Novel radio-photoluminescence materials and applications

Go OKADA$^{1,2}$

$^1$Department of Applied Chemistry, Kanazawa Institute of Technology, 7–1 Ohgigaoka, Nonoichi, Ishikawa 921–8501, Japan
$^2$Co-creative Research Center of Industrial Science and Technology, Kanazawa Institute of Technology, 3–1 Yatsukaho, Hakusan, Ishikawa 924–0838, Japan

Radio-photoluminescence (RPL) is a phenomenon whereby a new luminescent centre is generated in a material by the interaction of an ionizing radiation with the medium. Despite the usefulness of RPL, e.g. in radiation measurements, there are only a limited number of RPL materials available today, which limits our understanding of the phenomenon as well as extending its use for new applications. In recent investigations, a large number of new RPL material systems have been proposed for radiation measurements. In particular, Sm-based RPL is one of the most intensively studied alternative systems, which shows RPL properties owing to the intravalence reduction of the Sm ion (Sm$^{3+}$ → Sm$^{2+}$) induced by ionizing radiation. The generated Sm$^{2+}$, as well as Sm$^{3+}$, acts as a luminescent centre and shows photoluminescence, typically around 700 nm. This approach has enabled us to explore a wider range of material choices and to find a new application of RPL. An example is microbeam radiation therapy (MRT), which requires the measurement of extremely large radiation dose distributions at a microscopic scale. Such a new class of RPL is not only limited to Sm-based materials but also to those doped with other rare earth ions (e.g., Eu and Yb) and undoped materials.

Key-words: Radio-photoluminescence, RPL, Phosphor, Radiation measurement

1. Introduction

Radio-photoluminescence (RPL) is a radiation-induced luminescence phenomenon in which a new luminescent centre is generated in a material by the absorption of ionizing radiation. In general, the generated luminescent centre is stable in a normal environment, and the number of generated luminescent centres increases with increasing radiation dose accumulated over a certain period of time. Since a luminescence centre typically has a photoluminescence (PL) property, the RPL phenomenon can be easily observed by a conventional PL technique, and the PL intensity is proportional to the radiation dose. For these reasons, the RPL can be used for radiation dosimetry applications.

Luminescence phenomena used for radiation measurements in RPL are well-known in scintillation,$^1$ thermally stimulated luminescence (TSL),$^2$ and optically stimulated luminescence (OSL).$^3,4$ A distinct difference of RPL from scintillation is that the RPL allows one to record a signal (dose and distribution) on a material itself. Further, compared with TSL and OSL, a recorded RPL signal can be nondestructively read out. Scintillation, TSL, and OSL have been engaged in the fields of radiation measurement for a number of decades, and there are a large number of material systems recognized to show these phenomena, and they have found many applications. In contrast, despite the unique properties and usefulness of RPL, the materials and applications are quite limited today compared with the above radiation-induced luminescence phenomena, mainly because it has been recognized relatively recently.

There are three representative RPL materials: Ag-doped sodium aluminophosphosphate (SAP) glass,$^5$ Al$_2$O$_3$·C·Mg,$^6$ and LiF.$^7$ The Ag-doped SAP glass is probably the most successful RPL material in industry since it has found an application in personnel routine dosimetry, which has been commercialized by Chiyoda Technol Corp. since 2000, and it is still used in Japan and worldwide today.$^8$ The RPL phenomenon is understood to be due to the valence change of doped Ag ion as the Ag$^+$ ion can capture both an electron and a hole and then convert to Ag$^0$ and Ag$^{2+}$ states, respectively, although the detailed process is still controversial.$^9$ Upon UV excitation, these states of Ag act as luminescent centres and show strong luminescence in the blue and orange colours, respectively. Al$_2$O$_3$·C·Mg is another class of material specifically developed for RPL. It shows RPL as it forms F-centres (F$_2$) by ionizing radiation, and F$_2$+(2Mg) shows appears as the main RPL peak at 750 nm which can be excited by 260,
335, and 620 nm of light. This material is specifically designed not for use in point dosimetry, unlike Ag-doped SAP glass, but as so-called nuclear track detector which is intended to detect the trajectory of a nuclear particle deposited in the material on a microscopic scale. LiF may be the most attractive material for personnel dosimetry applications for its effective atomic number is equivalent to that of a biological soft tissue (~7.4). When it is irradiated, as for Al₂O₃:C,Mg, two different F-centres are formed. One is F₃⁺ which shows an emission band peaking at 530 nm while the other is F₂ showing an emission band peaking at 640 nm. Both the F-centres can be excited at 450 nm. The RPL of LiF has insufficient sensitivity in the μGy–mGy; therefore increasing its sensitivity is one of the most important issues for LiF to be used in major industrial applications.

