacuum. On the first day, both the samples exhibited a dominant band at 520 nm, which was not observed in the X-ray-induced radioluminescence spectra. The photoluminescence intensity of the appropriate crystal was less than 10% of that of the inappropriate crystal. This band was observed only in the photoluminescence spectra and may be attributed to some defects near the surface on which photoexcitation occurs. In addition to this band, a band at 560 nm appeared on the second and third day for both the crystals. Since no impurity was added between the first and second day, the band at 560 nm can be attributed to some defects introduced during the thermal cycle from room temperature to 5 K and back to room temperature. This result strongly suggests that the band at 560 nm in the photoluminescence and X-ray-induced radioluminescence band are correlated to the defects introduced by distortion, e.g. dislocation in the crystal. Figure 4 shows the photoluminescence spectra of the appropriate and inappropriate crystals on the third day and first day, respectively, at different temperatures. The band at 560 nm was seen for both the crystals at least up to 50 K, which is consistent with their behavior in the X-ray-induced radioluminescence spectra. The similar temperature dependence of the band at 560 nm in both the spectra confirms that

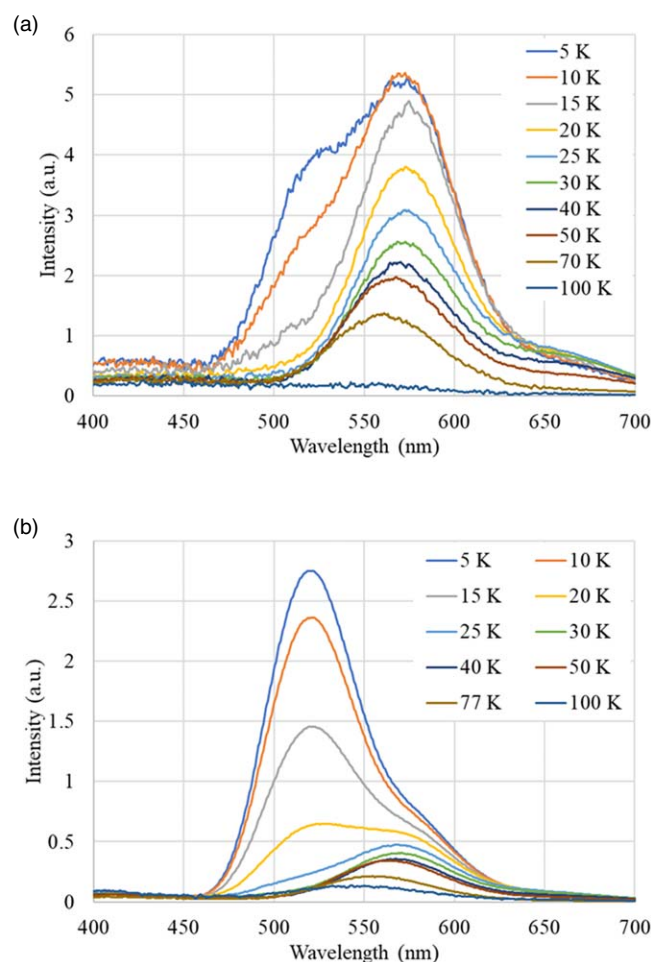


Fig. 4. (Color online) Photoluminescence spectra of the (a) appropriate crystal on the third day and (b) inappropriate crystal on the first day at different temperatures.

the origin of the band is the same for both photoexcitation and X-ray irradiation.

Figures 5 and 6 show the photoluminescence temporal profiles up to 100 μ s, 1.4 ms, and 5.5 ms for the appropriate and inappropriate crystals after recording their photoluminescence spectra on the third day and second day, respectively. The initial decay profiles were different in different time ranges, mainly because long excitation pulses were used for the measurements up to 1.4 and 5.5 ms. The temporal profiles did not obey a single exponential decay function, and the decay was observed from several tens of microseconds to several milliseconds. For the temporal profiles at 520 and 560 nm, we found a difference in the decay behavior within several tens of microseconds, while the decay was quite similar at longer time scales. The decay profile over the long time scale cannot be explained with one-component first order kinetics with a single exponential decay function. It can, however, be explained with multiple decay processes with different time scales ranging from micro- to milliseconds.

4. Conclusions

We investigated the photoluminescence and X-ray-induced radioluminescence properties of TlBr crystals. We investigated the samples cut from two parts of the crystal that are empirically known to be appropriate and inappropriate for

