

Optically Stimulated Luminescence Properties of Eu-doped BaAl₂S₄

Yuma Takebuchi,^{1*} Mao Morioka,¹ Yuki Nakashima,¹ Keitaro Tezuka,¹
Hiromi Kimura,² Shota Otake,³ and Takayuki Yanagida³

¹Faculty of Engineering, Utsunomiya University, 7-1-2 Yoto, Utsunomiya, Tochigi 321-8585, Japan

²National Institute of Advanced Industrial Science and Technology (AIST),

1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

³Division of Materials Science, Nara Institute of Science and Technology (NAIST), Ikoma, Nara 630-0192, Japan

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Undoped and Eu-doped BaAl₂S₄ samples were synthesized by sulfurization using N₂/CS₂ gas flow. The XRD measurement indicated that the synthesized samples were a single phase of cubic BaAl₂S₄. The Eu-doped sample exhibited photoluminescence and optically stimulated luminescence (OSL) emissions originating from the 5d–4f transitions of Eu²⁺. In OSL dose response functions, the Eu-doped sample showed a sublinear response between 10 mGy and 10 Gy with X-rays.

1. Introduction

Phosphors are often used for ionizing radiation detection.^(1–11) Among the phosphors, those capable of storing ionizing radiation energy are useful for dosimetry applications, such as personal dosimetry and medical imaging.^(12–15) The development of higher-performance phosphors provides radiation protection and early detection of disease. Storage-type phosphors for dosimetry applications exhibit two types of luminescence: optically stimulated luminescence (OSL) and thermally stimulated luminescence (TSL). OSL has some advantages compared with TSL. The dose assessment time using OSL is generally shorter, and the cost of the reader system is lower than that using TSL. In addition, OSL prevents thermal quenching and is expected to show a higher luminescence intensity than TSL. On the other hand, few materials are used as OSL-type phosphors in practical applications.

To date, oxide and halide materials have been mainly researched,^(16–31) and there are only a few studies on sulfide materials in dosimetry fields. In particular, the reports are limited only to binary sulfide materials as far as we know.^(32–34) Since some ternary sulfide materials show good luminescence properties,^(35,36) there is room to develop ternary sulfide materials for dosimetry applications. Eu-doped BaAl₂S₄ is known to exhibit bright blue luminescence.^(37–39) According to a previous report, the internal PL quantum yield is more than 60%.⁽⁴⁰⁾ Although

*Corresponding author: e-mail: takebuchi@a.utsunomiya-u.ac.jp
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the luminescence properties of Eu-doped BaAl₂S₄ were reported more than 50 years ago,⁽⁴¹⁾ no dosimetric properties of this material have been reported. In this study, we synthesized undoped and Eu-doped BaAl₂S₄ samples and investigated their PL and OSL properties.

2. Materials and Methods

Undoped and Eu-doped BaAl₂S₄ samples were synthesized by the following procedure: The starting powders used were BaCO₃ (3N, Kanto Chemical), Al₂O₃ (4N, High Purity Chemical), and Eu₂O₃ (3N, Nippon Yttrium). The chemical compositions of the prepared samples were BaAl₂S₄ and Ba_{0.99}Eu_{0.01}Al₂S₄. First, BaAl₂O₄ precursors were prepared by the solid-state reaction. After mixing, the powders were calcined at 800 °C for 12 h and then sintered at 1200 °C for 12 h in the air. The oxide precursors were sulfurized at 1000 °C for 12 h in a N₂/CS₂ gas flow created by bubbling with N₂ carrier gas through liquid CS₂. The obtained samples were pressed into pellets and sintered again at 1000 °C for 12 h in a N₂/CS₂ gas flow. The crystal phase of the samples was checked by X-ray diffraction (XRD) measurement using an X-ray diffractometer (Rigaku, Ultima IV). Photoluminescence (PL) excitation and emission spectra were measured using a spectrofluorometer (JASCO, FP-6500). The PL decay curve was measured using Quantaurs-τ (Hamamatsu Photonics, C11367) and approximated using the following formula:

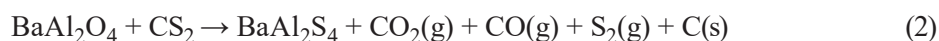
$$I(t) = I_0 \exp(-t/\tau). \quad (1)$$

Here, $I(t)$ represents the intensity at time t , and I_0 and τ mean the initial intensity and the decay time constant, respectively.

