Scintillation and Optical Stimulated Luminescence of Ce doped CaF₂

Takayuki Yanagida^{a*}, Yutaka Fujimoto^a, Kenichi Watanabe^b, Kentaro Fukuda^c, Noriaki Kawaguchi^d, Yuka Miyamoto^e, Hidehito Nanto^f

^aKyushu Institute of Technology, 2-4 Hibikino, Wakamatsu-ku, Kitakyushu 808-0196 Japan

^bDepartment of Quantum Engineering, Nagoya Univ., Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

^cTokuyama Corporation, Shibuya 3-chome, Shibuya-ku, Tokyo 150-8383 Japan

^dA&T Corporation, 2023-1 Endo, Fujisawa, Kanagawa 252-0816 Japan

^eChiyoda Technol Corporation, 3681 Narita-cho, Oarai-machi, Higashi-ibaraki-gun, Ibaraki 311-1313, Japan

^fKanazawa Institute of Technology, 3-1 Yatsukaho, Hakusann-shi, Ishikawa 924-0838, Japan

Abstract

Scintillation and optical stimulated luminescence of Ce 0.1-20% doped CaF₂ crystals prepared by Tokuyama Corp. were investigated. In X-ray induced scintillation spectra, luminescence due to Ce³⁺ 5d-4f transition appeared around 320 nm with typically 40 ns decay time. By ²⁴¹Am 5.5 MeV α -ray irradiation, 0.1% doped one showed the highest scintillation light yield and the light yield monotonically decreased with Ce concentrations. Optically stimulated luminescence after X-ray irradiation was observed around 320 nm under 550 or 830 nm stimulation in all samples. As a result, intensities of optically stimulated luminescence were proportional to Ce concentrations. Consequently, scintillation and optically stimulated luminescence resulted to have a complementary relation in Ce-doped CaF₂ system.

Keywords: Scintillation; Scintillator; OSL; Ce³⁺; CaF₂

* Corresponding author. Present address: Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu-ku, Kitakyushu 808-0196, Japan
Tel.: +81 93 695 6049; fax: +81 93 695 6049.
E-mail address: yanagida@lsse.kyutech.ac.jp (Takayuki Yanagida)

1. Introduction

In ionizing radiation detectors, luminescent materials were used to visualize invisible radiations by visible photons. Among such luminescent materials, scintillators which convert a single high energy ionizing radiation to thousands of ultraviolet-visible photons immediately (Yanagida 2013) is the most famous type and has a wide spread of applications such as medical (Yanagida et al., 2010), security (Totsuka et al., 2012), well-logging (Yanagida et al., 2013), and high energy physics (Yamaoka et al., 2005; Ito et al., 2007). On the other hand, another luminescent type detector, dosimeter stores the absorbed energy for several weeks and release the energy by optical (optically stimulated luminescence, OSL) or thermal (thermally stimulated luminescence, TSL) stimulation. The main application of OSL (Yukihara and McKeever 2011) or TSL (McKeever 1985) dosimeters is a personal dosimetry to measure ionizing radiation.

Historically, scintillators and dosimeters were investigated and developed by different communities due to differences of detection techniques and time scales while their purpose was the same, to detect ionizing radiation by luminescent materials. However, if we assume the energy conservation, scintillation and OSL/TSL should be complementary in some material systems. When some energies are absorbed in materials, some parts are released by luminescence immediately (scintillation). The simple question occurs why some scintillators are bright and the others are not. In other words, where remaining energies has gone in dark scintillator materials? In this case, some portion of remaining energies are storage in the material and they can be released by stimulation (OSL or TSL). In other cases, remaining portions of energy are converted to thermal energies which are used in calorimeter for radiation detection. Therefore we suppose scintillation and OSL/TSL can be treated unity concerning the energy income and expenditure in some material systems, and the understanding of this relation will be a great benefit for future scintillator/dosimeter developments.