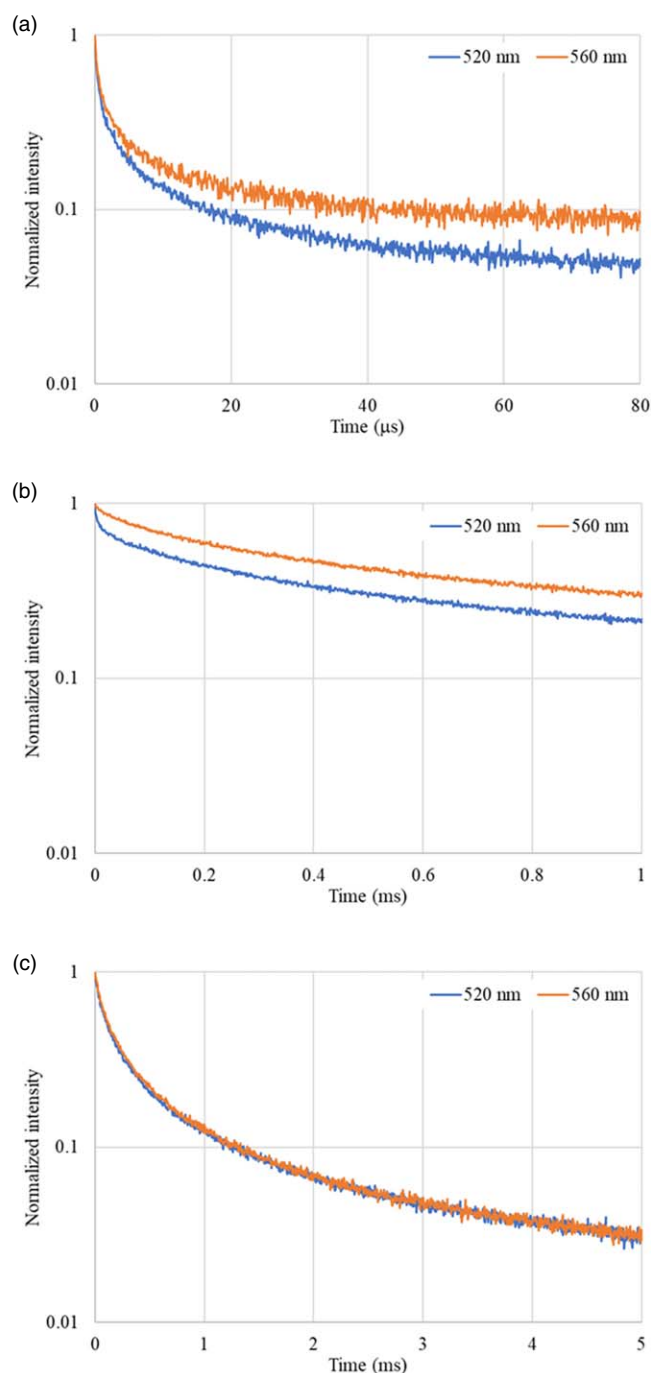


Fig. 5. (Color online) Photoluminescence temporal profiles up to (a) 100 μ s, (b) 1.4 ms, and (c) 5.5 ms of the appropriate crystal after recording its photoluminescence spectrum on the third day.

semiconductor detectors. We found a significant difference in the X-ray-induced radioluminescence spectra of the two parts of the crystal. An emission band at 560 nm was observed only for the inappropriate crystal. In addition, we observed an emission band at 560 nm in the photoluminescence spectra, which emerged after the thermal cycle from room temperature to 5 K and back to room temperature. In the absence of any introduced impurity, it was assumed that the sample was distorted during the thermal cycle, and the emission band at 560 nm originated owing to some defects related to the distortion, such as dislocations. Our results strongly suggest that the difference in the appropriate and inappropriate crystals is related to the distortion induced in the crystal structure.

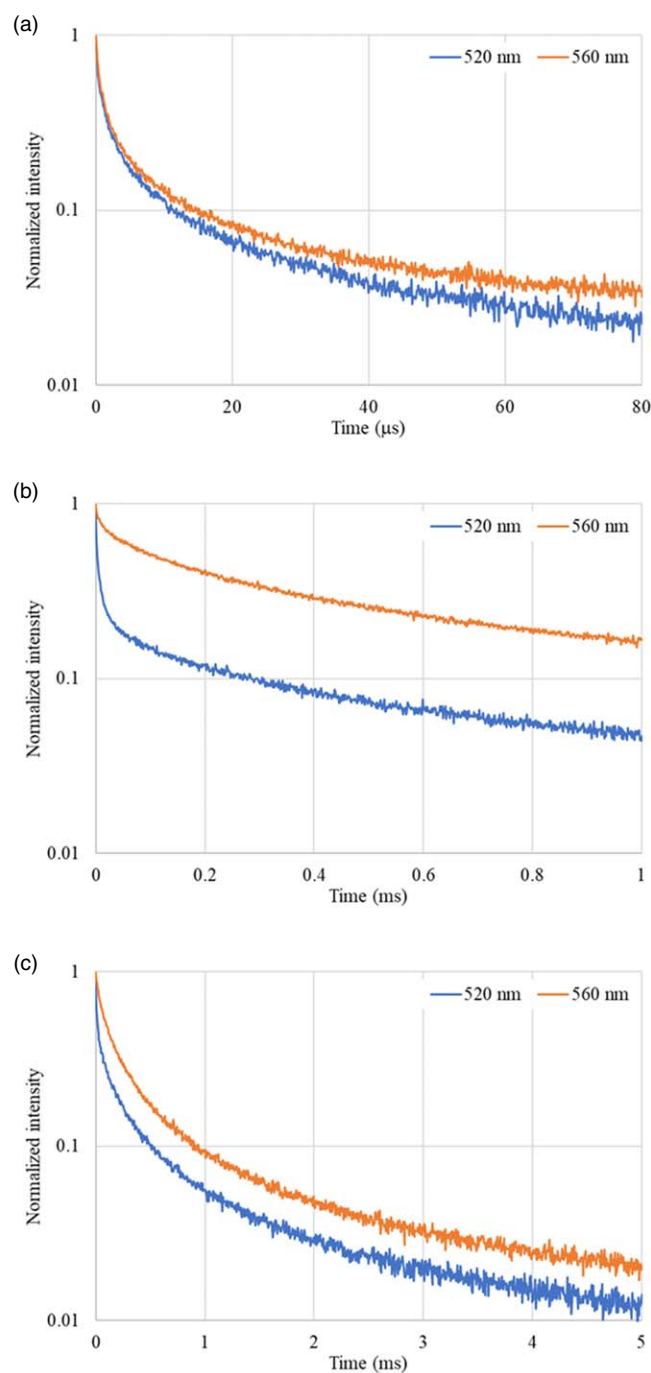


Fig. 6. (Color online) Photoluminescence temporal profiles up to (a) 100 μ s, (b) 1.4 ms, and (c) 5.5 ms of the inappropriate crystal after recording its photoluminescence spectrum on the second day.

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