Scintillation properties of CdF$_2$ crystal

Takayuki Yanagida [a,*], Yutaka Fujimoto [b], Masanori Koshimizu [b], Kentaro Fukuda [c]

[a] Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu, Kitakyushu, Fukuoka 808-0196, Japan
[b] Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
[c] Tokuyama Corp., 1-1 Mikage-cho, Shunan-shi, Yamaguchi 745-8648 Japan

ABSTRACT

CdF$_2$ single crystal was prepared by Tokuyama Corp. with the μ-PD method to investigate Auger free luminescence of this material. From optical transmittance spectrum, bandgap wavelength was around 280 nm. In X-ray induced radioluminescence spectrum, emission lines appeared around 350 nm and 420 nm. Excitation wavelength was investigated and excitation peak was around 250 nm. Photoluminescence and scintillation decay times were evaluated and decay time was few ns. Temperature dependence of X-ray induced radioluminescence was compared with conventional BaF$_2$ scintillator and scintillation of CdF$_2$ decreased when the temperature increased. Consequently, scintillation of CdF$_2$ is possibly emission at color centers or exciton related one.

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1. Introduction

Scintillators are widely used in various ionizing radiation detection applications such as medical, security, and high energy physics. Most common type of inorganic scintillators are rare-earth activated scintillators [1]. This kinds of scintillators have been widely used in medical [2], security [3], and high energy physics [4]. They exhibit high light yield with medium fast decay times of several tens nanoseconds. On the other hand, intrinsic luminescence of halide scintillators has also attracted considerable attention. The most famous one is Auger-free luminescence (AFL) of BaF$_2$. AFL is caused by transitions from the valence band to the top of outermost core levels. In general description, AFL shows a fast decay time, a high thermal stability, and a relative high yield. AFL of BaF$_2$ shows sub-ns decay time and BaF$_2$ was once investigated to apply TOF-PET [5]. Unfortunately, due to a low light yield and short emission wavelength in vacuum ultraviolet, BaF$_2$ did not reach to practical applications of medical imaging. CsF is also a famous scintillator exhibiting AFL [6]. Compared with BaF$_2$, CsF had an advantage of visible wavelength emission while huge hygroscopicity prevented to be practically used.

In addition to BaF$_2$ and CsF, CdF$_2$ is predicted to show AFL in ultraviolet or visible wavelength theoretically [7]. However, AFL of CdF$_2$ has not been experimentally confirmed yet. A half-century ago, one paper suggested the existence of fast luminescence [8]. In

1990's, scintillation properties of powder CdF$_2$ was investigated and 420 nm emission with few and few tens ns decay times were reported [9]. Recently, rare-earth element doped CdF$_2$ was investigated and they also examined X-ray induced radioluminescence of nondoped CdF$_2$ at 80 K [10]. In [10], presented spectrum differed with us (described later) possibly due to a difference of sample production techniques.

In the present work, we investigated optical and scintillation properties of CdF$_2$ crystal to examine the theoretical prediction about AFL. Fig. 1 demonstrates a picture of CdF$_2$ crystal prepared in Tokuyama by using μ-PD method. The sample was cut and polished for scintillation study. As shown in Fig. 1, the sample was colorless. In an evaluation of temperature dependence, BaF$_2$ crystal with a size of $2 \times 7 \times 1$ mm^3 was used for a comparison. This reference BaF$_2$ was also fabricated by Tokuyama Corp. In addition, excitation spectrum in the vacuum ultraviolet (VUV) region of CdF$_2$ was observed in order to confirm the occurrence of the AFL.

2. Experimental procedures

In-line transmittance was measured by using JASCO V670 spectrometer with a wavelength step of 1 nm from 190 to 2700 nm. Photoluminescence (PL) excitation spectrum monitoring at 350 nm was evaluated by using JASCO FP8600 spectrofluorometer at wavelength longer than 200 nm. At wavelength shorter than 200 nm, we evaluated at Synchrtron facility (UVSOR, beam line BL7B) from 50 to 200 nm. In UVSOR, 282 nm and 340 nm data

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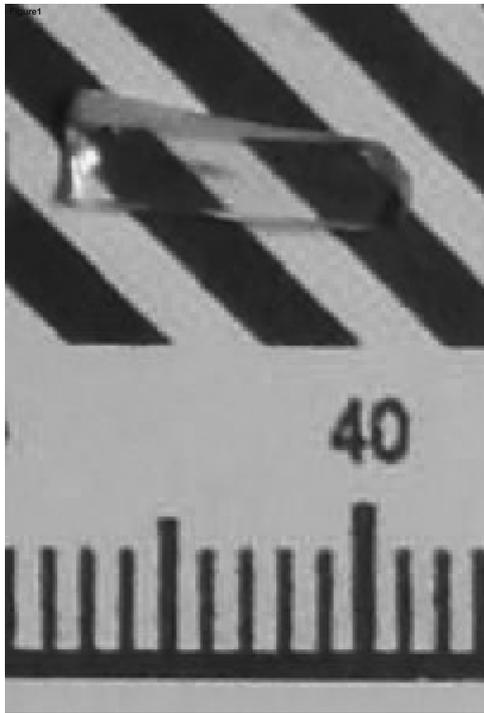
Fig. 1. Photographs of CdF$_2$ crystal.