In addition to the above conventional RPL materials, a large number of recent studies have focused on a search of new RPL materials and applications. This paper reviews recently investigated alternative RPL materials as well as new potential applications of RPL.

2. Alternative RPL materials

Today, materials recognized to show RPL phenomenon are very limited compared to those of scintillation, TSL, and OSL. In recent years, in addition to the conventional RPL materials, other classes of RPL materials have been intensively studied. One of the most actively studied material systems involves the Sm-ion. Sm³⁺ ion doped in a selected material is known to be reduced to Sm²⁺ by irradiating with ionizing radiation. One of the first studies on the reduction and PL of Sm²⁺ was due to Qiu et al. in the early 2000s, and the purpose was to obtain Sm²⁺ from Sm³⁺ ion by the trapping of phosphorus-oxygen hole burning for high-density optical memory applications. About 10 years later, the author and his colleagues at the University of Saskatchewan, the Victoria University of Wellington and the Canadian Light Source (CLS) have focused on the latter Sm-based RPL phenomenon for applications in radiation measurements.

As an example of RPL based on Sm³⁺, Fig. 1 shows the PL spectra of Sm-doped fluorophosphate glass as a function of X-ray dose. Without X-ray irradiation, the material shows luminescence bands peaking approximately at 560, 600, 640, and 700 nm. The origin of these emissions is attributed to the so-called 4f-4f transitions of Sm³⁺ ion, which are electronic transitions between the 4f orbitals. After X-ray irradiation, in contrast, there appears an evident difference in the PL spectrum in the long spectral region where sharp luminescence peaks appear at 680, 700, 720, 760, and 810 nm. The origin of these peaks is attributed to the 4f-4f transitions of Sm²⁺. In addition, the intensity of the latter emission peaks increases with increasing irradiation dose. The above observation clearly shows that the Sm²⁺ ion is generated by irradiating with X-rays.

Figure 2 shows an RPL response (which is equivalent to the PL intensity of Sm²⁺ ion) of Sm-doped fluorophosphate glasses as a function of X-ray irradiation dose. It is clearly seen that the response value increases with increasing irradiation dose, and the response saturates above a few thousand grays. In addition, the figure compares the response function with that of radiation induced absorbance in the UV region (denoted as G₁, G₂, and G₃). The origin of absorbance is due to a phosphorus-oxygen hole centre (POHC). A notable fact is that, as for the PL intensity of Sm²⁺, the intensity of absorbance by POHC increases with irradiation dose, and their increase rates are quite equivalent. In addition, the absorbance signal saturates in the same dose region as that of PL. These facts suggest that the generation of Sm²⁺ and POHC are closely connected as expressed in the below equations:

\[
\text{Sm}^{3+} + \text{PO} \xrightarrow{\text{irrad}} \text{Sm}^{3+} + \text{PO} + (e^- + h^+) \quad (1)
\]
\[
\text{Sm}^{3+} + e^- \xrightarrow{\text{migration}} (\text{Sm}^{3+} + e^-) + (\text{PO} + h^+) \quad (2)
\]
\[
\text{Sm}^{2+} + \text{POHC} \quad (3)
\]

First, at the initial state, the Sm-ion is in its trivalent state and the glass matrix contains a PO bonding network. When it is irradiated, a numerous number of electrons and...
Table 1. Recently investigated materials that show RPL for radiation measurement applications

| #  | Host Material          | Activator |
|----|------------------------|-----------|
| 1  | Li2CO3                  | n/a       |
| 2  | Li3PO4-Al(PO4)2         | Ag        |
| 3  | LiCuAlF6                | Sm        |
| 4  | Na2CO3                  | n/a       |
| 5  | NaCl                     | Yb        |
| 6  | MgF2                    | n/a       |
| 7  | MgF2                    | Sm        |
| 8  | MgF2·MgO·F2O3-B2O3·Sm   | Sm        |
| 9  | MgF2·AlF3·SrF2·YF·BaF2  | Sm        |
| 10 | MgF2·AlF3·CaF2·SrF2·Sr(PO3)12 (Fluorophosphate) | Sm |
| 11 | MgSiO2                  | n/a       |
| 12 | KBr                     | Sm        |
| 13 | K2CO3                   | n/a       |
| 14 | CaF2                    | Sm        |
| 15 | Ca2SiO4                 | Eu        |
| 16 | CaSO4                   | n/a       |
| 17 | CaSO4·1.32              | Sm        |
| 18 | SrBr2                   | Sm        |
| 19 | SrBPO3                  | Sm        |
| 20 | SrSO4                   | Sm        |
| 21 | BaBPO3                  | Sm        |
| 22 | BaSO4                   | Sm        |
| 23 | BaAlBO3·F3              | Eu        |
| 24 | BaAlBO3·F3              | Sm        |
| 25 | CsCl                    | Ag        |
| 26 | CsBr                    | Sm        |

