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Radio-photoluminescence phenomenon in non-doped CaF_2 ceramic

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ABSTARCT

We discovered that a CaF_2 ceramic showed a radio-photoluminescence (RPL) phenomenon by X-ray irradiation. The RPL observed in the non-doped CaF_2 ceramic as a generation of photoluminescence (PL) emission bands peaking at 660 nm under excitations at 370 and 560 nm, and 760 nm under excitations at 390 and 610 nm. The emission bands at 660 and 760 nm are due to F_2^+ and $(F_2^+)_A$ centers, respectively.

1. Introduction

Storage phosphors are often used as radiation detectors such as personal dosimeters and imaging plates. Such materials have a function to store and accumulate absorbed energy of incident radiations as a form of trapped electrons and holes. Radio-photoluminescence (RPL) is recognized as a phenomenon in which stable photoluminescence (PL) centers are newly occurred via interactions with radiations. In common cases of practical applications, the RPL is described as a valence change including Ag ion ($Ag^+ \rightarrow Ag^0$ and Ag^{2+}) in Ag-doped phosphate glass [1–4] or generation of defect centers such as F_2 and F_2^+ (2 Mg) in Al_2O_3:C, Mg [5,6]. The Ag-doped phosphate glass is a well-known material used for personnel dosimetry, which is commercialized by Chiyoda Technol Corp. while Al_2O_3:C, Mg was created by Landauer Inc. for particularly nuclear track detections. In RPL phenomenon, the number of newly occurred PL centers depends on the radiation dose deposited to the phosphor. For this reason, we can apply the PL intensity as a measurment of radiation dose, so the RPL is utilized in applications of personal dosimetery. In comparison with thermally stimulated luminescence (TSL) and optically stimulated luminescence (OSL) dosimeters, RPL dosimeters have a notable advantage that a luminescence intensity corresponding to deposited radiation dose can be read out several time without fading of the luminescence intensity [3,4]. In spite of such advantage, only little phosphors are known to possess RPL properties; for example, Ag-doped phosphate glasses [2], Cu-doped aluminoborosilicate glass [7], Al_2O_3:C, Mg [6], Eu-doped material [8], Sm-doped material [9], Yb-doped NaCl [10], LiF [11], MgF_2 [12], Mg_2SiO_4 [13], K_2CO_3 [14] and Na_2CO_3 [15].

In this study, we discovered and reported RPL properties of a non-doped CaF_2 ceramic for the first time. CaF_2 has been known as fluorite for a long time, which is applied to optical lens for high power laser, astronomical telescope and industrial inspection equipment having a wide band gap and high durability. In radiation detection field, Dy, Tm and Mn-doped CaF_2 are used as TSL dosimeter because its Z_{eff} is close to the soft tissue [16–18]. Furthermore, OSL properties of CaF_2 doped with rare earth or transition metal were also investigated [19–21]; however, to the best of our knowledge, there was no study concerning RPL properties of the non-doped CaF_2.

2. Material and methods

The CaF_2 ceramic sample was prepared by the spark plasma sintering (SPS) method using Sinter Land LabX-100. The sintering was carried out by following method in a vacuum. The sintering temperature was raised from 25 to 800 °C with a heating rate of 80 °C/min, and then the sintering condition was maintained at 800 °C with 10 MPa pressure for 10 min. Afterwards, the sintering temperature was furthermore raised to 1070 °C with a heating rate of 90 °C/min, and the state was maintained with 70 MPa pressure for 15 min, and then the sintering was ended.

The X-ray generator (XRB80N100/CB, Spellman) was used as radiation source, which equipped with an X-ray tube having a W anode target. The irradiation dose was fixed to 20 Gy. The PL excitation and emission maps and quantum yields were measured by Hamamatsu Quantaurus QY. The PL excitation and emission maps were measured over the excitation wavelengths of 250–700 nm with 10 nm interval. The PL decay curves monitored at 660 and

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760 nm were evaluated by using Hamamatsu Quantaurus-τ. Here, the PL decay constants were estimated by least-square fitting of decay curve by an exponential decay function. This device is equipped with seven excitation sources of 280, 340, 365, 405, 470, 590 and 630 nm.

3. Results and discussion

Fig. 1 illustrates an appearance of the non-irradiated and irradiated samples under LED and UV (365 nm) light. It seems like that there is no difference of the appearance between both non-irradiated and irradiated samples under LED light,. In comparison with the non-irradiated and irradiated samples under UV light, the irradiated sample showed red luminescence although the non-irradiated sample showed no luminescence. This phenomenon assists an idea that new emission centers were occurred by X-ray irradiation, which is one of the evidence of RPL phenonmenon.

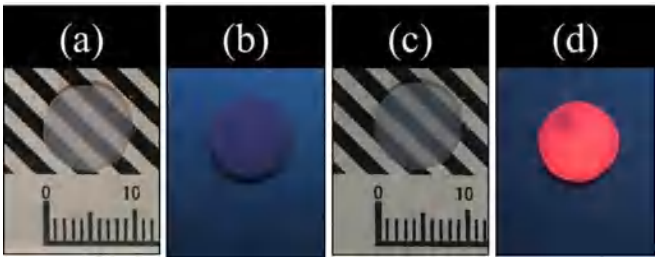

Fig. 1. (a) Non-irradiated and (c) irradiated samples under LED light, and (b) non-irradiated and (d) irradiated samples under UV light (365 nm).