1 In the present work, we examine the hypothesis that scintillation and OSL have a
2 complementary relation in some material systems experimentally. For this purpose, Ce 0.1, 0.5,
3 1, 3, 5, 10, and 20% doped Ce^{3+} -doped CaF_2 crystals were prepared by Tokuyama Corp. using
4 the simple solidification method (Kawaguchi et al., 2013). The reason to choose $\text{CaF}_2:\text{Ce}$ is that
5 it can emit detectable scintillation and OSL signals. Figure 1 demonstrates samples for
6 evaluations. They all had similar sizes, typically 10 mm diameter and 1 mm thickness.

17 2. Experimental procedures

19 To evaluate basic optical property, optical in-line transmittance was evaluated by using
20 JASCO V670 spectrometer. Then, as basic scintillation properties, X-ray induced
21 radioluminescence spectra (Yanagida et al., 2013b) and decay time profiles (Yanagida et al.,
22 2010b; Yanagida et al., 2013c) were investigated. The aim of this work was to investigate a
23 basic relation of scintillation and OSL. For this purpose, the confirmation that our samples
24 had typical scintillation responses of $\text{CaF}_2:\text{Ce}$ was important. Scintillation light yield were
25 determined by pulse height with our standard setup (Yanagida et al., 2013d). Because γ -ray
26 sensitivity of CaF_2 was not so high due to low effective atomic number ($Z_{\text{eff}} = 16.4$) and
27 density (3.2 g/cm^3), ^{241}Am 5.5 MeV α -ray (4 MBq) was selected as the excitation source.

41 OSL properties were evaluated by photoluminescence (PL) quantum yield (QY) with
42 Hamamatsu Quantaurus-QY after X-ray exposure (0.5-4 Gy). The bias voltage and tube
43 current of X-ray generator were 40 kV and 5.2 mA, respectively. The exposure dose was
44 evaluated by X-ray ionization chamber. The absolute QY was calculated by the following
45 equation, $QY = N_{\text{emit}}/N_{\text{absorb}}$ where N_{emit} and N_{absorb} were number of emission and absorption
46 photons, respectively (e.g., Yanagida et al., 2013e). One of the problems of OSL evaluations
47 is that OSL intensity is a qualitative value while irradiated dose is quantitative. In this paper,
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we used PL QY as the OSL intensity because it was largely used to evaluate emission intensity of general phosphors as well as luminosity (Cd/cm^2).

3. Results and discussion

Figure 2 represents optical in-line transmittance spectra of Ce-doped CaF_2 from 190 to 320 nm. Absorption bands at 200, 240, and 300 nm were ascribed to Ce^{3+} 4f-5d transition and absorption depths were in proportion to nominal Ce concentrations. Transmittance at wavelength longer than 350 nm was typically 80-90% without noticeable absorption lines.

Then, we investigated basic luminescence properties. Figure 3 represents X-ray induced radioluminescence spectra of Ce differently doped CaF_2 scintillators. 300-360 nm luminescence peaks were originated from Ce^{3+} 5d-4f transition. In low Ce concentration samples, self-trapped exciton luminescence at 270 nm was observed. A sharp line around 300 nm in Ce 20% doped sample was a noise due to a direct hit of X-ray or background cosmic ray to CCD. Figure 4 demonstrates the relation between scintillation decay times and Ce concentrations. Scintillation decay times monotonically became faster when the Ce concentrations increased. Finally, scintillation decay time reached ~ 30 ns in Ce 20% doped sample. Based on these optical and scintillation evaluations, it was confirmed that our Ce-doped CaF_2 crystals exhibited typical properties of this material system.

To evaluate scintillation light yield, all samples were irradiated with 5.5 MeV α -rays of ^{241}Am . Figure 5 exemplifies relation between the scintillation light yield and the dopant concentration. As a representative, the pulse height spectrum of Ce 0.1% doped sample is demonstrated in the inset and α -ray full energy peak was clearly observed. Taking into account the quantum efficiency of the used PMT around 320 nm, scintillation light yield was deduced. Scintillation light yields monotonically decreased with Ce concentrations and this tendency was consistent with previous result (Gektin et al., 2009; Yanagida et al., 2010c).