OSL emission and excitation spectra, decay curves, and dose-response functions were acquired using a spectrofluorometer (JASCO, FP-8600). An X-ray generator (Spellman, XRB80N100/CB) with 40 kV bias voltage was used for X-ray irradiation.

3. Results and Discussion

Figure 1 shows the XRD patterns of the undoped and Eu-doped BaAl₂S₄ samples. The inset shows the appearance of the samples under room light and 364 nm UV light. Both XRD patterns are consistent with a BaAl₂S₄ reference pattern (ICSD 035136), and no impurity phases are detected. Therefore, the obtained samples are a single phase of cubic BaAl₂S₄. Since the Eu-doped sample exhibits luminescence due to Eu²⁺ (described later) despite the BaAl₂O₄ precursor exhibiting red luminescence, Eu³⁺ could be reduced to Eu²⁺ during sulfurization. In the sulfurization process, the following reaction would occur.⁽⁴²⁾



The carbon would act as a reducer. BaAl₂S₄ has three cation sites: 6 and 12 coordinated Ba²⁺ sites (1.35 and 1.61 Å) and 4 coordinated Al³⁺ sites (0.39 Å).⁽⁴⁰⁾ Eu²⁺ (1.17 Å) occupies 6

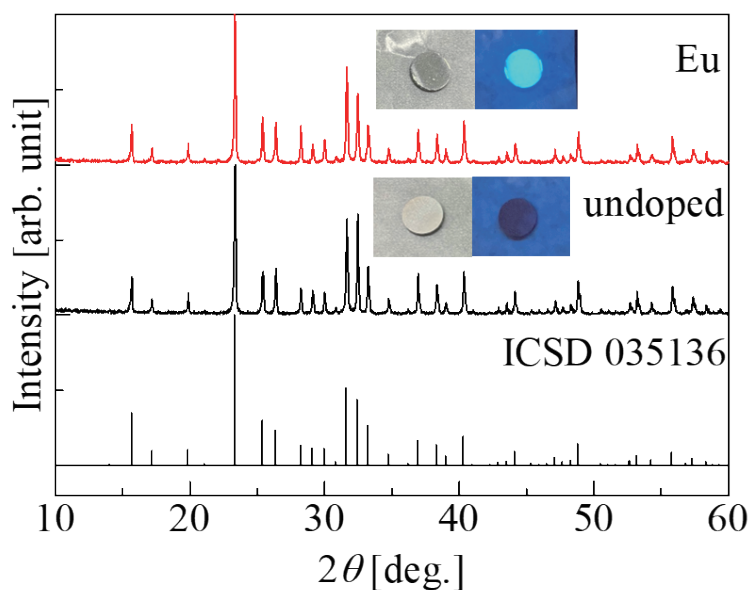


Fig. 1. (Color online) XRD patterns of undoped and Eu-doped BaAl_2S_4 samples. The inset shows the photos of the samples under (left) room light and (right) 364 nm UV light.

coordinated Ba^{2+} sites because of ionic radii and valence.⁽⁴³⁾ The samples are 9 mm in diameter, 3 mm in thickness, and gray. The color has been reported in a previous study and explained by carbon deposition.⁽⁴²⁾ However, the present samples show no carbon diffraction peaks because of a light element and low amount. Under UV irradiation, only the Eu-doped sample exhibits blue emission. Therefore, the luminescence properties of the Eu-doped sample were researched.