Fig. 2 shows the PL excitation and emission maps before and after X-ray irradiation. The non-irradiated sample showed no emission bands. In contrast, the irradiated sample showed emission bands peaking around 660 nm with an excitation bands peaking around 370 and 560 nm, and 760 nm with an excitation bands peaking around 390 and 610 nm. The maximum PL quantum yield was 42.6%. According to the previous study, CaF_2 shows the emission band peaking around 645 nm under 360 and 545 nm excitations due to F_2^+ center [22]. Hence, it is considered that the emission at 660 nm observed in our samples arises from F_2^+ center. On the other hand, the excitation wavelengths at 390 and 610 nm were approximately consistent with the absorption wavelengths of $(F_2^+)_A$ center [23]; thus, there is a high possibility that the emission at 760 nm is due to $(F_2^+)_A$ center.

Fig. 3 represents the PL decay time profiles monitored at 660 nm under 340 and 590 nm excitations, and 760 nm under 405 and 630 nm excitations with an instrumental response function (IRF). Both the decay curves were well-approximated by an exponential decay function. The derived decay constants monitored at 660 nm under 340 and 590 nm excitations were 15.9 and 16.8 ns, respectively. In contrast, the obtained decay constants

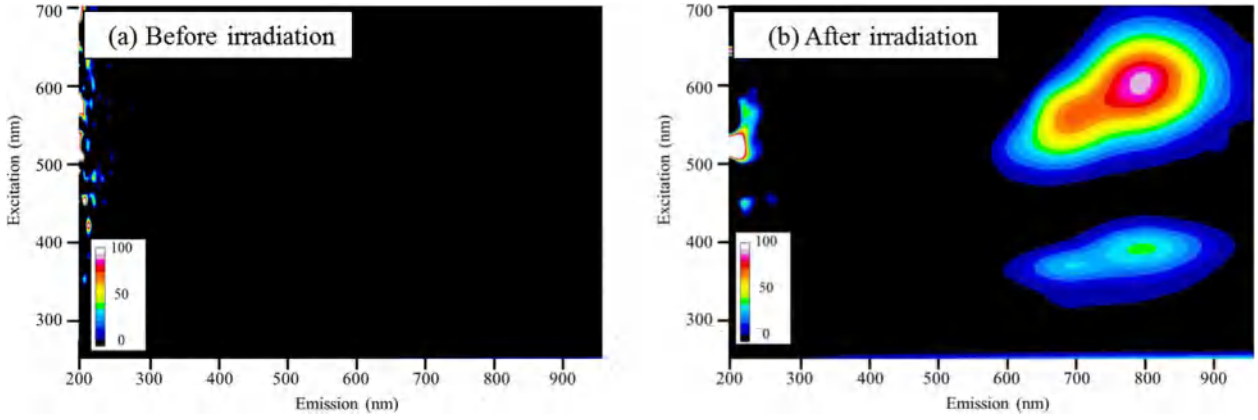

Fig. 2. PL excitation and emission maps of the (a) non-irradiated and (b) irradiated samples. The horizontal and vertical axes show emission and excitation wavelengths, respectively.

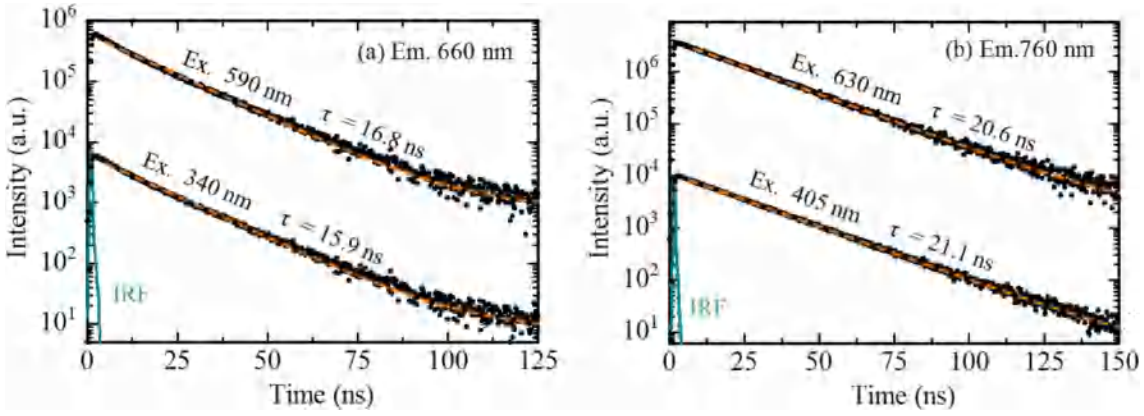

Fig. 3. PL decay time profiles monitored at (a) 660 nm under 340 and 590 nm excitations, and (b) 760 nm under 405 and 630 nm excitations with the instrumental response function.

monitored at 760 nm under 405 and 630 nm excitations were 21.1 and 20.6 ns, respectively. These results back up the above argument that the origins of the emissions are caused by defects since significantly short decay constant is a representative feature of luminescences from defects [12,14]. It should be stressed that conventional materials showing RPL based on the generation of defects are only LiF, MgF_2, Al_2O_3:C, Mg, Na_2CO_3 and K_2CO_3 so far [5,11–15].

4. Conclusions

We prepared the non-doped CaF_2 ceramic by the SPS method, and then discovered that the CaF_2 ceramic showed RPL phenomenon. The X-ray irradiated sample showed the broad emissions peaking at 660 nm under 370 and 560 nm excitations, and 760 nm under 390 and 610 nm excitations. Judging from the excitation wavelengths, the former and latter emissions are due to F_2^+ and $(F_2^+)_A$ center.

CRediT authorship contribution statement

Takumi Kato: Conceptualization, Data curation, Writing - review & editing. **Daisuke Nakauchi:** Investigation. **Noriaki Kawaguchi:** Investigation. **Takayuki Yanagida:** Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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