

# Scintillation Properties of Cr-doped LiTaO<sub>3</sub> Single Crystal

Toshiaki Kunikata,<sup>1\*</sup> Kai Okazaki,<sup>1</sup> Hiromi Kimura,<sup>2</sup> Shunta Takase,<sup>1</sup>  
Takumi Kato,<sup>1</sup> Daisuke Nakauchi,<sup>1</sup> Noriaki Kawaguchi,<sup>1</sup> and Takayuki Yanagida<sup>1</sup>

<sup>1</sup>Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma 630-0192, Japan

<sup>2</sup>National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba 305-8568, Japan

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A 0.5% Cr-doped LiTaO<sub>3</sub> single crystal was synthesized by the optical floating zone technique, and its scintillation properties were investigated. The X-ray diffraction pattern of the synthesized sample was ascribed to that of LiTaO<sub>3</sub>. The sample showed a scintillation spectrum peak at around 950 nm. The scintillation intensity of the sample in the near-infrared range linearly increased with the X-ray dose rate from 0.05 to 50 Gy/h.

## 1. Introduction

Scintillators are phosphors that immediately convert high-energy ionizing radiation such as  $\gamma$ - and X-rays into low-energy photons. Scintillators are used for radiation detectors and contribute to various applications such as security scanning, medical imaging, industrial inspection, and scientific analysis. Although the required characteristics for scintillators differ depending on their applications, chemical stability, high radiation resistance, large effective atomic number, high density, high light yield, and suitable emission wavelength for the photodetector are particularly important. Since there have been no scintillators that satisfy all the required characteristics, various materials such as single crystals,<sup>(1–5)</sup> ceramics,<sup>(6–9)</sup> glasses,<sup>(10–14)</sup> organic-inorganic composites,<sup>(15)</sup> and other forms<sup>(16,17)</sup> have been studied as scintillators up to now.

Scintillators are used with photodetectors such as Si photodiodes and photomultiplier tubes (PMTs). Their emission wavelengths need to match the sensitivities of photodetectors. Typical PMTs are sensitive in the visible-to-ultraviolet (UV) wavelength range. Since PMTs have been mainly used as photodetectors in scintillation detectors, visible- or UV-light-emitting scintillators have been widely used. However, near-infrared (NIR)-light-emitting scintillators have recently been studied more intensively with the spread of InGaAs-based photodetectors.<sup>(18–21)</sup> NIR-light-emitting scintillators are expected for monitoring applications in nuclear reactors because there is little overlap with the wavelength of Cherenkov radiation.

In this research, we focused on LiTaO<sub>3</sub> (LT) as a host crystal of NIR-light-emitting scintillators. LT is suitable for X- and  $\gamma$ -ray detection, because it has a large effective atomic

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\*Corresponding author: e-mail: [kunikata.toshiaki.kt1@ms.naist.jp](mailto:kunikata.toshiaki.kt1@ms.naist.jp)  
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number of 68.3, a high density of  $7.46 \text{ g/cm}^3$ , and non-hygroscopicity. Furthermore, the LT single crystal can be grown by the melt growth method, which is advantageous for mass production. According to previous reports, LT:Cr shows photoluminescence at around 950 nm.<sup>(22,23)</sup> Thus, this material has potential for use as an NIR light-emitting scintillator. We grew a 0.5% Cr-doped LT single crystal by the optical floating zone (OFZ) method and investigated its NIR scintillation properties.

## 2. Materials and Methods

An LT:Cr single crystal was grown by the OFZ technique. As raw materials,  $\text{Li}_2\text{CO}_3$  (4N),  $\text{Ta}_2\text{O}_5$  (4N), and  $\text{Cr}_2\text{O}_3$  (4N) powders were used, and they were mixed in a mole ratio of 0.995:1:0.005 for Li:Ta:Cr. The mixed powders were heated in air at  $650 \text{ }^\circ\text{C}$  for 8 h using an electric furnace to remove carbonates from the raw materials. Then, the obtained powder was additionally heated in air at  $850 \text{ }^\circ\text{C}$  for 8 h using the same furnace to synthesize the Cr-doped  $\text{LiTaO}_3$  powder. After heating, the obtained powder was formed into a rod shape by hydrostatic pressing. The shaped rod was sintered at  $1200 \text{ }^\circ\text{C}$  for 10 h. Then, crystal growth was conducted in air using an OFZ furnace (FZD0192, Canon Machinery). Although both pulling up and down can be done to move the molten zone when using this furnace, we selected pulling up because the molten Cr-doped  $\text{LiTaO}_3$  easily dropped when it was pulled down. The pull-up and rotation speeds were 3 mm/h and 7 rpm, respectively. After the LT:Cr single crystal was obtained, it was polished using a polishing machine (Buehler, MetaServ 250).

