

Relationship between Lifetime and Emission Wavelength in Scintillation and Photoluminescence from the Same Excited State

Takayuki Yanagida,* Takumi Kato, Daisuke Nakauchi, and Noriaki Kawaguchi

Nara Institute of Science and Technology, 8916-5 Takayama-cho, Ikoma City, Nara 630-0192, Japan

(Received October 20, 2023; accepted December 27, 2023)

Keywords: scintillation, photoluminescence, decay time, lifetime, emission wavelength

The relationship between the lifetimes and emission wavelengths of scintillation and photoluminescence, when the initial excited state was the same, was studied. When the rate equation is dominant, lifetime should be the same at different emission wavelengths. However, we have observed the dependence of lifetime on emission wavelength in common scintillators.

1. Introduction

Photoluminescence (PL) and scintillation (SC) are close but different phenomena. When the luminescence center is excited, dynamics including excitation and emission (relaxation) processes at the localized luminescence center can be observed, and such a phenomenon is PL. In SC, after the absorption of ionizing radiation, the excitation of the host and the transportation of energy from the host to luminescence centers occur in addition to the PL process.^(1–3) In terms of practical applications of scintillators, SC lifetime (decay time) is important since it is a dominant factor of the timing resolution of radiation detectors.⁽⁴⁾ Despite such importance, no theories for scintillation lifetime have been established, and that for PL⁽⁵⁾ has been used for a long time instead of the original theory. In PL, the lifetime can be expressed as

$$\Gamma = -\frac{1}{\tau} \propto \frac{n}{\lambda^3} \left(\frac{n^2 + 2}{3} \right)^2 \sum_f |f| |\mu| |i|^2, \quad (1)$$

where G , t , n , and l represent the decay rate of an excited state, decay time, refractive index, and emission wavelength, respectively. The matrix element connecting the initial state $|i\rangle$ with the final state $|f\rangle$ via the dipole operator m will only be of appreciable size for transitions between states of different parities. Although Eq. (1) is offered for PL, the relationship has also been confirmed in SC.⁽⁶⁾ In our previous work,⁽⁶⁾ Eq. (1) was confirmed only for scintillators with different excited states, such as 5d–4f transitions of Ce³⁺, Pr³⁺, and Nd³⁺. However, if one considers the common rate equation, one may consider that lifetime will be the same when the excited state is the same. The common and simple rate equation is expressed as

*Corresponding author: e-mail: yanagida.takayuki@naist.ac.jp
<https://doi.org/10.18494/SAM4748>

$$\frac{dN}{dt} = -kN, \quad (2)$$

where N , t , and k mean the number of excited states (excited electrons), time, and rate constant, respectively. In this relationship, lifetime should be the same when the excited state is the same. In other words, the rate equation does not care about excitation processes.

The aim of the current work is to study whether Eq. (1) is still dominant for different initial excited states. If Eq. (1) is dominant, a correlation between emission wavelength and lifetime can be observed. To exemplify them, the generality of samples is important. In terms of material forms, single crystals,^(7–23) ceramics,^(24–34) and glasses^(35–54) are common forms of scintillators, and samples with these forms are selected.

2. Materials and Methods

Sample materials are Ce³⁺-doped Lu₃Al₅O₁₂,⁽⁵⁵⁾ Gd₃Al₂Ga₃O₁₂,⁽⁵⁵⁾ Y₃Al₅O₁₂,⁽⁵⁵⁾ LuAlO₃,⁽⁵⁶⁾ YAlO₃,⁽⁵⁶⁾ Y₂SiO₅,⁽⁵⁷⁾ Gd₂SiO₅,⁽⁵⁸⁾ Lu₂SiO₅,⁽⁵⁹⁾ (Lu,Y)₂SiO₅,⁽⁵⁹⁾ LiCaAlF₆,⁽⁶⁰⁾ Eu²⁺-doped CaAl₂O₄,⁽¹⁵⁾ SrAl₂O₄,⁽¹⁵⁾ BaAl₂O₄,⁽¹⁵⁾ LiCaAlF₆,⁽⁶¹⁾ and LiSrAlF₆,⁽⁶²⁾ in single crystal or ceramic forms. Except for CaAl₂O₄, SrAl₂O₄, BaAl₂O₄, and LiSrAlF₆, all the samples are commercially available. PL spectra and lifetimes were evaluated using Quantaaurus-QY and Quantaaurus-τ (both by Hamamatsu), respectively. SC spectra⁽⁶³⁾ and lifetimes⁽⁶⁴⁾ were measured using our original setups.

