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Radiation-induced Luminescence Properties of Ce-doped $ZnBr_2$-based Glasses

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Ce-doped 20CsBr-20$BaBr_2$-60$ZnBr_2$ glasses were synthesized by the conventional melt quenching method, and their photoluminescence (PL) and scintillation properties were investigated. In the PL and scintillation spectra, all the Ce-doped glasses showed broad emissions due to the 5d–4f transitions of Ce^{3+} ions. Under ^{241}Am α-rays, the light yield of 0.05% Ce-doped glass was 40 photons/5.5 MeV-α.

1. Introduction

Scintillation detectors have been used in various fields such as medicine,[1] security,[2] well logging,[3,4] environmental monitoring,[5,6] and high-energy physics.[7] They are composed of a scintillator and a photodetector.[8] The scintillator has a function to instantaneously convert the absorbed energy of ionizing radiation into a large number of low-energy photons, and the photodetector can convert the photons into electric signals. The performance of scintillation detectors strongly depends on the properties of the scintillator. The scintillators for X- and γ-ray detectors generally require a large effective atomic number, a high density, a high light yield (*LY*), a short lifetime, and a low afterglow.[9–12]

Single crystals have mainly been used as the material form for X-ray and γ-ray detectors because of their high transmission and high density.[13–22] In addition, commercial scintillators such as Tl-doped NaI,[23] Tl-doped CsI,[24] Ce-doped Gd_2SiO_5,[25] and Ce-doped $Gd_3(Ga,Al)_5O_{12}$[26] show high *LY*s. On the other hand, although glasses have some merits including a high transparency, a low production cost, and a high moldability, the only commercial scintillator in the form of glass for neutron detectors is Ce-doped Li_2O-MgO-Al_2O_3-SiO_2 (GS20, Saint-Gobain).[27,28] Therefore, the development of glass scintillators for X- and γ-ray detectors is expected.

The scintillation properties of various oxide glass scintillators such as borate,[29–32] silicate,[33–38] phosphate,[39–44] and tellurite glasses[45–47] have been reported. In recent years,

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Ce-doped oxyhalide and halide glasses have attracted much attention because of advantages including a low synthesis temperature and a low phonon energy compared with oxide glasses.[48–52] In addition, Ce-doped oxyhalide glasses show high *LY*s compared with those reported for glass scintillators; for example, the *LY*s reported for Ce-doped BaF_2-Al_2O_3-B_2O_3,[53] CsCl-$Al(PO_3)_3$-$CsPO_3$,[54] and CsBr-$Al(PO_3)_3$-$CsPO_3$[55] were 1800, 2100, and 2700 photons/MeV, respectively. In the case of halide glasses, Ce-doped $ZnCl_2$-based glasses such as CsCl-$CaCl_2$-$ZnCl_2$[56] and CsCl-$BaCl_2$-$ZnCl_2$[57] showed high quantum yields (*QY*) of ~87.6 and ~75.7, respectively. However, there are no reports on the scintillation properties of Ce-doped $ZnBr_2$-based glasses even though the phonon energy of bromide glasses is lower than that of chloride glasses. In this study, we synthesized Ce-doped CsBr-$BaBr_2$-$ZnBr_2$ glasses and investigated their photoluminescence (PL) and scintillation properties.

2. Materials and Methods

We synthesized 0.01, 0.05, 0.1, and 0.5% Ce-doped 20CsBr-20$BaBr_2$-60ZnBr glasses by the conventional melt quenching method. As raw powders, CsBr (99.99%, Furuuchi Chemical), $BaBr_2$ (99.9%, Furuuchi Chemical), $ZnBr_2$ (99.99%, High Purity Chemicals), and $CeBr_3{\cdot}6H_2O$ (>99%, Mitsuwa Chemicals) were used. Detailed information on the synthesis is given in our past reports.[58] The synthesized glasses were then evaluated as follows.

For PL properties, the PL excitation/emission map and *QY* were measured using a Quantaurus-QY system (Hamamatsu Photonics, C11347). In addition, PL decay curves were evaluated using a Quantaurus-τ system (Hamamatsu Photonics, C11367). To evaluate scintillation properties, X-ray-induced scintillation spectra were measured using a laboratory-built setup reported previously.[26] X-ray-induced decay curves were evaluated using an afterglow characterization system.[59] To estimate scintillation *LY*s, pulse height spectra were measured using our original setup.[26]

3. Results and Discussion

Figure 1 shows photographs of the 0.01, 0.05, 0.1, and 0.5% Ce-doped 20CsBr-20$BaBr_2$-60$ZnBr_2$ glasses. The thickness of the synthesized glasses was fixed at 1.0 mm, and all the glasses were transparent. The glasses with higher Ce concentrations were yellow, which would be due to the Ce absorption. The surfaces of all the glasses became slightly cloudy after a few minutes because they were deliquescent.