Figure 2 shows the PL excitation and emission spectra and decay curve of the Eu-doped sample. The Eu-doped sample exhibits a broad emission peak centered at 475 nm. The emission wavelength is consistent with the visual color shown in the inset in Fig. 1. For the 475 nm emission, two excitation peaks at 295 and 350 nm are observed. The spectral shapes of the emission peak remain constant regardless of excitation wavelength, and the emission intensity becomes the highest with 350 nm excitation. On the basis of the PL excitation and emission spectra, the excitation and monitoring wavelengths for the PL decay curve were set to 340 and 475 nm, respectively. The obtained decay time constant is 0.33 μs . The spectral shapes of the excitation and emission spectra well agree with previous studies,^(42,44,45) and the decay time constant is typical for the 5d–4f transitions of Eu^{2+} .^(46–50) Therefore, the luminescence center is attributed to Eu^{2+} . The carbon contamination would decrease the luminescence intensity by self-absorption, while the overall spectral shape remains unaffected.

Figure 3 shows the OSL stimulation and emission spectra and decay curve of the Eu-doped sample. After X-ray irradiation, the Eu-doped sample exhibits an emission peak around 475 nm with light stimulation. Judging from the spectral shape, the luminescence origin is the 5d–4f transitions of Eu^{2+} as well as PL. The OSL intensity increases as the stimulation wavelength shortens. The stimulation and monitoring wavelengths for the OSL decay curve were set to 475 and 610 nm, respectively. The emission intensity gradually decreases with continued irradiation by light stimulation. The decay curve is evidence that the emission peak shown in Fig. 3 is due to

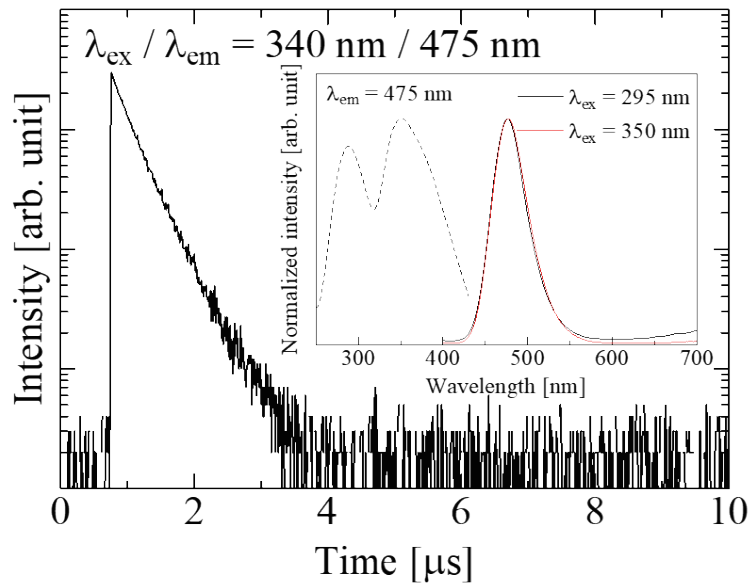


Fig. 2. (Color online) PL excitation and emission spectra (inset) and decay curve of Eu-doped BaAl₂S₄.