The diffuse transmittance spectrum was measured using a spectrophotometer (Shimadzu, SolidSpec-3700). The X-ray diffraction (XRD) pattern was measured using an X-ray diffractometer (Rigaku, MiniFlex600). The recorded XRD pattern was compared to the reference data from the Crystallography Open Database (COD). The NIR scintillation spectrum was measured using our customized measurement system.<sup>(24)</sup> To evaluate the performance of the LT:Cr single crystal as the NIR scintillation detector, the relationship between the NIR scintillation intensity and the X-ray dose rate was evaluated using another measurement system that we constructed.<sup>(18–21)</sup>

## 3. Results and Discussion

The diffuse transmittance spectrum and appearance of the obtained LT:Cr single crystal are shown in Fig. 1(a). The LT:Cr sample showed a high transmittance of approximately 70% in the wavelength range from 800 to 1400 nm. The LT:Cr sample is green due to absorption bands of  $\text{Cr}^{3+}$ . Absorption peaks at around 470 and 640 nm were ascribed to the  ${}^4\text{A}_2\text{--}{}^4\text{T}_1$  (470 nm) and  ${}^4\text{A}_2\text{--}{}^4\text{T}_2$  (640 nm) transitions of  $\text{Cr}^{3+}$  ions.<sup>(22,23)</sup> Figure 1(b) shows the XRD pattern of the LT:Cr sample and the reference XRD pattern of LT (COD, 2101846). The observed XRD peaks of LT:Cr coincided with those of LT, and no secondary phases were observed.

Figure 2(a) shows the X-ray-induced NIR scintillation spectrum of the LT:Cr sample. The NIR scintillation peak due to the  ${}^4\text{T}_2\text{--}{}^4\text{A}_2$  transitions of  $\text{Cr}^{3+}$  ions was detected at around

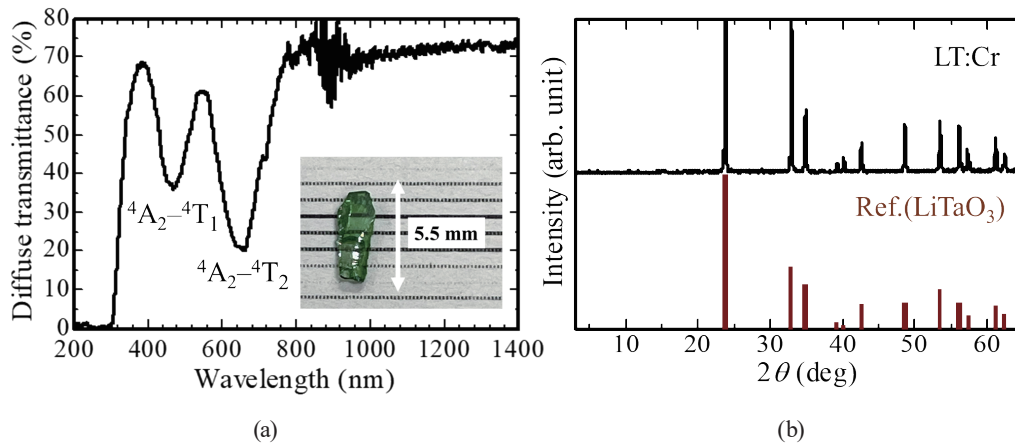


Fig. 1. (Color online) (a) Diffuse transmittance spectrum and appearance of obtained LT:Cr single crystal. (b) XRD pattern of obtained LT:Cr single crystal and reference XRD pattern of LiTaO<sub>3</sub>.