The PL excitation/emission map of the 0.5% Ce-doped glass is illustrated in Fig. 2 as a representative map. Here, the vertical and horizontal axes correspond to the excitation and emission wavelengths, respectively. All the Ce-doped glasses showed a broad emission peak around 380 nm under excitation wavelengths of 290 and 320 nm. The peak positions of the excitation and emission bands were consistent with this in past reports on Ce-doped glasses. [56,57] The *QY*s of the 0.01, 0.05, 0.1, and 0.5% Ce-doped glasses were 4.4, 2.2, 1.4, and 1.6%, respectively, which were comparable to that of Eu-doped 20CsBr-20$BaBr_2$-60$ZnBr_2$ glasses (~6.4%).[58]

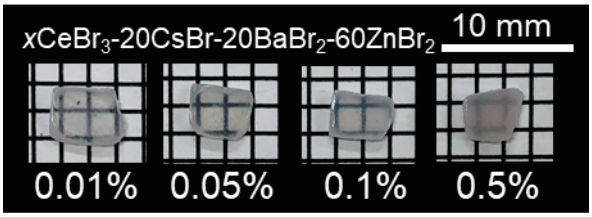

Fig. 1. (Color online) Photographs of 0.01, 0.05, 0.1, and 0.5% Ce-doped 20CsBr-20$BaBr_2$-60$ZnBr_2$ glasses.

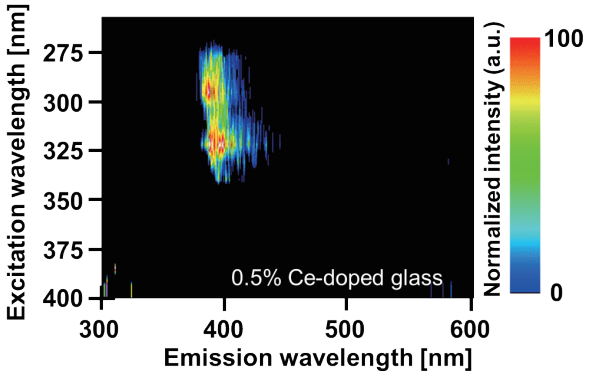

Fig. 2. (Color online) PL excitation/emission map of 0.5% Ce-doped 20CsBr-20$BaBr_2$-60$ZnBr_2$ glass.

Figure 3 shows PL decay curves of the Ce-doped glasses for a monitoring wavelength of 380 nm and an excitation wavelength of 280 nm. All the curves were well fitted by the sum of the two exponential decay functions we used to estimate the lifetimes. The lifetimes of the two components of all the glasses were 3.7–6.3 and 19.6–21.2 ns. The faster component was assigned using the instrumental response function (IRF), and the slower component was a typical value for the 5d–4f transitions of Ce^{3+}.[56,57,60]

Figure 4 presents X-ray-induced scintillation spectra of the Ce-doped glasses. The 0.5% Ce-doped glass showed broad emission peaks around 400 and 500 nm. The peak position of the emission around 400 nm was slightly shifted to the longer-wavelength side compared with the result for PL. This behavior was observed in previous studies on Ce-doped $ZnCl_2$-based glasses and is due to the self-absorption of Ce.[56,57] In a previous report on non-doped $ZnCl_2$-based glasses, there was a broad emission peak around 500 nm due to self-trapped excitons (STEs).[61] Therefore, the origin of the broad emission peak around 500 nm is also expected to be STEs in Ce-doped $ZnBr_2$-based glasses.

