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Radiophotoluminescence Properties of Bi-doped $CaBPO_5$

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Bi-doped $CaBPO_5$ was synthesized by the solid-state reaction method, and its radiophotoluminescence (RPL) properties were subsequently examined. Steady-state photoluminescence (PL) studies suggest that Bi^{2+} ions are generated upon X-ray irradiation, resulting in a PL emission band with a peak at 630 nm. The RPL-related PL signal is unstable at room temperature, decreasing to approximately 50% of its initial intensity within 20 min. Heat treatment accelerates the signal decay, with the signal minimized after heating to 500 °C. Following signal erasure via heat treatment at 500 °C, the material sensitivity to X-ray irradiation shows a slight increase with repeated cycles, rising by approximately 40% of the original sensitivity after 10 cycles.

1. Introduction

Radiophotoluminescence (RPL) has attracted significant attention in the field of luminescence dosimetry owing to its utility in radiation detection.[1–3] RPL is defined as a phenomenon wherein luminescence centers are generated through interactions with ionizing radiation. These luminescence centers, which can be detected by conventional photoluminescence (PL) techniques, exhibit an intensity directly proportional to the accumulated radiation dose, thus enabling the quantification of radiation exposure. Despite the effectiveness of RPL, conventional dosimetric materials remain limited to Ag-doped phosphate glass,[4–6] LiF,[7,8] and Al_2O_3:C,Mg.[9,10] Recent research, however, has identified additional viable materials, including

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Sm-doped,[11–18] Eu-doped,[19–22] Yb-doped,[23] and Bi-doped[24] compounds, as well as certain undoped compounds.[25–28]

In this study, we explore the development of novel RPL materials by synthesizing Bi-doped $CaBPO_5$ by the solid-state reaction method. $CaBPO_5$ is an attractive host as the effective atomic number is reasonably low (Z_{eff} ~ 14.7), and it consists of B, thus having the potential for neutron detection owing to the nuclear reaction: $^{10}B + n \rightarrow {}^{7}Li + {}^{4}He$. The Bi-doped $CaBPO_5$ compound demonstrated RPL characteristics, affirming its potential for use in dosimetric applications. A detailed discussion on the origin of its RPL properties and its suitability for radiation measurement is presented, underscoring the compound's value as a potential addition to the spectrum of materials available for advanced dosimetry.

2. Materials and Methods

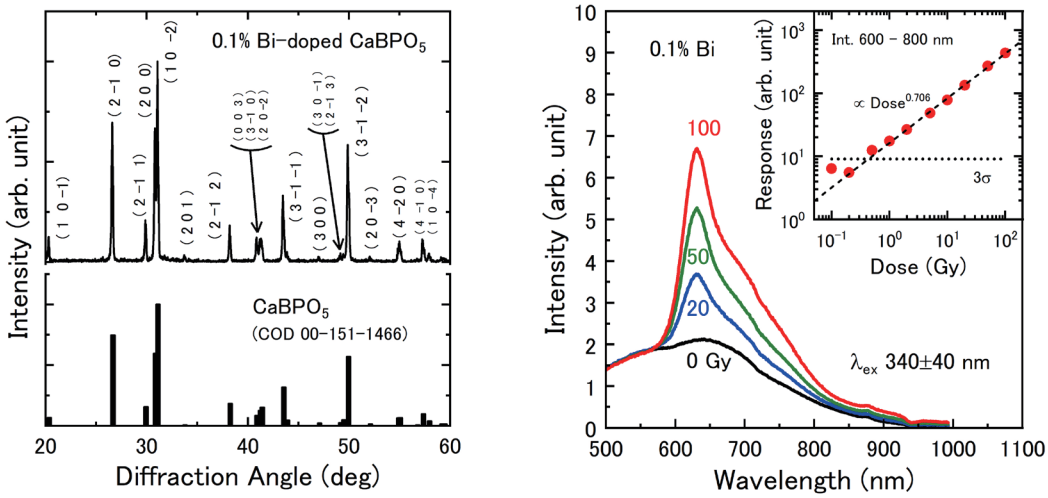
Bi-doped $CaBPO_5$ was prepared by the solid-state reaction method. The starting materials—$CaCO_3$ (99.99%), $NH_4H_2PO_4$ (99.999%), H_3BO_3 (99.99%), and Bi_2O_3 (99.9%)—were weighed to the stoichiometric ratio and then thoroughly mixed for 20 min using a mortar and pestle, with the addition of 10 mol% Na_2CO_3 (99.9%) as a sintering aid. The Bi concentrations were 0.1, 0.2, 0.5, and 1.0%. The resulting mixture was transferred to an alumina crucible and subjected to a two-step sintering process: first at 200 °C for 2 h, followed by a secondary sintering at 950 °C for 4 h, performed in an electric furnace (FT-101FMW, Full-Tech).