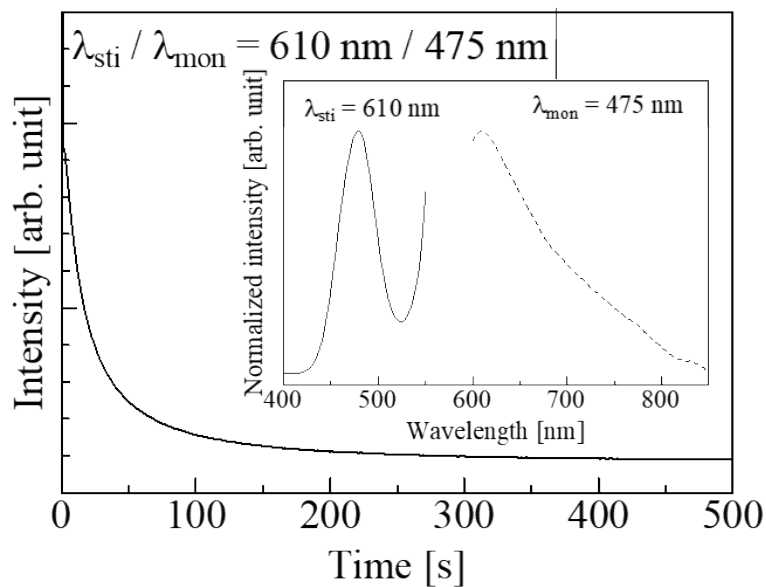


Fig. 3. OSL emission and stimulation spectra (inset) and decay curve of Eu-doped BaAl₂S₄.

the OSL phenomenon. According to a previous report, Eu²⁺ acts not only as luminescence centers but also as hole trapping centers.⁽⁵¹⁾ In addition, S vacancies act as electron trapping centers.⁽⁵²⁾ Therefore, Eu²⁺ and S vacancies may drive as trapping centers in Eu-doped BaAl₂S₄.

Figure 4 shows the OSL dose-response function of the Eu-doped sample. The OSL intensity is defined as the integrated intensity of OSL decay curves for each irradiation dose. The Eu-doped sample shows sublinearity between 10 mGy and 10 Gy. During the measurement,

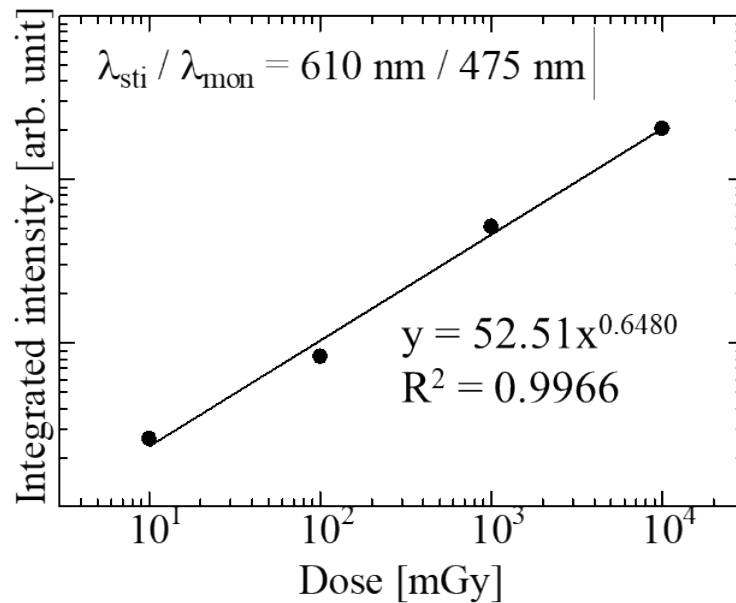


Fig. 4. OSL dose-response function of Eu-doped BaAl₂S₄.

BaAl₂S₄ was hydrolyzed by moisture and decreased the luminescence intensity.⁽⁵³⁾ Therefore, the OSL intensity in the higher dose range measured later was underestimated, and the dose-response function showed sublinearity. The results comprise the first report on the OSL properties of ternary sulfide materials, although the lower detection limit of 10 mGy is worse than those of some commercial dosimeters.^(16,54) The gray color shown in Fig. 1 causes self-absorption and decreases the OSL intensity. Therefore, the sensitivity can be improved by preventing carbon deposition, for example, by using H₂S gas instead of CS₂ for sample synthesis. In addition, sealing should also be considered to prevent hydrolysis.

4. Conclusions

In this study, the PL and OSL properties of Eu-doped BaAl₂S₄ were investigated. This is the first report on the OSL properties of ternary sulfide materials. The synthesized samples were a single phase of cubic BaAl₂S₄. Under UV irradiation, Eu-doped BaAl₂S₄ exhibited an emission peak around 475 nm, and the decay time constant was 0.33 μ s. The emission peak was attributed to the 5d–4f-transitions of Eu²⁺. In OSL, Eu²⁺ acted as a luminescence center as well as PL. A sublinear response between 10 mGy and 10 Gy was observed in the OSL dose-response functions. Eu-doped BaAl₂S₄ demonstrated that ternary sulfide materials are suitable for dosimetry application, although the lower detection limit of the present sample was worse than that of a commercial dosimeter. The OSL properties could be enhanced to improve the synthesis method.