X-ray-induced scintillation decay curves of the Ce-doped glasses are shown in Fig. 5. The decay curves of all the Ce-doped glasses consisted of a sum of two exponential decay functions, and the faster and slower lifetimes were 0.8–1.1 and 25.8–36.8 ns, respectively. Since these values were consistent with those of Ce-doped $ZnCl_2$-based glasses,[56,57] the faster and slower lifetimes are concluded to be due to the IRF and the 5d–4f transitions of

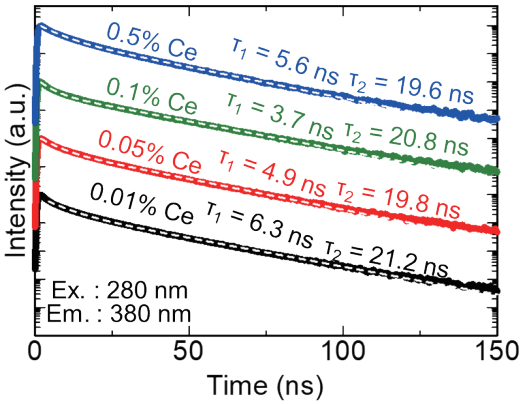

Fig. 3. (Color online) PL decay curves of Ce-doped 20CsBr-20$BaBr_2$-60$ZnBr_2$ glasses for a monitoring wavelength of 380 nm and an excitation wavelength of 280 nm.

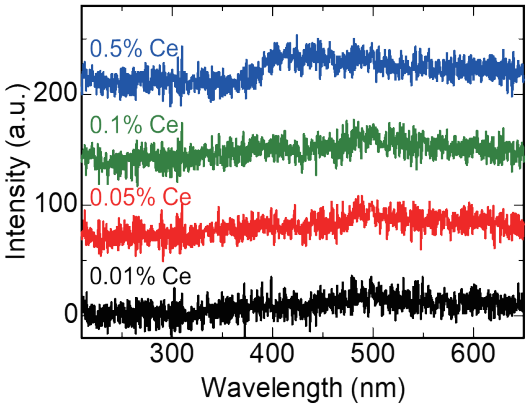

Fig. 4. (Color online) X-ray-induced scintillation spectra of Ce-doped 20CsBr-20$BaBr_2$-60$ZnBr_2$ glasses.

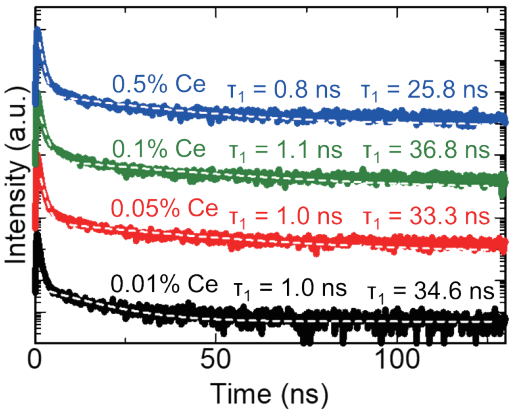

Fig. 5. (Color online) X-ray-induced scintillation decay curves of Ce-doped 20CsBr-20$BaBr_2$-60$ZnBr_2$ glasses.

Ce^{3+} ions, respectively. Compared with the result for PL, the lifetime for the scintillation was long. A similar trend was observed in previous studies.[61–63]

Figure 6 shows the pulse height spectra of the Ce-doped $ZnBr_2$-based glasses under ^{241}Am α-rays. The inset shows the pulse height spectra of Ce-doped Lu_2SiO_5 under ^{137}Cs γ-rays as a reference. Here, Ce-doped Lu_2SiO_5 has an *LY* of 8700 photons/MeV.[64] For the 0.05% Ce-doped glass, the full energy peak was observed around 105 ch. In contrast, no full energy peak was clearly confirmed for the other glasses. As possible reasons for this observation, the synthesized glasses may have been inhomogeneous and the *LY*s of the glasses were very low. The estimated *LY* of the 0.05% Ce-doped glass was 40 photons/5.5 MeV-α with a typical error of ±10%. Table 1 shows the *QY*s and *LY*s for previously reported $ZnCl_2$ and $ZnBr_2$-based glasses and the values obtained in this study. The *QY* and *LY* of the Ce-doped $ZnBr_2$-based glasses were lower than those of the Ce-doped $ZnCl_2$-based and Eu-doped $ZnBr_2$-based glasses. In general, Ce can take the state of Ce^{3+} or Ce^{4+} in glasses, although the emission around 400 nm is not related to Ce^{4+}. If the present glasses had been prepared in a reducing environment, Ce^{4+} would have been converted to Ce^{3+}, and their *QY*s and *LY*s may have been improved.

Table 1
*QY*s and *LY*s for previously reported $ZnCl_2$-based and $ZnBr_2$-based glasses and glasses in this study.