Characterizations were conducted using the TSL/OSL/RPL Automated and Integrated Measurement System (TORAIMS). Details of the system are available elsewhere;[29] however, a brief overview is provided here. TORAIMS comprises an X-ray tube (XRB80N, Spellman), a Xenon lamp (LAX-C100, Asahi Spectra), a multichannel spectrometer (QEPro, Ocean Optics), and a ceramic heater (WALN-3H, Sakaguchi), facilitating the X-ray irradiation, PL spectrum measurements, and thermal treatment of the sample. These components are managed through computer-controlled software that enables a customizable measurement sequence, thereby ensuring highly reproducible and reliable characterizations by minimizing potential deviations associated with manual operations.

3. Results and Discussion

Figure 1(a) shows the X-ray diffraction (XRD) pattern of a representative 0.1% Bi-doped $CaBPO_5$ sample, compared with a standard reference pattern from the Crystallography Open Database (COD) (00-151-1466). The experimental and reference patterns show excellent agreement, confirming that the synthesized sample exists as a single phase of $CaBPO_5$. It is considered that the introduced Bi ion substitutes the Ca site owing to the similarity of ionic radii.

Figure 1(b) shows the PL spectra of a 0.1% Bi-doped $CaBPO_5$ sample as a function of X-ray irradiation dose. Prior to X-ray irradiation (0 Gy), the sample exhibits a broad luminescence band spanning 500–800 nm, suggesting that the luminescence originates from a defect center. Following X-ray irradiation, an additional luminescence band appears, peaking at 630 nm, with its intensity increasing proportionally to the X-ray dose. The emergence of this luminescence



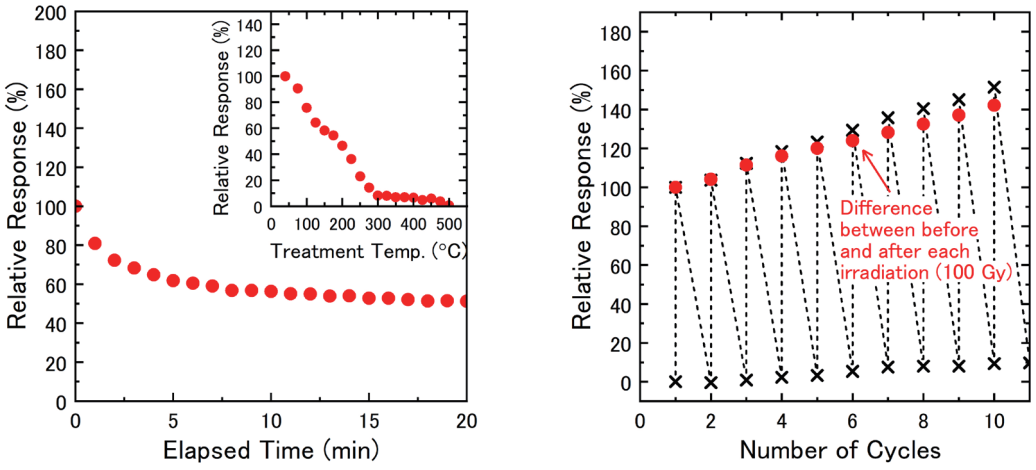
(a) (b)

Fig. 1. (Color online) (a) XRD pattern of 0.1% Bi-doped $CaBPO_5$ compared with a reference pattern (COD 00-151-1466). (b) PL spectra of 0.1% Bi-doped $CaBPO_5$ measured as a function of X-ray irradiation dose. The inset shows a dose response function.

band indicates the formation of luminescent centers due to X-ray irradiation, confirming the RPL properties of Bi-doped $CaBPO_5$. A similar RPL behavior was observed in previous research by Nakamura *et al.*, who reported that Bi-doped $NaCaBO_3$ exhibits RPL due to the formation of Bi^{2+} centers upon interaction with ionizing radiation.[24] This suggests that a similar mechanism may be responsible in the present material.