Figures 1 and 2 show examples of results in this work. After PL and SC spectra were measured, 2–4 monitoring wavelengths for lifetimes were determined. In PL, the excitation level of 5d¹ was selected as the excitation wavelength, which was determined to be 280 nm for most materials and 470 nm for Ce-doped garnet materials. The number of monitoring points depended on the width of the emission peak. As exemplified in Fig. 1, each monitoring band was separated without any overlapping as much as possible. Technically, perfect separation was impossible since such a broad spectrum contained several emission peaks with a Gaussian-like shape, and tail parts of Gaussian overlapped each other. However, in such a case, the dominant lifetime originated from the target emission band. Moreover, strictly, some materials such as rare-earth silicate materials (e.g., Lu₂SiO₅) have different sites for dopant Ce³⁺, and emissions from different sites show slightly different lifetimes.⁽⁶⁵⁾ In such a case, since the observed values will be an average lifetime of every component, such an effect was not considered. After selecting the monitoring wavelengths, wavelength-resolved PL and scintillation time profiles were measured, as shown in Fig. 2, and the obtained time profiles were analyzed by single exponential approximation.

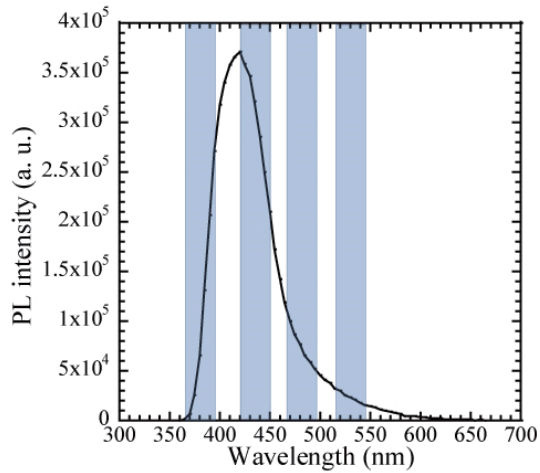


Fig. 1. (Color online) PL spectrum of Ce-doped Y_2SiO_5 crystal under 280 nm excitation. Hatched ranges were monitoring points of lifetimes.

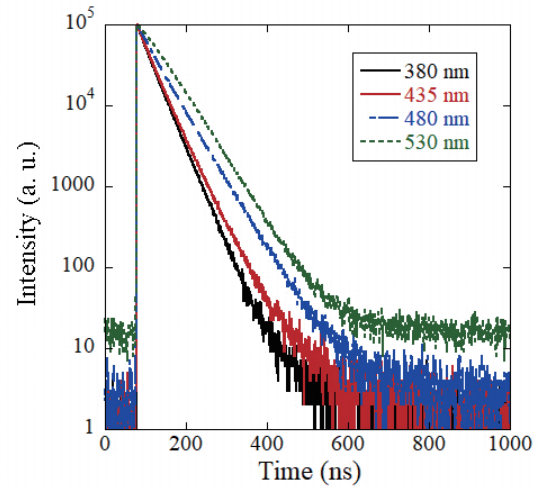


Fig. 2. (Color online) Time profiles of Ce-doped Y_2SiO_5 crystal monitoring at various wavelengths under 280 nm excitation.

3. Results

Figures 3(a)–3(c) show the relationship between emission wavelength and lifetime. Since the measurement ranges of Ce- and Eu-doped samples were markedly different, they were separately plotted in different panels. In Ce-doped materials, a relationship of $t \sim \lambda^{1.5}$ was observed, and a proportional relationship was confirmed. Equation (1) assumes a perfect crystal with an ideal energy structure, and differences with actual materials (e.g., defects) will be a reason for the difference between theory and experiments. Proportion was also confirmed in Eu-doped AEAl_2O_4 (AE = alkali earth) samples. Since the number of data points was limited, the multiplier (n) increased. In panel (c), no proportional relationship was observed. The main reason can be blamed for technical matters. Eu-doped LiCaAlF_6 and LiSrAlF_6 showed similar emission spectra peaking at 370 nm with an FWHM of ~ 10 nm. In these samples, the wavelength separation was not enough.