Fig. 2. Transmittance of CdF$_2$ crystal. Inset shows the transmittance below 350 nm.

Fig. 3. Excitation spectrum of CdF$_2$ monitoring at 350 nm. Below 200 nm, data was obtained at UVSOR and beyond 200 nm by FP8600 spectrofluorometer.

was also measured for the crosscheck with FP8600 excitation spectrum. In UVSOR, PL decay time profiles under 200 and 282 nm monitoring at 420 nm were evaluated since we could not detect 350 nm emission due to a low emissivity.

X-ray induced radioluminescence spectrum at room temperature was corrected and the geometry of the setup was described previously [11]. The supplied bias voltage and tube current for X-ray generator was 80 kV and 2.5 mA, respectively. Scintillation decay time profiles were evaluated by two instruments. One was pulse X-ray equipped streak camera system which enabled us to observe wavelength resolved scintillation decay [12]. By using this instrument, monitoring wavelengths were 350 ± 15 and 420 ± 15 nm. The other was the pulse X-ray equipped afterglow characterization system in the fast mode [13]. In this instrument, wavelength was not resolved so that we could observe scintillation decay similar to practical uses. Temperature dependence of X-ray induced radioluminescence of CdF$_2$ was compared with conventional BaF$_2$ from −60 to 140 °C since it was a common knowledge that AFL was relatively stable in the temperature change [14,15]. The sample was put in a constant temperature bath (Espec SH661) with an optical fiber and 80 kV X-ray was irradiated to the sample through an irradiation port. The X-ray generator and CCD based spectrometer connected with the optical fiber were outside the temperature bath. Therefore, temperature dependence of scintillator sample itself was observed.

3. Experimental results and discussion

In order to compare the excitation below and beyond (scintillation) the bandgap, optical properties were evaluated at first. Fig. 2 represents in-line transmittance spectrum of CdF$_2$. CdF$_2$ showed a high transmittance around 90% at wavelength longer than 300 nm and absorption bands at wavelength shorter than 280 nm was observed. This absorption band was longer than the bandgap of CdF$_2$ (~8 eV = 155 nm) estimated based on reflection spectrum [17]. The intense absorption within the bandgap energy strongly suggests that color centers influence the optical properties in the
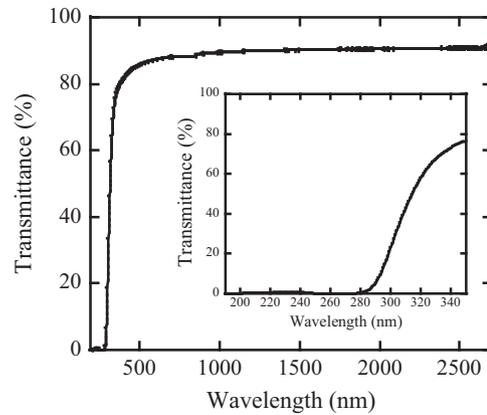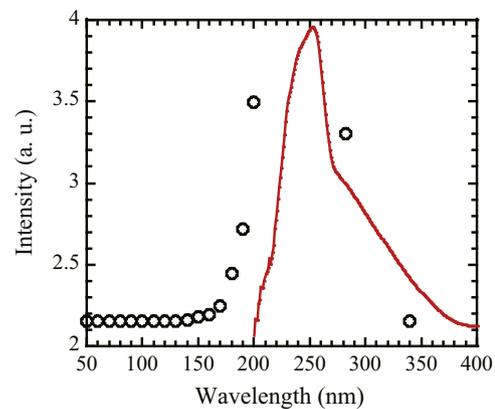
crystal. PL excitation spectra monitoring at 350 nm is shown in Fig. 3. Below 160 nm, no emission was observed and this wavelength corresponded to the bandgap of CdF$_2$. As a result, spectral features roughly overlapped in UVSOR and FP8600 results and the excitation band appeared around 250 nm. Though we observed two emission peaks around 350 and 420 nm (described later in X-ray induced radioluminescence), the excitation band of both emissions was around 250 nm. Considering the bandgap energy, this excitation band is located within the bandgap. It should be noted that the luminescence band was not effectively induced by core level excitation, which corresponds to the wavelength of approximately 100 nm according to the energy split between the conduction band minimum and the outermost core level (Cd^{2+} 4d orbital) [18,19]. PL decay time profile of CdF$_2$ under 200 nm excitation monitoring at 420 nm is demonstrated in Fig. 4. Decay time was deduced to 2.8 ns. Decay time profile under 282 nm excitation was quite similar with Fig. 4 and no specific difference was observed. When we tried to detect 350 nm decay time profile, low signal intensity prevented us from the measurement.