The X-ray sensitivity varies with Bi concentration, with the 0.1% Bi-doped sample demonstrating the highest sensitivity among the tested concentrations (0.1, 0.2, 0.5, and 1.0%). The inset of Fig. 1(b) shows the dose response function for the 0.1% Bi-doped sample, defined as the RPL intensity as a function of the delivered X-ray dose. Here, the RPL response is measured as the induced, integrated PL signal across 600–800 nm. The results indicate a monotonic increase in intensity with dose, with a slope of approximately 0.7 on a log-log scale. The intersection with the 3σ line, representing three times the standard deviation of the signal from the reader instrument, occurs at approximately 0.4 Gy, establishing the lowest detectable dose (LDD) for the TORAIMS reader instrument at 0.4 Gy. It should be noted that further optimization of the reader system could lower the LDD; however, this falls outside the scope of this study.

Figure 2(a) shows the stability of the RPL signal, which corresponds to the stability of Bi^{2+} centers formed following X-ray irradiation at a total dose of 100 Gy. The response value shows a remarkable decrease within the first few minutes, with intensity declining to approximately 50% of its initial value after 20 min. For precise dose estimation, it is therefore crucial to utilize the stabilized signal value rather than the initial, halved sensitivity. The inset in Fig. 2(a) shows the relative response signal as a function of heat-treatment temperature. Heat treatment was applied for 100 s at each temperature, followed by PL spectrum measurement to assess the effect of temperature on signal stability. The data reveal a steep reduction in intensity as the treatment temperature increases from 100 to 300 °C, indicating that Bi^{2+} centers are effectively eliminated



(a) (b)

Fig. 2. (Color online) (a) Relative RPL response as a function of elapsed time after X-ray irradiation (100 Gy). The inset shows relative RPL response as a function of heat treatment temperature determined after X-ray irradiation of 100 Gy and before readout at room temperature. Each treatment time is 100 s. (b) Cycle testing of RPL with X-ray irradiation of 100 Gy and heat treatment of 500 °C for 200 s. The circle plots represent response values by 100 Gy at each cycle.

by heat treatment and exhibit high sensitivity to temperature, even at levels near room temperature. This suggests that the observed signal fading at room temperature, as shown in Fig. 2(a), is largely attributable to thermal effects. Moreover, when the treatment temperature is raised to 500 °C, the response signal is almost completely erased, indicating the potential for reusing the material.

Figure 2(b) illustrates the reproducibility of RPL in Bi-doped $CaBPO_5$. For this characterization, the sample was subjected to X-ray irradiation at a dose of 100 Gy, followed by heat treatment at 500 °C for 200 s to eliminate the response signal. This irradiation and heat-treatment cycle was repeated 10 times to assess the reproducibility of the RPL response. As shown in the figure, during the first cycle, the signal increases following irradiation and then decreases markedly after heat treatment. In the second cycle, the response to 100 Gy irradiation is slightly higher than in the first cycle, with the signal effectively reduced by subsequent heat treatment. With repeated cycles, the sensitivity of the sample gradually increases, with the response signal rising by approximately 40% compared with the original value. This behavior suggests that the RPL of Bi-doped $CaBPO_5$ lacks complete reproducibility without further treatment. However, as the sensitivity increase correlates well with the number of cycles, it could be accounted for through appropriate calibration.

4. Conclusions

Bi-doped $CaBPO_5$ was synthesized by the solid-state reaction method, and RPL properties were confirmed, attributed to the formation of Bi^{2+} ions induced by ionizing radiation. The dosimetric properties of the RPL were further investigated: the PL intensity of Bi^{2+} increases with radiation dose but shows instability at room temperature, decreasing to approximately 50%

of its initial value within 20 min. The RPL signal can be reset through heat treatment at 500 °C for 200 s; however, the sensitivity gradually increases with repeated cycles.

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