holes are generated in the matrix [Eq. (1)]. Next, these generated charges migrate in the matrix and then meet Sm3+ and PO, respectively [Eq. (2)]. Last, the electron is trapped by Sm3+, which becomes Sm2+, while the hole is trapped by PO, which becomes POHC [Eq. (3)]. With the presence of POHC, the charge compensation is maintained, and the Sm2+ ion can be stable in the matrix. There are several different RPL materials reported in the literature, and they do not always contain PO molecules. Therefore, the destination of free holes should vary by the host material system. Table 1 summarizes a list of new alternative RPL materials studied for radiation measurements. The material system for Sm-based RPL is not just limited to fluorophosphates but oxides, oxyfluorides, halides, carbonates, and sulfates. Because there are a large number of Sm-doped materials listed in the table, it seems that any materials doped with Sm3+ ions show RPL properties, but the fact is that it is very rare and only a limited number of Sm-doped materials show RPL. There are also other classes of RPL materials based on Ag, Eu, and Yb activators. The Eu- and Yb-based RPL are explained by the reduction of the trivalent state to divalent as for the Sm-based RPL.

One may wonder by what material properties the occurrence of RPL is controlled. As discussed above, the charge compensation should be one of important aspects as we generally understand by the knowledge of Electrochemistry whereas Fig. 3 proposes an additional aspect. The figure summarizes whether or not RPL properties are effective for a set of Sm-doped materials as a function of band gap energy of the host material. It is clearly demonstrated that those with relatively smaller band gap energy do not show RPL while those with larger band gap energy do show RPL. Further, the threshold between these opposite types of behaviour appears around 7 eV. Therefore, it suggests that having a larger band gap energy is an important aspect to consider for a host material of the Sm3+ ion in order to obtain an RPL property. An interpretation for the reason why the band gap energy matters is as follows. As discussed above, the RPL of Sm-doped materials can be interpreted by a charge trapping process of electrons and holes generated by the ionizing radiation. The Sm3+ ion acts as an electron trapping centre, so Sm3+ acquires an electron and then becomes Sm2+. Considering the potential energy of the Sm-ions, it is well-understood that Sm2+ is located at a higher potential energy than Sm3+. 37) As depicted in the inset of Fig. 3, Sm2+ locates within the forbidden band when the band gap energy is sufficiently large, which confirms that the trapped electron at Sm2+ stays as it is. When the band gap energy is smaller, however, the location of Sm2+ becomes inside or close to the bottom of the conduction band, so the captured electron can easily escape into the conduction band, hence the Sm2+ loses an electron and then reverts back to Sm3+. With the above knowledge, in fact, the band gap energy should be considered just as an indirect indicator for the right material choice. A more important aspect should be the energy gap between the bottom of the conduction band and Sm2+; therefore, it is probably more appropriate to discuss the phenomenon with the latter energy gap than simply the band gap energy.

3. Applications in microbeam radiation therapy (MRT)

Conventionally, RPL phenomenon has been considered for a number of applications such as individual routine dosimetry,38) environmental dosimetry,39) nuclear track detection,40) and high density optical memory.41) Recently, highly controlled beam irradiation has attracted considerations for a new generation of radiation therapy. One
example is the MRT. Figure 4 illustrates the principle of MRT. In MRT, an array of multiple micro-structured X-ray beams is used to treat a cancer tumour. The radiation dose at the centres of the microbeams are on an order of hundreds or thousands of grays, which is extremely high for radiation therapy, whereas those at the valleys of beams should be controlled below 20 Gy. It is extremely important to experimentally measure the distribution of the radiation dose in addition to just a computer simulation, in order to advance the technology into the clinical stage. However, due to the highly unusual characteristics of the treatment beam in terms of the large dose range and microscale distribution, no existing radiation detectors could satisfy the requirements of both the dynamic range and spatial resolution together.