Chemical composition	*QY* (%)	*LY* (photons/5.5 MeV-α)	Reference
Ce:20CsCl-20$CaCl_2$-60$ZnCl_2$	~87.6	No data	(56)
Ce:20CsCl-20$BaCl_2$-60$ZnCl_2$	~75.7	127	(57)
Eu:20CsCl-20$BaCl_2$-60$ZnCl_2$	~3.3	No data	(61)
Ce:20CsBr-20$BaBr_2$-60$ZnBr_2$	~4.4	40	This work
Eu:20CsBr-20$BaBr_2$-60$ZnBr_2$	~6.4	100	(58)

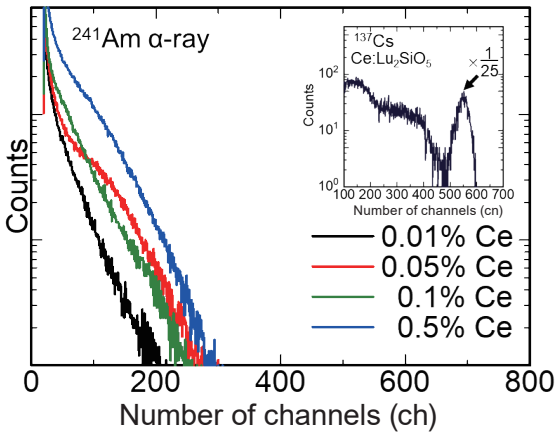

Fig. 6. (Color online) Pulse height spectra of Ce-doped 20CsBr-20$BaBr_2$-60$ZnBr_2$ glasses under ^{241}Am α-rays. The inset shows the pulse height spectrum of a Ce-doped Lu_2SiO_5 scintillator.

4. Conclusions

We prepared 0.01, 0.05, 0.1, and 0.5% Ce-doped 20CsBr-20$BaBr_2$-60$ZnBr_2$ glasses by the conventional melt quenching method and investigated their PL and scintillation properties. All the glasses were transparent when the thickness was fixed at 1.0 mm. Under UV and X-ray irradiations, all the glasses showed a broad emission peak around 380 and 400 nm, respectively, which was due to the 5d–4f transitions of Ce^{3+} ions. Under ^{241}Am α-rays, the *LY* of the 0.05% Ce-doped glass was 40 photons/5.5 MeV-α, and we investigated the scintillation properties of Ce-doped $ZnBr_2$-based glasses for the first time.