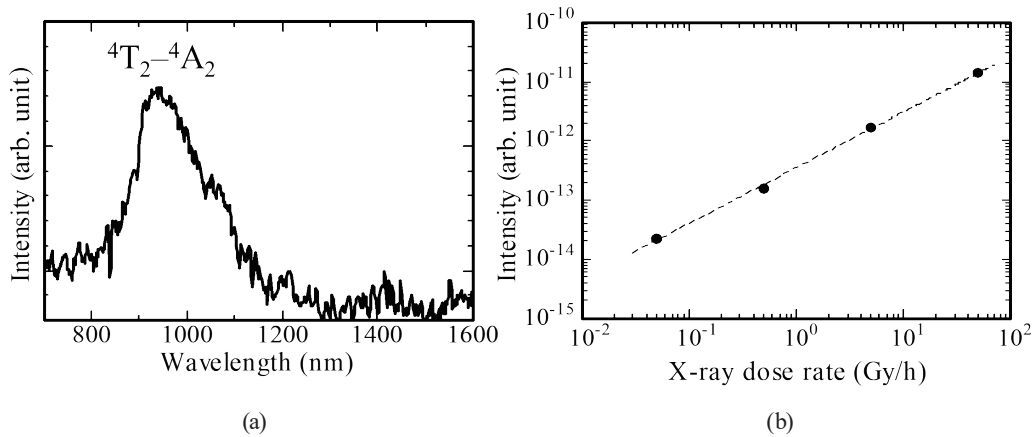


Fig. 2. (a) X-ray-induced NIR scintillation spectrum of LT:Cr single crystal. (b) Relationship between NIR emission intensity and X-ray dose rate.

950 nm.<sup>(22,23)</sup> Figure 2(b) shows the relationship between the NIR emission intensity (vertical axis) and the X-ray dose rate (horizontal axis). The scintillation intensity increased linearly with the X-ray dose rate in the range from 0.05 to 50 Gy/h. The lower measurement limit was inferior to those of Nd-doped GdVO<sub>4</sub> (0.006 Gy/h),<sup>(25)</sup> Nd-doped Ca<sub>3</sub>TaGa<sub>3</sub>Si<sub>2</sub>O<sub>14</sub> (0.001 Gy/h),<sup>(26)</sup> and Nd-doped CaYAl<sub>3</sub>O<sub>7</sub> (0.001 Gy/h).<sup>(27)</sup> However, it was almost the same as those of Tm-doped Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> (0.03 Gy/h),<sup>(24)</sup> Nd-doped CaWO<sub>4</sub> (0.06 Gy/h),<sup>(28)</sup> and Er-doped Mg<sub>4</sub>Ta<sub>2</sub>O<sub>9</sub> (0.06 Gy/h).<sup>(20)</sup> The lower measurement limit of the LT:Cr sample is acceptable for radiation monitoring in nuclear facilities, according to a previous report.<sup>(29)</sup>

#### 4. Conclusions

An LT:Cr single crystal was grown using an OFZ furnace. The obtained LT:Cr single crystal showed high transparency and was green. The transmittance at 800–1400 nm was approximately 70%, and the absorption peaks due to Cr<sup>3+</sup> ions were observed at around 470

and 640 nm. The NIR scintillation peak due to the  ${}^4T_2-{}^4A_2$  transitions of  $Cr^{3+}$  ions was confirmed. The NIR scintillation intensity of the LT:Cr single crystal increased linearly with the X-ray dose rate from 0.05 to 50 Gy/h.