X-ray induced radioluminescence spectrum of CdF$_2$ is presented in Fig. 5. Intense emission appeared at 420 nm with a weak emission around 350 nm. Theoretical calculation expected AFL from 300 to 600 nm [7] with 2.3/7.9 ns decay time so that the experimental emission peaks well coincided with the prediction at least in scintillation spectrum. Previously, 420 nm scintillation with 5, 24, and 78 ns decay time components was reported [9]. Very recently, only 370 nm scintillation from CdF$_2$ crystal with a decay time of 18 ns was reported and they concluded the origin of this emission
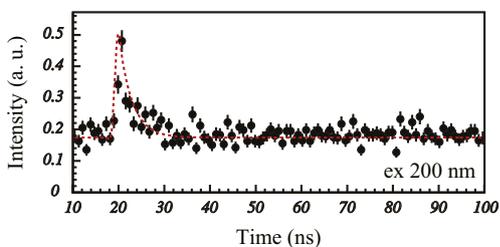
Fig. 4. PL decay time profile of 420 nm emission under 200 nm excitation at UVSOR.
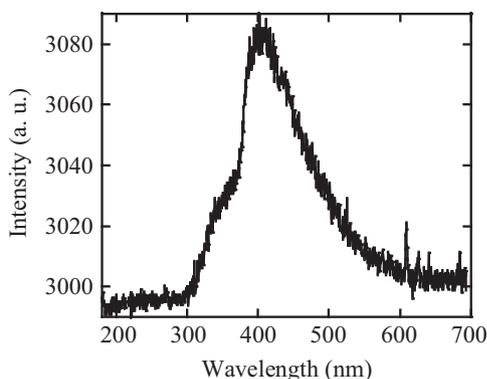
Fig. 5. X-ray excited radioluminescence spectrum.

Fig. 6. X-ray induced scintillation decay time profile. Wavelength was not resolved.

was the exciton [10]. Therefore, our sample showed both reported emission peaks in one sample. Though we challenged to evaluate pulse height under ^{137}Cs γ-ray irradiation and we could not detect clear photoabsorption peak. The upper limit of scintillation light yield of CdF_2 was around 100 ph/MeV and the light yield of CdF_2 was smaller than AFL of BaF_2 at least one digit.

In Fig. 6, wavelength not resolved scintillation decay time profile under pulse X-ray excitation is shown. Since we could not observe the instrumental response of the pulse X-ray equipped afterglow characterization system, tail part was fitted by double exponential function. 1.75 and 25.5 ns decay times were deduced by the analysis. In wavelength resolved observations, significant difference with the wavelength not resolved one did not appear. Two reasons are possible to explain the present result. One possibility is that the origin of 350 and 420 nm emissions are same. The other is that wavelength resolution was not enough since these two emission bands obviously overlapped in Fig. 5. Compared with previous results, 25 ns component in powder sample [9] and similar value of 18 ns [10] were reported recently. Though the signal intensity ratio generally depends on the wavelength sensitivity of PMT, we calculated relative intensity of the fast (1.75 ns) and the slow (25.5 ns) components. As a result, the slow emission was dominant ∼70%.