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References

- 1 T. Yanagida and M. Koshimizu Eds.: Phosphors for Radiation Detectors (Wiley, 2022). <https://doi.org/10.1002/9781119583363>
- 2 T. Yanagida, T. Kato, D. Nakauchi, and N. Kawaguchi: Jpn. J. Appl. Phys. **62** (2023) 010508. <https://doi.org/10.35848/1347-4065/ac9026>
- 3 Y. Takebuchi, K. Watanabe, M. Koshimizu, K. Ichiba, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Radiat. Phys. Chem. **223** (2024) 111917. <https://doi.org/10.1016/j.radphyschem.2024.111917>
- 4 M. Koshimizu: Jpn. J. Appl. Phys. **62** (2023) 010503. <https://doi.org/10.35848/1347-4065/ac94fc>
- 5 K. Ichiba, Y. Takebuchi, H. Kimura, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: J. Mater. Sci. Mater. Electron. **33** (2022) 13634. <https://doi.org/10.1007/s10854-022-08298-3>
- 6 M. Koshimizu, K. Oba, Y. Fujimoto, and K. Asai: Sens. Mater. **36** (2024) 565. <https://doi.org/10.18494/SAM4761>
- 7 Y. Takebuchi, A. Masuno, D. Shiratori, K. Ichiba, A. Nishikawa, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Sens. Mater. **36** (2024) 579. <https://doi.org/10.18494/SAM4751>
- 8 Y. Takebuchi, D. Shiratori, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Sens. Mater. **35** (2023) 507. <https://doi.org/10.18494/SAM4142>
- 9 Y. Takebuchi, M. Koshimizu, K. Ichiba, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Materials (Basel) **16** (2023) 4502. <https://doi.org/10.3390/ma16134502>
- 10 Y. Takebuchi, K. Watanabe, D. Nakauchi, H. Fukushima, T. Kato, N. Kawaguchi, and T. Yanagida: J. Ceram. Soc. Japan **129** (2021) 397. <https://doi.org/10.2109/jcersj2.20233>
- 11 Y. Endo, K. Ichiba, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: Sens. Mater. **36** (2024) 473. <https://doi.org/10.18494/SAM4758>
- 12 H. Nanto: Sens. Mater. **30** (2018) 327. <https://doi.org/10.18494/SAM.2018.1803>
- 13 H. Nanto and G. Okada: Jpn. J. Appl. Phys. **62** (2023) 010505. <https://doi.org/10.35848/1347-4065/ac910614> K. Shinsho, R. Oh, M. Tanaka, N. Sugioka, H. Tanaka, G. Wakabayashi, T. Takata, W. Chang, S. Matsumoto, G. Okada, S. Sugawara, E. Sasaki, K. Watanabe, Y. Koba, K. Nagasaka, S. Yoshihashi, A. Uritani, and T. Negishi: Jpn. J. Appl. Phys. **62** (2023) 010502. <https://doi.org/10.35848/1347-4065/ac971e>
- 14 E. G. Yukihara, S. W. S. McKeever, C. E. Andersen, A. J. J. Bos, I. K. Bailiff, E. M. Yoshimura, G. O. Sawakuchi, L. Bossin, and J. B. Christensen: Nat. Rev. Methods Prim. **2** (2022) 26. <https://doi.org/10.1038/s43586-022-00102-0>
- 15 K. Ichiba, Y. Takebuchi, H. Kimura, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Sens. Mater. **35** (2023) 475. <https://doi.org/10.18494/SAM4143>
- 16 T. Kato, H. Kimura, K. Okazaki, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Sens. Mater. **35** (2023) 483. <https://doi.org/10.18494/SAM413718>
- 17 H. Ezawa, Y. Takebuchi, K. Okazaki, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Sens. Mater. **36** (2024) 465. <https://doi.org/10.18494/SAM4757>
- 18 R. Tsubouchi, H. Fukushima, T. Kato, D. Nakauchi, S. Saijo, T. Matsuura, N. Kawaguchi, T. Yoneda, and T. Yanagida: Sens. Mater. **36** (2024) 481. <https://doi.org/10.18494/SAM4763>
- 19 S. Otake, H. Sakaguchi, Y. Yoshikawa, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Sens. Mater. **36** (2024) 539. <https://doi.org/10.18494/SAM4759>
- 20 T. Kato, Y. Takebuchi, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Radiat. Meas. **135** (2020) 106341. <https://doi.org/10.1016/j.radmeas.2020.106341>
- 21 Y. Takebuchi, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Sens. Mater. **34** (2022) 645. <https://doi.org/10.18494/SAM3685>
- 22 K. Ichiba, Y. Takebuchi, H. Kimura, D. Shiratori, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Sens. Mater. **34** (2022) 677. <https://doi.org/10.18494/SAM3680>
- 23 K. Ichiba, Y. Takebuchi, H. Kimura, T. Kato, D. Shiratori, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Radiat. Phys. Chem. **202** (2023) 110515. <https://doi.org/10.1016/j.radphyschem.2022.110515>
- 24 Y. Takebuchi, M. Koshimizu, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: J. Lumin. **251** (2022) 119247. <https://doi.org/10.1016/j.jlumin.2022.119247>