Figure 4 shows the current results in addition to previous results of Ce^{3+} , Pr^{3+} , and Nd^{3+} -doped samples in PL,⁽⁶⁾ and Fig. 5 is the same plot for SC. Here, a clear correlation between emission wavelength and lifetime was confirmed. Throughout the work, Eq. (1) is confirmed to be dominant even when the phenomenon starts from the same excited state. Since the rate equation does not consider any states before excitation, the present result suggests that excitation processes will affect a behavior of lifetime. Even in PL, the excitation source has a few ns pulse width, and the condition changes from an ideal rate equation, which assumes the full occupation of the excited state under the initial condition.

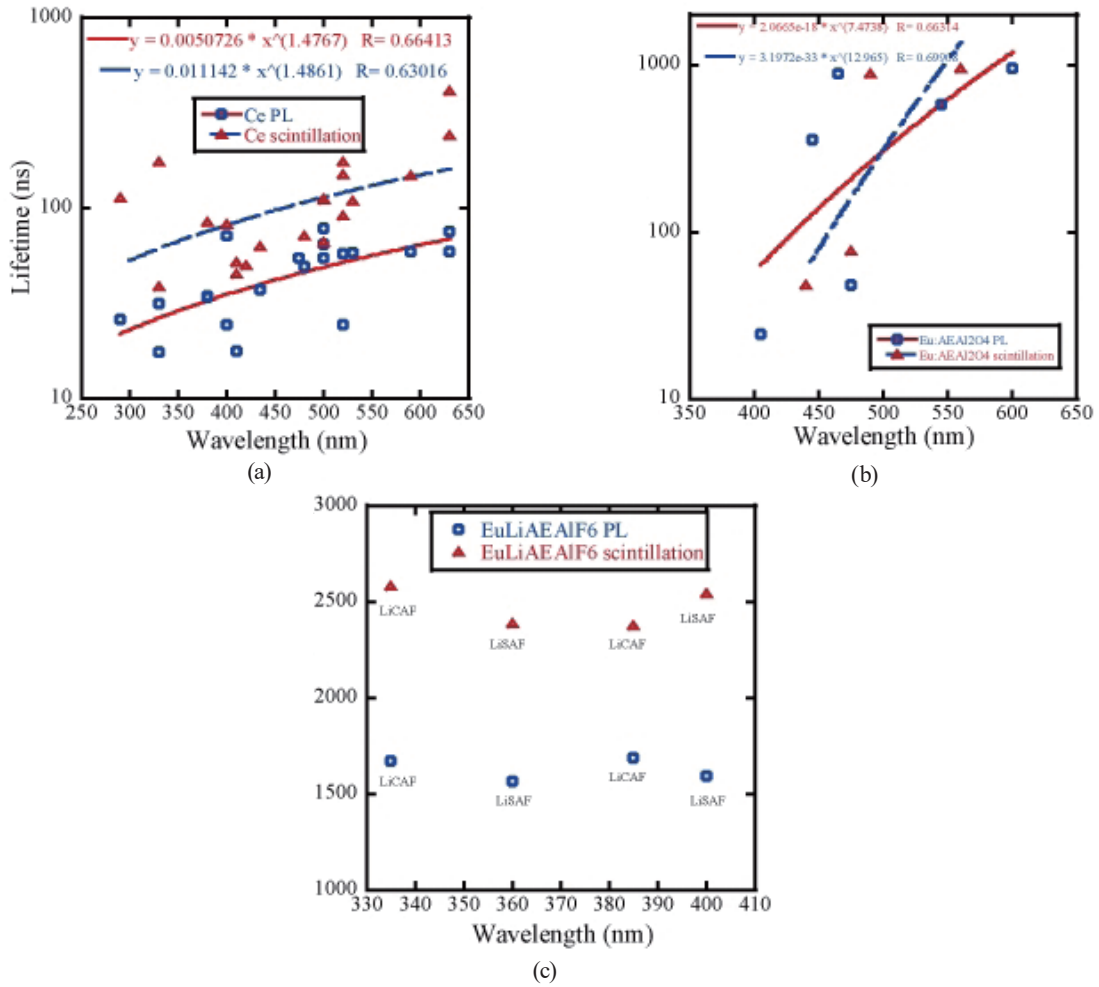


Fig. 3. (Color online) Relationship between emission wavelength (horizontal axis) and lifetime (vertical axis) of PL and SC in (a) Ce-doped scintillators, (b) Eu-doped AEAl₂O₄, and (c) Eu-doped LiAEAlF₆. Circles and triangles represent PL and SC, respectively. In (a) and (b), approximation by $\tau = A\lambda^n$ is also plotted, where A and n are positive number constants.