Figure 6 depicts OSL emission map of Ce 20% doped CaF_2 . OSL appeared around 320 nm with 550 and 830 nm stimulation. Throughout OSL evaluations, QY was deduced by summing up these 550 and 830 nm emission peaks. Among present samples, Ce 20% doped CaF_2 exhibited the highest OSL intensity since it had a large number of defects due to a charge imbalance of Ce^{3+} and Ca^{2+} . Then in figure 7, the relation between the OSL intensity after 2 Gy X-ray exposure and the dopant concentration is shown. Unlike the similar plot in scintillation light yield, OSL intensity monotonically increased with the Ce concentration.

Finally, the relation between the scintillation light yield under ^{241}Am α -ray irradiation and OSL intensities after 0.5-4 Gy X-ray exposure is demonstrated in figure 8. Though it was obvious from figure 5 and 7, a reverse proportional relation between the scintillation light yield and the OSL intensity was clearly observed and our assumption of the complementary relation of scintillation and OSL was experimentally confirmed in Ce-doped CaF_2 system. If we used X- or γ -ray as an excitation source to evaluate scintillation light yield, the observed relation will be similar since charged particle and high energy photon induced light yields are in proportion but the energy conversion efficiency is different. This conversion efficiency is called α/β (or α/γ) ratio and this ratio shows little dependence on dopant concentrations (e.g., the case in LuAG:Pr, Yanagida et al., 2012). Except Ce 20% doped one, OSL intensities systematically decreased when X-ray exposure increased and it was suggested that OSL responses in Ce 0.1-1% doped samples saturated around few Gy exposure. Simply, OSL response was improved in higher Ce concentration sample by creation of defects due to the charge imbalance. Of course, the complementary relation of scintillation and OSL is not always observed in all material systems because there are some competing processes with OSL/TL in energy storage processes of dosimeter materials (e.g., tunnelling). In such material systems, most part of the absorbed energy would be converted to thermal form and we could not observe the complementary relation in such material systems.

4 Conclusion

Ce 0.1-20% doped CaF_2 crystals were prepared by Tokuyama Corp. using the simple solidification method. By optical transmittance, radioluminescence, and scintillation decay, it was confirmed that Ce-doped CaF_2 used in this work exhibited typical properties of this material system. Scintillation light yield had an inverse proportionality to Ce concentrations while OSL intensity was in proportion to dopant concentrations. The hypothesis that the scintillation and OSL had a complementary relation in some material systems was confirmed experimentally.

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Figure Captions

Figure 1 Ce-doped CaF_2 crystals illuminated by UV-lamp.

Figure 2 Transmittance spectra of Ce-doped CaF_2 crystals in the wavelength range from 190 to 320 nm.

Figure 3 X-ray induced radioluminescence spectra of Ce-doped CaF_2 scintillators in the wavelength range from 180 to 700 nm. The supplied bias voltage and tube current were 80 kV and 1 mA, respectively. The X-ray exposure time was 10 s for each integration.

Figure 4 X-ray induced scintillation decay times of Ce-doped CaF_2 plotted against Ce concentrations. The inset shows a decay time profile of Ce 5% doped CaF_2 . The excitation X-ray had a spectral form of Bremsstrahlung with the energy endpoint of 40 keV. The timing resolution was 80 ps.

Figure 5 Scintillation light yield plotted against Ce concentrations. The inset shows ^{241}Am α -ray spectrum of Ce 0.1% doped CaF_2 . The shaping time was 2 μs and 5.5 MeV peak channel was determined by a single gaussian fitting.

Figure 6 OSL emission map of Ce 20% doped CaF_2 . The horizontal axis shows the stimulation wavelength and the vertical axis exhibits emission wavelength with 10 nm step.

Figure 7 OSL intensity (QY , %) plotted against Ce concentrations after 2 Gy exposure. QY was calculated by summing up of 550 and 830 nm stimulation.

Figure 8 Relation between the scintillation light yield (ph/5.5 MeV- α) and OSL intensity (QY , %) after 0.5, 1, 2, and 4 Gy X-ray exposure.

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