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### References

- 1 T. Kunikata, P. Kantuptim, D. Shiratori, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **36** (2024) 457. <https://doi.org/10.18494/SAM4754>
- 2 K. Ichiba, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **36** (2024) 451. <https://doi.org/10.18494/SAM4752>
- 3 D. Yuan, E. G. Villora, N. Kawaguchi, D. Nakauchi, T. Kato, T. Yanagida, and K. Shimam: *Jpn. J. Appl. Phys.* **62** (2023) 010614. <https://doi.org/10.35848/1347-4065/aca3e5>
- 4 K. Miyazaki, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **36** (2024) 515. <https://doi.org/10.18494/SAM4756>
- 5 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>
- 6 T. Kunikata, T. Kato, D. Shiratori, P. Kantuptim, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **36** (2023) 491. <https://doi.org/10.18494/SAM4145>
- 7 H. Kimura, T. Kato, T. Fujiwara, M. Tanaka, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *Jpn. J. Appl. Phys.* **62** (2023) 0101504. <https://doi.org/10.35848/1347-4065/ac916c>
- 8 T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *Jpn. J. Appl. Phys.* **62** (2023) 010604. <https://doi.org/10.35848/1347-4065/ac94ff>
- 9 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>
- 10 Y. Oshima, K. Watanabe, H. Shiga, and G. Wakabayashi: *Sens. Mater.* **35** (2023) 545. <https://doi.org/10.18494/SAM4148>
- 11 D. Shiratori, H. Fukushima, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: *Jpn. J. Appl. Phys.* **62** (2023) 010608. <https://doi.org/10.35848/1347-4065/ac90a4>
- 12 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>
- 13 H. Kawamoto, Y. Fujimoto, and K. Asai: *Sens. Mater.* **36** (2024) 607. <https://doi.org/10.18494/SAM4766>
- 14 M. Koshimizu, K. Oba, Y. Fujimoto, and K. Asai: *Sens. Mater.* **36** (2024) 565. <https://doi.org/10.18494/SAM4761>
- 15 R. Nagaoka, N. Kawano, Y. Takebuchi, H. Fukushima, T. Kato, D. Nakauchi, and T. Yanagida: *Jpn. J. Appl. Phys.* **61** (2022) 110621. <https://doi.org/10.35848/1347-4065/ac943d>
- 16 M. Koshimizu, Y. Fujimoto, and K. Asai: *Sens. Mater.* **35** (2023) 521. <https://doi.org/10.18494/SAM4149>
- 17 A. Ito and S. Matsumoto: *Jpn. J. Appl. Phys.* **62** (2023) 010612. <https://doi.org/10.35848/1347-4065/aca249>
- 18 D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: *Radiat. Meas.* **175** (2024) 107174. <https://doi.org/10.1016/j.radmeas.2024.107174>
- 19 K. Okazaki, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: *Radiat. Phys. Chem.* **220** (2024) 111700. <https://doi.org/10.1016/j.radphyschem.2024.111700>
- 20 T. Hayashi, K. Ichiba, D. Nakauchi, K. Okazaki, T. Kato, N. Kawaguchi, and T. Yanagida: *Photonics* **10** (2023) 654. <https://doi.org/10.3390/photonics10060654>
- 21 K. Okazaki, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: *Nucl. Instrum. Methods Phys. Res., Sect. B* **547** (2024) 165197. <https://doi.org/10.1016/j.nimb.2023.165197>
- 22 I. Sokólska and S. Kück: *Spectrochim. Acta, Part A.* **54** (1998) 1695. [https://doi.org/10.1016/S1386-1425\(98\)00099-7](https://doi.org/10.1016/S1386-1425(98)00099-7)

- 23 W. Ryba-Romanowski, S. Gołab, W. A. Pisarski, G. Dominiak-Dzik, M. N. Palatnikov, N. V. Sidorov, and V. T. Kalinnikov: *Appl. Phys. Lett.* **70** (1997) 2505. <https://doi.org/10.1063/1.118904>
- 24 M. Akatsuka, H. Kimura, D. Onoda, D. Shiratori, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **33** (2021) 2243. <https://doi.org/10.18494/SAM.2021.3319>
- 25 K. Okazaki, D. Nakauchi, H. Fukushima, T. Kato, N. Kawaguchi, and T. Yanagida: *Sens. Mater.* **35** (2023) 459. <https://doi.org/10.18494/SAM4144>
- 26 K. Okazaki, M. Koshimizu, D. Nakauchi, T. Kunikata, T. Kato, N. Kawaguchi, and T. Yanagida: *J. Alloys Compd.* **1008** (2024) 176788. <https://doi.org/10.1016/j.jallcom.2024.176788>
- 27 A. Nishikawa, K. Ichiba, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: *Appl. Radiat. Isot.* **214** (2024) 111559. <https://doi.org/10.1016/j.apradiso.2024.111559>
- 28 K. Okazaki, D. Nakauchi, H. Fukushima, T. Kato, N. Kawaguchi, and T. Yanagida: *Appl. Sci.* **12** (2022) 11624. <https://doi.org/10.3390/appl122211624>
- 29 E. Takada, A. Kimura, Y. Hosono, H. Takahashi, and M. Nakazawa: *J. Nucl. Sci. Technol.* **36** (1999) 641. <https://doi.org/10.1080/18811248.1999.9726250>