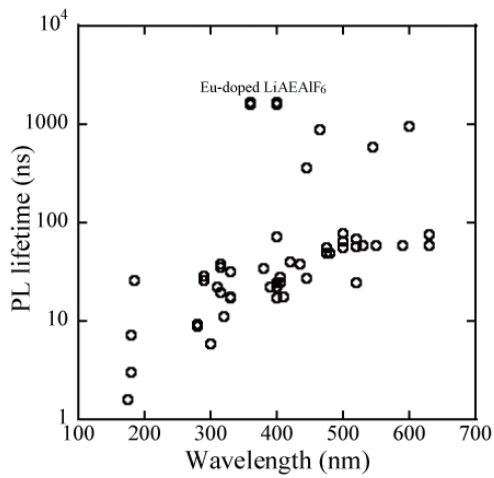


Fig. 4. Distribution of PL emission wavelength (horizontal axis) and PL lifetime (vertical axis).

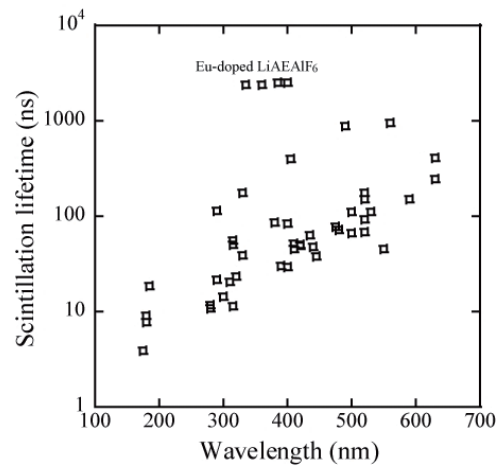


Fig. 5. Distribution of scintillation emission wavelength (horizontal axis) and scintillation lifetime (vertical axis).

4. Conclusions

When the initial excited state was the same, the relationship between emission wavelength and lifetime in PL and SC was studied. Their clear correlation was observed in both phenomena. In addition to different excited states, even in the same excited state, emission wavelength and lifetime were confirmed to be correlated.

Acknowledgments

This work was supported by MEXT Grants-in-Aid for Scientific Research A (22H00309), Scientific Research B (21H03733, 21H03736, and 22H03872), and Exploratory Research (22K18997), and Cooperative Research Project of the Research Center for Biomedical Engineering.