Temperature dependences of scintillation at −60, 20, and 140 °C of CdF_2 and BaF_2 are depicted in Fig. 7. Since we used to detect scintillation photons via 3 m optical, AFL of BaF_2 at 190 nm was not observed due to an absorption of vacuum ultraviolet photons by oxygen in air. In BaF_2 (Fig. 7(a)), AFL at 220 nm and self-trapped exciton (STE) emission around 300 nm were detected. Although the tendency of STE was consistent with previous studies [12], AFL exhibited a temperature dependence at higher temperature. The root of the common knowledge about the temperature stability of AFL was based on the report in 1985 [16] and the temperature dependence was examined from 198 K (= −75 °C) to 358 K (=85 °C). We measured spectra at 20 °C step and till 80 °C AFL at 220 nm was relatively stable. However at
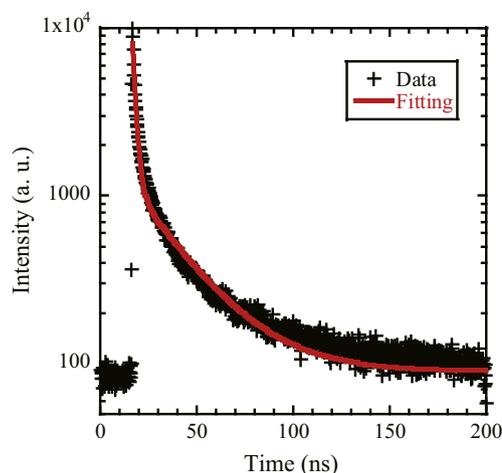
temperature higher than 100 °C, AFL rapidly decreased. Therefore, temperature stability is not an evidence of AFL. On the other hand in CdF_2 (Fig. 7(b)), whole emission monotonically decreased when the temperature increased and the decreasing rate was an intermediate level between AFL and STE of BaF_2. Taking into account that the slow component possibly due to STE was dominant in scintillation decay, similar temperature dependence on STE of BaF_2 would be valid.

Throughout the present study, PL spectrum and decay curve, scintillation spectrum and its temperature dependence on a comparison with BaF_2, and scintillation decay time profile were evaluated. In scintillation spectrum, 350 nm emission observed in [10] and 420 nm emission detected in [9] appeared in one sample. Taking into account excitation wavelengths and scintillation decay times were quite similar, origin of these two emissions would be the same. From the theoretical prediction, AFL of CdF_2 should appear around 300–600 nm with 2.3/7.9 ns decay time. In these points, experimental results, 350–420 nm and 1.75/25.5 ns, were consistent with the prediction. However, the excitation spectrum in the VUV region strongly suggests that the AFL hardly occurs in this crystal. The basis of AFL of previous studies was the light yield stability against the temperature and this basis was not true even in conventional BaF_2 at higher temperature. Concerning these results, a valid scenario of CdF_2 emission would be a marginal emission at color centers or exciton related one and these emission wavelengths would be quite overlapped.

4. Conclusion and future prospects

CdF_2 single crystal was prepared by Tokuyama Corp. with the μ-PD technique. In optical transmittance, absorption bands were observed below 280 nm. Emission peaks appeared around 350 and 420 nm in photo- and radio-luminescence spectra. Excitation bands of these peaks were around 250 nm. Photoluminescence and scintillation decay time of these emissions were fast few ns. When the temperature dependence of scintillation light yield of CdF_2 was compared with conventional BaF_2, emission intensity of CdF_2 decreased at higher temperature and the same tendency was observed in AFL and STE of BaF_2. Taking into account optical and scintillation properties in present work, a valid scenario of CdF_2 emission would be a marginal emission at color centers or exciton related one and these emission wavelengths would be quite overlapped.
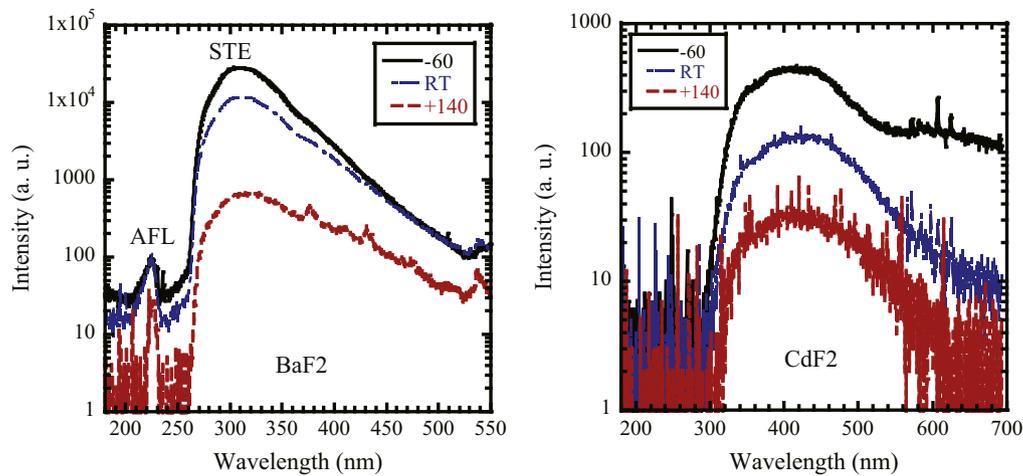
Fig. 7. Temperature dependence of BaF$_2$ (a) and CdF$_2$ (b) under X-ray excitation.

Acknowledgments

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