Acknowledgments

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References

1 S. Yamamoto, S. Okumura, N. Kato, and J. Y. Yeom: J. Instrum. **10** (2015) T09002.
2 J. Glodo, Y. Wang, R. Shawgo, C. Brecher, R. H. Hawrami, J. Tower, and K. S. Shah: Phys. Procedia **90** (2017) 285.
3 N. Kawaguchi, G. Okada, K. Fukuda, and T. Yanagida: Nucl. Instrum. Methods Phys. Res., Sect. A **954** (2020) 161518.
4 C. L. Melcher: Nucl. Instrum. Methods Phys. Res., Sect. B **40**–**41** (1989) 1214.
5 L. Salonen: Sci. Total Environ. **130**–**131** (1993) 23.
6 Y. Shirakawa: Nucl. Instrum. Methods Phys. Res., Sect. B **263** (2007) 58.
7 T. Itoh, T. Yanagida, M. Kokubun, M. Sato, R. Miyawaki, K. Makishima, T. Takashima, T. Tanaka, K. Nakazawa, T. Takahashi, N. Shimura, and H. Ishibashi: Nucl. Instrum. Methods Phys. Res., Sect. A **579** (2007) 239.
8 T. Yanagida: Proc. Japan Acad. Ser. B **94** (2018) 75.
9 M. J. Weber: J. Lumin. **100** (2002) 35.
10 C. W. E. van Eijk: Nucl. Instrum. Methods Phys. Res., Sect. A **392** (1997) 285.
11 T. Yanagida, T. Kato, D. Nakauchi, and N. Kawaguchi: Jpn. J. Appl. Phys. **62** (2023) 010508.
12 P. Lecoq: Nucl. Instrum. Methods Phys. Res., Sect. A **809** (2016) 130.
13 M. Koshimizu, N. Kawano, A. Kimura, S. Kurashima, M. Taguchi, Y. Fujimoto, and K. Asai: Sens. Mater. **33** (2021) 2137.
14 H. Fukushima, M. Akatsuka, H. Kimura, D. Onoda, D. Shiratori, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: Sens. Mater. **33** (2021) 2235.
15 Y. Fujimoto, D. Nakauchi, T. Yanagida, M. Koshimizu, and K. Asai: Sens. Mater. **33** (2021) 2147.
16 E.V.D. van Loef, P. Dorenbos, C. W. E. van Eijk, K. Krämer, and H. U. Güdel: Appl. Phys. Lett. **77** (2000) 1467.
17 P. Kantuptim, H. Fukushima, H. Kimura, D. Nakauchi, T. Kato, M. Koshimizu, N. Kawaguchi, and T. Yanagida: Sens. Mater. **33** (2021) 2195.
18 Y. Fujimoto, D. Nakauchi, T. Yanagida, M. Koshimizu, and K. Asai: Sens. Mater. **34** (2022) 629.
19 T. Yanagida, T. Kato, D. Nakauchi, and N. Kawaguchi: Sens. Mater. **34** (2022) 595.
20 A. Canning, A. Chaudhry, R. Boutchko, and N. Grønbech-Jensen: Phys. Rev. B **83** (2011) 125115.
21 D. Nakauchi, H. Fukushima, T. Kato, N. Kawaguchi, and T. Yanagida: Sens. Mater. **34** (2022) 611.
22 L. Pidol, A. Kahn-Harari, B. Viana, B. Ferrand, P. Dorenbos, J. T. M. de Haas, C. W. E. van Eijk, and E. Virey: J. Phys. Condens. Matter **15** (2003) 2091.
23 E. Sakai: IEEE Trans. Nucl. Sci. **34** (1987) 418.
24 M. Moszynski, M. Kapusta, M. Mayhugh, D. Wolski, and S. O. Flyckt: IEEE Trans. Nucl. Sci. **44** (1997) 1052.
25 M. Balcerzyk, M. Moszynski, M. Kapusta, D. Wolski, J. Pawelke, and C. L. Melcher: IEEE Trans. Nucl. Sci. **47** (2000) 1319.
26 T. Yanagida, K. Kamada, Y. Fujimoto, H. Yagi, and T. Yanagitani: Opt. Mater. **35** (2013) 2480.
27 J. Czirr, G. MacGillivray, R. MacGillivray, and P. Seddon: Nucl. Instrum. Methods Phys. Res., Sect. A **424** (1999) 15.
28 A. Ishikawa, A. Yamazaki, K. Watanabe, S. Yoshihashi, A. Uritani, Y. Sakurai, H. Tanaka, R. Ogawara, M. Suda, and T. Hamano: Sens. Mater. **32** (2020) 1489.
29 N. Kawano, N. Kawaguchi, G. Okada, Y. Fujimoto, and T. Yanagida: J. Non. Cryst. Solids **482** (2018) 154.
30 H. Kimura, H. Masai, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: J. Mater. Sci. Mater. Electron. **31** (2020) 3017.
31 H. Masai, Y. Suzuki, T. Yanagida, and K. Mibu: Bull. Chem. Soc. Jpn. **88** (2015) 1047.
32 N. Kawaguchi, H. Masai, M. Akatsuka, D. Nakauchi, T. Kato, and T. Yanagida: Sens. Mater. **33** (2021) 2215.
33 Y. Isokawa, H. Kimura, T. Kato, N. Kawaguchi, and T. Yanagida: Opt. Mater. **90** (2019) 187.
34 D. Shiratori, H. Kimura, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: Radiat. Meas. **134** (2020) 106297.
35 W. Chewpraditkul, Y. Shen, D. Chen, B. Yu, P. Prusa, M. Nikl, A. Beitlerova, and C. Wanarak: Opt. Mater. **34** (2012) 1762.
36 H. Fukushima, D. Shiratori, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: Sens. Mater. **34** (2022) 717.
37 H. Masai, H. Kimura, M. Akatsuka, T. Kato, N. Kitamura, and T. Yanagida: J. Lumin. **241** (2022) 118481.
38 K. Ichiba, Y. Takebuchi, H. Kimura, D. Shiratori, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Sens. Mater. **34** (2022) 677.
39 T. Yanagida, Y. Fujimoto, H. Masai, G. Okada, T. Kato, D. Nakauchi, and N. Kawaguchi: Sens. Mater. **33** (2021) 2179.