- 26 Y. Takebuchi, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *J. Alloys Compd.* **1002** (2024) 175334. <https://doi.org/10.1016/j.jallcom.2024.175334>
- 27 Y. Takebuchi, H. Fukushima, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *Optik (Stuttg)* **231** (2021) 166498. <https://doi.org/10.1016/j.ijleo.2021.166498>
- 28 Y. Takebuchi, H. Fukushima, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **32** (2020) 1405. <https://doi.org/10.18494/SAM.2020.2717>
- 29 N. Kurata, N. Kubota, Y. Takei, and H. Nanto: *Radiat. Prot. Dosimetry* **119** (2006) 398. <https://doi.org/10.1093/rpd/nci515>
- 30 G. Fiksel, F. J. Marshall, C. Mileham, and C. Stoekli: *Rev. Sci. Instrum.* **83** (2012) 086103. <https://doi.org/10.1063/1.4739771>
- 31 K. Okazaki, T. Kato, Y. Takebuchi, H. Kimura, K. Ichiba, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *Radiat. Meas.* **175** (2024) 107156. <https://doi.org/10.1016/j.radmeas.2024.107156>
- 32 A. N. Yazici, M. Öztaş, and M. Bedir: *Opt. Mater. (Amst)*. **29** (2007) 1091. <https://doi.org/10.1016/j.optmat.2006.04.010>
- 33 M. Isik, M. Yüksel, M. Topaksu, and N. M. Gasanly: *J. Lumin.* **225** (2020) 117362. <https://doi.org/10.1016/j.jlumin.2020.117362>
- 34 D. Lapraz, H. Prévost, K. Idri, G. Angellier, and L. Dusseau: *Phys. Status Solidi* **203** (2006) 3793. <https://doi.org/10.1002/pssa.200622054>
- 35 J. E. Van Haecke, P. F. Smet, and D. Poelman: *J. Lumin.* **126** (2007) 508. <https://doi.org/10.1016/j.jlumin.2006.10.001>
- 36 Y. Nanai, Y. Sakamoto, and T. Okuno: *Jpn. J. Appl. Phys.* **52** (2013) 04CG15. <https://doi.org/10.7567/JJAP.52.04CG1537> G. Runhong, N. Miura, H. Matsumoto, and R. Nakano: *J. Rare Earths* **24** (2006) 119. [https://doi.org/10.1016/S1002-0721\(07\)60338-X](https://doi.org/10.1016/S1002-0721(07)60338-X)
- 38 W. A. Thornton: *Phys. Rev.* **102** (1956) 38. <https://doi.org/10.1103/PhysRev.102.38>
- 39 P. F. Smet, I. Moreels, Z. Hens, and D. Poelman: *Materials (Basel)* **3** (2010) 2834. <https://doi.org/10.3390/ma3042834>
- 40 K. T. Le Thi, A. Garcia, F. Guillen, and C. Foussaier: *Mater. Sci. Eng. B* **14** (1992) 393. [https://doi.org/10.1016/0921-5107\(92\)90080-S](https://doi.org/10.1016/0921-5107(92)90080-S)