References

- 1 T. Yanagida: Proc. Jpn. Acad. Ser. B **94** (2018) 75. <https://doi.org/10.2183/pjab.94.007>
- 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 T. Yanagida, T. Kato, D. Nakauchi, and N. Kawaguchi: Sens. Mater. **35** (2023) 423. <https://doi.org/10.18494/SAM4135>
- 4 W. Choong: Phys. Med. Biol. **54** (2009) 6495. <https://doi.org/10.1088/0031-9155/54/21/004>
- 5 B. Henderson and G. F. Imbush: Optical Spectroscopy of Inorganic Solids (Clarendon Press, Oxford, 1989). <https://doi.org/10.1002/0470016043>
- 6 T. Yanagida, Y. Fujimoto, A. Yamaji, N. Kawaguchi, K. Kamada, D. Totsuka, K. Fukuda, K. Yamanoi, R. Nishi, S. Kurosawa, T. Shimizu, and N. Sarukura: Radiat. Meas. **55** (2013) 99. <https://doi.org/10.1016/j.radmeas.2012.05.014>
- 7 H. Fukushima, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: Sens. Mater. **35** (2023) 429. <https://doi.org/10.18494/SAM4139>
- 8 D. Onoda, M. Akatsuka, N. Kawano, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Sens. Mater. **34** (2022) 585. <https://doi.org/10.18494/SAM3679>
- 9 R. Nagaoka, N. Kawano, Y. Takebuchi, H. Fukushima, T. Kato, D. Nakauchi, and T. Yanagida: Jpn. J. Appl. Phys. **61** (2022) 110601. <https://doi.org/10.35848/1347-4065/ac943d>
- 10 D. Shiratori, H. Fukushima, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: Sens. Mater. **35** (2023) 439. <https://doi.org/10.18494/SAM4140>
- 11 T. Yanagida, T. Kato, D. Nakauchi, and N. Kawaguchi: Sens. Mater. **34** (2022) 595. <https://doi.org/10.18494/SAM3684>
- 12 T. Suto, N. Kawano, K. Okazaki, Y. Takebuchi, H. Fukushima, T. Kato, D. Nakauchi and T. Yanagida: Jpn. J. Appl. Phys. **62** (2023) 010610. <https://doi.org/10.35848/1347-4065/ac8f02>
- 13 P. Kantuptim, T. Kato, D. Nakauchi, N. Kawaguchi, K. Watanabe, and T. Yanagida: Sens. Mater. **35** (2023) 451. <https://doi.org/10.18494/SAM4141>
- 14 P. Kantuptim, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: Sens. Mater. **34** (2022) 603. <https://doi.org/10.18494/SAM3690>
- 15 D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: Jpn. J. Appl. Phys. **62** (2023) 010607. <https://doi.org/10.35848/1347-4065/ac9181>
- 16 K. Okazaki, D. Nakauchi, H. Fukushima, T. Kato, N. Kawaguchi, and T. Yanagida: Sens. Mater. **35** (2023) 459. <https://doi.org/10.18494/SAM4144>
- 17 D. Nakauchi, H. Fukushima, T. Kato, N. Kawaguchi, and T. Yanagida: Sens. Mater. **34** (2022) 611. <https://doi.org/10.18494/SAM3696>
- 18 Y. Fujimoto and K. Asai: Jpn. J. Appl. Phys. **62** (2023) 010605. <https://doi.org/10.35848/1347-4065/ac9348>
- 19 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>