40 J. Zhou, J. Zhong, J. Dai, Z. Xiao, J. Zhang, Q. Su, and S. Pan: Sci. Adv. Mater. **9** (2017) 424.
41 S. Akiyama, A. Sasaki, R. Nakajima, D. Hasegawa, K. Iizuka, S. Kimura, T. Akagami, Y. Kitagawa, O. Hanaizumi, and W. Kada: Sens. Mater. **34** (2022) 735.
42 D. Yodkantee, A. Prasatkhetragarn, N. Chanthima, Y. Tariwong, S. Kothan, S. Rujirawat, R. Yimnirun, P. Kidkhunthod, H. J. Kim, P. Limsuwan, and J. Kaewkhao: Radiat. Phys. Chem. **185** (2021) 109496.
43 N. Kawaguchi, D. Nakauchi, T. Kato, Y. Futami, and T. Yanagida: Sens. Mater. **34** (2022) 725.
44 D. Shiratori, Y. Takebuchi, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Sens. Mater. **34** (2022) 745.
45 N. Kawano, H. Kimura, D. Nakauchi, K. Shinozaki, and T. Yanagida: Solid State Sci. **100** (2020) 106111.
46 R. Nakamori, N. Kawano, A. Takaku, D. Onoda, Y. Takebuchi, H. Fukushima, T. Kato, K. Shinozaki, and T. Yanagida: Sens. Mater. **34** (2022) 707.
47 R. Nakamori, N. Kawano, A. Takaku, D. Nakauchi, H. Kimura, M. Akatsuka, K. Shinozaki, and T. Yanagida: Mater. Res. Bull. **145** (2022) 111547.
48 T. Tsuneoka, K. Kojima, and S. Bojja: J. Non. Cryst. Solids **202** (1996) 297.
49 M. Shojiya, M. Takahashi, R. Kanno, Y. Kawamoto, and K. Kadono: J. Appl. Phys. **82** (1997) 6259.
50 Y. Yao, L. Liu, Y. Zhang, D. Chen, Y. Fang, and G. Zhao: Opt. Mater. **51** (2016) 94.
51 X. Sun and S. Huang: Nucl. Instrum. Methods Phys. Res., Sect. A **621** (2010) 322.
52 Y. Du, S. Han, Y. Zou, J. Yuan, C. Shao, X. Jiang, and D. Chen: Opt. Mater. **89** (2019) 243.
53 H. Samizo, K. Shinozaki, T. Kato, G. Okada, N. Kawaguchi, H. Masai, and T. Yanagida: Opt. Mater. **90** (2019) 64.
54 K. Kagami, Y. Fujimoto, M. Koshimizu, T. Yanagida, K. Shinozaki, and K. Asai: J. Mater. Sci. - Mater. Electron. **31** (2020) 4488.
55 Y. Nakabayashi, Y. Fujimoto, M. Koshimizu, and K. Asai: J. Mater. Sci. - Mater. Electron. **33** (2022) 19846.
56 G. Ito, H. Kimura, D. Shiratori, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: Sens. Mater. **34** (2022) 685.
57 G. Ito, H. Kimura, D. Shiratori, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: Optik **226** (2021) 165825.
58 H. Kimura, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Sens. Mater. **34** (2022) 691.
59 T. Yanagida, Y. Fujimoto, T. Ito, K. Uchiyama, and K. Mori: Appl. Phys. Express **7** (2014) 062401.
60 H. Kimura, K. Shinozaki, G. Okada, N. Kawaguchi, and T. Yanagida: J. Non. Cryst. Solids **508** (2019) 46.
61 G. Ito, H. Kimura, D. Shiratori, K. Hashimoto, D. Nakauchi, M. Koshimizu, T. Kato, N. Kawaguchi, and T. Yanagida: J. Mater. Sci. - Mater. Electron. **32** (2021) 8725.
62 H. Kimura, F. Nakamura, T. Kato, D. Nakauchi, N. Kawano, G. Okada, N. Kawaguchi, and T. Yanagida: Optik **157** (2018) 421.
63 F. Nakamura, T. Kato, G. Okada, N. Kawaguchi, K. Fukuda, and T. Yanagida: J. Alloys Compd. **726** (2017) 67.
64 K. Ichiba, Y. Takebuchi, H. Kimura, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: J. Mater. Sci. - Mater. Electron. **32** (2021) 25065.