For the highly challenging dosimetric applications in MRT, Sm-doped RPL materials have been considered, because a dose level can be recorded as RPL on a detector plate, and the distribution can be read out by using a confocal fluorescent microscope with a microscale resolution. The same approach was applied by using RPL of Al2O3:C,Mg, but it can only detect the radiation dose approximately below 50 Gy. Furthermore, RPL response of Ag-doped SAP glass is also known to saturate above 50 Gy, and LiF does not have sufficient sensitivity to low doses. Figure 5 compares dose response functions of several different Sm-doped RPL materials considered for dosimetric applications in MRT. The dynamic range strongly varies by the host material, and it also depends on the concentration of Sm. Dose detection range required in MRT is said to be from a few Gy to over 1000 Gy, so 1% Sm-doped fluoroaluminate glass is considered as a promising candidate. Some polycrystalline materials were also tested in the initial stage; however, severe light scattering during the readout process due to the polycrystalline nature of the sample dramatically decreases the image resolution.

The recorded RPL signal on a glass plate is intended to be read out by using a confocal laser scanning fluorescent microscope. The instrumental details can be found elsewhere. Figure 6 shows a dose distribution of microbeam X-ray obtained by using a Sm-doped fluoroaluminate glass plate as an RPL detector. Figure 6(a) demonstrates the two-dimensional features as a function of the entrance dose (dose measured at the upstream of multislit collimator), and Fig. 6(b) demonstrates the profiles in the one-dimensional scale. It is clearly demonstrated that the dose values of both in and between the adjacent beams are successfully detected. In addition, the distribution features such as flat structures on top of the beams, sharp edges, and tail structures are well represented.

Figure 7 compares dose distribution profiles of microbeams at the CLS, Canada, European Synchrotron Research Facility (ESRF), France, and SPring-8, Japan. The profiles are also compared with a result of Monte Carlo Simulations for various radiation sources and microbeam energies.
Carlo simulation performed by Nettlebeck et al. The experimental profiles are very well correlated with the simulation data which convinces that the present approach is a very promising technique for MRT. In addition, the experimental data clearly indicate the difference of distribution shape, or the dose contrast between the peak and valley, between the synchrotron facilities. It is said that the larger the contrast, the more effective for a cancer treatment. In this context, the treatment beam at SPring-8 has the best quality while the one at ESRF is the poorest. The reason for the low contrast at ESRF was considered to be due to a large number of collimation components installed in the beam path. In addition, at the time of the irradiation at the CLS, the multi-slit collimator was misaligned only by a rotation angle of 0.03° with respect to the beam axis. (Notice that the beam width is slightly smaller than the others.) After realignment, the peak shape became identical to that of SPring-8. These results, as well as a recent extended work, indicate that the dose contrast is very sensitive to the collimator alignment while the present technique is a very powerful tool to detect the error and evaluate the beam quality.

4. Conclusions

Recently, RPL phenomenon has attracted increasing interests for its uniqueness and usefulness especially in the field of materials science and radiation measurement. Conventionally, Ag-doped SAP glass, Al2O3:C,Mg, and LiF are well recognized as RPL material standards while a limited number of available materials are problematic in terms of a comprehensive understanding of the phenomenon as well as extending into new applications. Recent intensive investigations on a search of new RPL materials have successfully increased the material choices, and a new class of RPL detectors (Sm-doped fluoroaluminate glass) found a promising application in high-dose and high-resolution dosimetry in MRT. A continuous search for new materials is believed to open the doors to new scientific discoveries and potential new applications.

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Go Okada received an M.Sc. and Ph.D. from the University of Saskatchewan, Saskatoon, Canada, under supervision of Prof. Safa Kasap. After his engagement as a Post-doctoral Research Fellow at Lakehead University, Thunder Bay, Canada, and the University of Saskatchewan, he joined the Graduate School of Materials Science, Nara Institute of Technology, Ikoma, Japan, as an Assistant Professor in 2015 to work with Prof. Takayuki Yanagida. Since 2018, he has joined the Department of Applied Chemistry and Co-creative Research Center of Industrial Science and Technology, Kanazawa Institute of Technology, Nonoichi, Japan, to start his own research laboratories as an Assistant Professor. His current research interest includes materials science and its applications in radiation measurement applications.