- 20 M. Akatsuka, N. Daisuke, K. Takumi, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **34** (2022) 619. <https://doi.org/10.18494/SAM3692>
- 21 D. Yuan, E. G. Villora, N. Kawaguchi, D. Nakauchi, T. Kato, T. Yanagida, and K. Shimamura: *Jpn. J. Appl. Phys.* **62** (2023) 010614. <https://doi.org/10.35848/1347-4065/aca3e5>
- 22 K. Okazaki, D. Onoda, D. Nakauchi, N. Kawano, H. Fukushima, T. Kato, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **34** (2022) 575. <https://doi.org/10.18494/SAM3678>
- 23 Y. Fujimoto, D. Nakauchi, T. Yanagida, M. Koshimizu, and K. Asai: *Sens. Mater.* **34** (2022) 629. <https://doi.org/10.18494/SAM3693>
- 24 Y. Shao, R. L. Conner, N. R. S. Souza, R. S. Silva, and L. G. Jacobsohn: *Jpn. J. Appl. Phys.* **62** (2023) 010601. <https://doi.org/10.35848/1347-4065/ac9941>
- 25 T. Kunikata, T. Kato, D. Shiratori, P. Kantuptim, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **35** (2023) 491. <https://doi.org/10.18494/SAM4145>
- 26 X. Huang, J. He, Y. Jiang, W. Chewpraditkul, and L. Zhang: *Ceram. Intr.* **48** (2022) 23571. <https://doi.org/10.1016/j.ceramint.2022.05.005>
- 27 N. Kawaguchi, T. Kato, D. Nakauchi, and T. Yanagida: *Jpn. J. Appl. Phys.* **62** (2023) 010611. <https://doi.org/10.35848/1347-4065/ac99c3>
- 28 M. Makowski, M. E. Witkowski, W. Drozdowski, G. Zhang, J. Li, and Y. Wu: *Radiat. Phys. Chem.* **208** (2023) 110896. <https://doi.org/10.1016/j.radphyschem.2023.110896>
- 29 T. Kunikata, T. Kato, D. Shiratori, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **34** (2022) 661. <https://doi.org/10.18494/SAM3683>
- 30 M. Rahimi, M. Zahedifar, R. Azimirad, and A. Faeghinia: *J. Lumin.* **221** (2020) 117040. <https://doi.org/10.1016/j.jlumin.2020.117040>
- 31 D. Shiratori, H. Fukushima, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: *Jpn. J. Appl. Phys.*, **62** (2023) 010608. [10.35848/1347-4065/ac90a4](https://doi.org/10.35848/1347-4065/ac90a4)
- 32 W. Wang, H. Kou, S. Liu, Y. Shi, J. Li, X. Feng, Y. Pan, Y. Li, and J. Guo: *Ceram. Intr.* **41** (2015) 2576. <https://doi.org/10.1016/j.ceramint.2014.11.005>
- 33 D. Nakauchi, F. Nakamura, T. Kato, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **35** (2023) 467. <https://doi.org/10.18494/SAM4138>
- 34 S. Blahuta, B. Viana, A. Bessière, E. Mattmann, and B. LaCourse: *Opt. Mater.* **33** (2011) 1514. <https://doi.org/10.1016/j.optmat.2011.02.040>
- 35 K. Shinozaki, G. Okada, N. Kawaguchi, and T. Yanagida: *Jpn. J. Appl. Phys.* **62** (2023) 010603. <https://doi.org/10.35848/1347-4065/ac95e6>
- 36 N. Kawaguchi, K. Watanabe, D. Shiratori, T. Kato, D. Nakauchi, and T. Yanagida: *Sens. Mater.* **35** (2023) 499. <https://doi.org/10.18494/SAM4136>
- 37 N. Wantana, E. Kaewnuam, Y. Tariwong, N. D. Quang, P. Pakawanit, C. Phoovasawat, N. Vittayakorn, S. Kothan, H. J. Kim, and J. Kaewkhao: *Jpn. J. Appl. Phys.* **62** (2023) 010602. <https://doi.org/10.35848/1347-4065/ac9876>
- 38 Y. Takebuchi, D. Shiratori, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **35** (2023) 507. <https://doi.org/10.18494/SAM4142>
- 39 Z. Wen, S. Xu, L. Li, J. Chen, L. Lei, T. Jiang, and H. Guo: *J. Lumin.* **263** (2023) 120086. <https://doi.org/10.1016/j.jlumin.2023.120086>
- 40 H. Masai and T. Yanagida: *Jpn. J. Appl. Phys.* **62** (2023) 010606. <https://doi.org/10.35848/1347-4065/ac91b88>
- 41 J. Tang, Z. Lin, D. Tu, T. Wei, R. Duan, and S. Zhou: *J. Non-crystalline Solids X* **15** (2022) 100110. <https://doi.org/10.1016/j.nocx.2022.100110>
- 42 H. Kimura, T. Fujiwara, M. Tanaka, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **35** (2023) 513. <https://doi.org/10.18494/SAM4146>
- 43 Y. Nakabayashi, Y. Fujimoto, M. Koshimizu, and K. Asai: *Opt. Mater.* **142** (2023) 114136. <https://doi.org/10.1016/j.optmat.2023.114136>
- 44 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>
- 45 L. Wang, F. Lu, X. Li, F. Hu, H. Guo, and R. Wei: *J. Lumin.* **257** (2023) 119751. <https://doi.org/10.1016/j.jlumin.2023.119751>
- 46 G. Ito, H. Kimura, D. Shiratori, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **34** (2022) 685. <https://doi.org/10.18494/SAM3681>
- 47 Z. Sun, X. Huang, J. Yang, S. Wang, and S. Wu: *Ceram. Intr.* **49** (2023) 15500. <https://doi.org/10.1016/j.ceramint.2023.01.135>