- 41 P. C. Donohue and J. E. Hanlon: *J. Electrochem. Soc.* **121** (1974) 137. <https://doi.org/10.1149/1.2396807>
- 42 V. Petrykin and M. Kakihana: *Chem. Mater.* **20** (2008) 5128. <https://doi.org/10.1021/cm801339p>
- 43 R. D. Shannon: *Acta Crystallogr. Sect. A* **32** (1976) 751. <https://doi.org/10.1107/S0567739476001551>
- 44 R. Yu, H. Mi Noh, B. K. Moon, B. C. Choi, J. H. Jeong, K. Jang, H. S. Lee, and S. S. Yi: *Ceram. Int.* **39** (2013) 9709. <https://doi.org/10.1016/j.ceramint.2013.04.041>
- 45 C. Barthou, R. B. Jabbarov, P. Benalloul, C. Chartier, N. N. Musayeva, B. G. Tagiev, and O. B. Tagiev: *J. Electrochem. Soc.* **153** (2006) G253. <https://doi.org/10.1149/1.2164693>
- 46 H. Ito, G. Okada, Y. Koguchi, W. Kada, K. Watanabe, and H. Nanto: *Sens. Mater.* **36** (2024) 559. <https://doi.org/10.18494/SAM4765>
- 47 I. Tanaka, Y. Inoue, K. Tanaka, and Y. Izumi: *J. Lumin.* **96** (2002) 69. [https://doi.org/10.1016/S0022-2313\(01\)00214-9](https://doi.org/10.1016/S0022-2313(01)00214-9)
- 48 T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **36** (2024) 531. <https://doi.org/10.18494/SAM4749>
- 49 K. Ichiba, H. Kimura, Y. Takebuchi, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *Appl. Radiat. Isot.* **214** (2024) 111528. <https://doi.org/10.1016/j.apradiso.2024.111528>
- 50 K. Miyazaki, D. Nakauchi, Y. Takebuchi, T. Kato, N. Kawaguchi, and T. Yanagida: *Radiat. Meas.* **173** (2024) 107102. <https://doi.org/10.1016/j.radmeas.2024.107102>
- 51 H. Nanto, T. Sato, N. Kashiwagi, M. Miyazaki, S. Nasu, E. Kusano, A. Kinbara, and Y. Douguchi: *Radiat. Prot. Dosimetry* **85** (1999) 305. <https://doi.org/10.1093/oxfordjournals.rpd.a03285752>
- 52 S. S. Pitale, S. K. Sharma, R. N. Dubey, M. S. Qureshi, and M. M. Malik: *J. Lumin.* **128** (2008) 1587. <https://doi.org/10.1016/j.jlumin.2008.03.002>
- 53 P. F. Smet, J. E. Van Haecke, R. L. Van Meirhaeghe, and D. Poelman: *J. Electron Spectros. Relat. Phenomena* **148** (2005) 91. <https://doi.org/10.1016/j.elspec.2005.04.001>
- 54 N. J. M. Le Masson, A. J. J. Box, C. W. E. Van Eijk, C. Furetta, and J. P. Chaminade: *Radiat. Prot. Dosimetry* **100** (2002) 229. <https://doi.org/10.1093/oxfordjournals.rpd.a005853>