- 48 H. Kimura, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **34** (2022) 691. <https://doi.org/10.18494/SAM3687>
- 49 A. Yokoyama, W. Kada, M. Sakai, K. Miura, and O. Hanaizumi: *Appl. Radiat. Isot.* **196** (2023) 110753. <https://doi.org/10.1016/j.apradiso.2023.110753>
- 50 R. Nakamori, N. Kawano, A. Takaku, D. Onoda, Y. Takebuchi, H. Fukushima, T. Kato, K. Shinozaki, and T. Yanagida: *Sens. Mater.* **34** (2022) 707. <https://doi.org/10.18494/SAM3689>
- 51 N. Luewarasirikul, S. Sarachai, S. Kothan, H. J. Kim, and J. Kaewkhao: *Optik* **292** (2023) 171385. <https://doi.org/10.1016/j.ijleo.2023.171385>
- 52 H. Fukushima, D. Shiratori, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **34** (2022) 717. <https://doi.org/10.18494/SAM3691>
- 53 K. Bansal, P. J. Singh, M. Tyagi, A. Kaur, and S. Singh: *J. Lumin.* **250** (2022) 119093. <https://doi.org/10.1016/j.jlumin.2022.119093>
- 54 N. Kawaguchi, D. Nakauchi, T. Kato, Y. Futami, and T. Yanagida: *Sens. Mater.* **34** (2022) 725. <https://doi.org/10.18494/SAM3705>
- 55 T. Yanagida, Y. Fujimoto, M. Koshimizu, K. Watanabe, H. Sato, H. Yagi, and T. Yanagitani: *Opt. Mater.* **36** (2014) 2016. <https://doi.org/10.1016/j.optmat.2013.12.043>
- 56 A. J. Wojtowicz, J. Glodo, W. Drozdowski, and K. R. Przegietka: *J. Lumin.* **79** (1998) 275. [https://doi.org/10.1016/S0022-2313\(98\)00039-8](https://doi.org/10.1016/S0022-2313(98)00039-8)
- 57 K. Ichiba, Y. Takebuchi, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *Jpn. J. Appl. Phys.* In press (2023). <https://doi.org/10.35848/1347-4065/acf4a7>
- 58 T. Yanagida, Y. Fujimoto, and K. Watanabe: *Radiat. Meas.* **61** (2014) 16. <https://doi.org/10.1016/j.radmeas.2013.12.006>
- 59 C. Wanarak, W. Chewpraditkul, and A. Phunpueok: *Proc. Eng.* **32** (2012) 765. <https://doi.org/10.1016/j.proeng.2012.02.010>
- 60 K. Watanabe, T. Yanagida, K. Fukuda, A. Koike, T. Aoki, and A. Uritani: *Sens. Mater.* **27** (2015) 269. <https://doi.org/10.18494/SAM.2015.1093>
- 61 T. Yanagida, M. Koshimizu, Y. Fujimoto, K. Fukuda, K. Watanabe, G. Okada, and N. Kawaguchi: *J. Lumin.* **191** (2017) 22. <https://doi.org/10.1016/j.jlumin.2017.01.029>
- 62 T. Yanagida, G. Okada, K. Fukuda, K. Watanabe, and N. Kawaguchi: *Radiat. Meas.* **106** (2017) 124. <https://doi.org/10.1016/j.radmeas.2016.11.010>
- 63 T. Yanagida, K. Kamada, Y. Fujimoto, H. Yagi, and T. Yanagitani: *Opt. Mater.* **35** (2013) 2480. <https://doi.org/10.1016/j.optmat.2013.07.002>
- 64 T. Yanagida, Y. Fujimoto, A. Yoshikawa, Y. Yokota, K. Kamada, Jan Pejchal, N. Kawaguchi, K. Fukuda, K. Uchiyama, K. Mori, K. Kitano, and M. Nikl: *Appl. Phys. Express* **3** (2010) 056202. <https://doi.org/10.1143/APEX.3.056202>
- 65 Y. Wu, J. Peng, D. Rutstrom, M. Koschan, C. Foster, and C. Melcher: *ACS Appl. Mater. Interfaces* **11** (2019) 8194. <https://doi.org/10.1021/acsami.8b19040>