1. Introduction

A scintillator is a phosphor which converts high energy ionizing radiation to thousands of visible photons, and scintillation detector consists of a pair of a scintillator and a photodetector such as a photomultiplier tube (PMT).\(^1\) The typical application fields are medical imaging,\(^2,3\) security,\(^4,5\) and astrophysics.\(^6,7\) In recent years, a development of neutron scintillators becomes attractive research topic due to a limitation of standard detector material, \(^3\)He\(^\text{gas}\) as a neutron capture element has been mainly used. Up to now, a proportional counter which encloses \(^3\)He gas. Until now, a proportional counter which encloses \(^3\)He gas as a neutron capture element has been mainly used as neutron detectors.\(^8-10\) However, demands of neutron detectors has increased with growth of security techniques, and shortage of \(^3\)He has been concerned for these 10 years.\(^11\) Therefore, neutron scintillators have been required as replacements to the gas proportional counter. Required properties of neutron scintillators are high light yield \((LY)\), fast decay time, small effective atomic number \((Z_{\text{eff}})\), and large cross section for neutron capture. In the case of scintillators containing \(^6\)Li, \(\alpha\)-ray and \(^3\)H are generated according to the following formula when a scintillator reacts with a neutron,

\[
^6\text{Li} + n \rightarrow ^3\text{H} (2.75 \text{ MeV}) + \alpha (2.05 \text{ MeV}).
\]

Then, generated \(\alpha\)-rays and \(^3\)H ionize and excite the emission centers of scintillators, and luminescence occurs.

Undoped and Ce-doped LiAlO\(_2\) single crystals, a novel neutron scintillator, were synthesized by the floating zone method, and the photoluminescence and scintillation properties were investigated. Under X-ray irradiation, all the synthesized crystals showed luminescence due to oxygen vacancies with decay time constants of 250 ns and 2 \(\mu\)s, and Ce-doped LiAlO\(_2\) crystals showed luminescence due to the 5d–4f transition of Ce\(^{3+}\) with a decay time constant of 40 ns as well. In the pulse height spectra under neutron irradiation from \(^{252}\)Cf, the synthesized crystals exhibited thermal neutron peak, and scintillation light yields increased by doping of Ce. Furthermore, neutron and gamma-ray pulse shape discrimination was examined, and 0.5 and 1.0 % Ce-doped ones showed a distinction of neutron and gamma-ray events.

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(99.99%, RARE METALLIC), Al₂O₃ (99.99%, TAIMEI CHEMICALS), and CeO₂ (99.99%, Furuuchi Chemical) powders were used as raw materials. The 20% excess of Li₂CO₃ were used to compensate for an incongruent Li evaporation. The mixed powders were taken into a balloon to form a cylindrical rod by applying hydrostatic pressure. The rod was calcined in the order at 600°C for 4 h, 1100°C for 8 h, and 1300°C for 8 h. The single crystals were synthesized in air, and the pull-down rate during the crystal growth was 5 mm/h. The crystals were cut and mechanically polished for measurement. The phase of crystals was examined by powder XRD analysis using an X-ray diffractometer (Rigaku, MiniFlex600).

The diffuse transmittance spectra were evaluated by the spectrophotometer (Shimadzu, SolidSpec-3700) in the spectral range of 250–800 nm. The PL excitation and emission spectra were evaluated by using a spectrofluorometer (JASCO, FP-8600). PL decay curves monitored at 400 nm under 340 nm excitation were measured using QuantaMaurus (Hamamatsu Photonics, C11367).

The X-ray-induced scintillation spectra were evaluated by using our original setup. The X-ray-induced scintillation decay curves was measured by an afterglow characterization system. To obtain LYs, the pulse height spectra with ²⁵²Cf neutron exposure were evaluated by our typical setup. In order to estimate the LY, Li-glass scintillator GS20 (7200 ph/n²) was used as a reference. The pulse shape discrimination (PSD) for neutron and gamma-ray events were evaluated by a similar setup with our previous work, and only the difference was that the digitizer used here was PicoScope 6402D (Pico Technology). Two dimensional plots of fast and slow integrations were obtained in 0.5 and 1.0% Ce-doped samples, while we could not detect clearly by undoped and 0.1% Ce-doped ones due to a low scintillation LY described later. When we set the time = 0 at the beginning of the scintillation light pulse, the fast and slow integration windows were set at were 0–192 ns and 0–12.8 μs, respectively.

3. Results and discussions

In the crystal growth by the FZ method, as-grown sample rods with typical size of 5 mm φ × 10 mm were obtained. After cut and polish, we prepared typically 5 mm φ × 1 mm crystals for characterizations. The remaining portion of as-grown samples were crushed for XRD measurement. Figure 1 shows the XRD patterns of the synthesized crystals. ICDD 73-1338 and 87-1278 were used as reference data of γ-LiAlO₂ and LiAl₅O₈, respectively. Undoped, and 0.1 and 0.5% Ce-doped crystals showed a single phase of γ-LiAlO₂, while the 1% Ce-doped crystal contained a LiAl₅O₈ phase. In the past studies, both Li and Al sites could be substituted by rare earth ions, and the site where Ce replaced was unclear in this measurement. No peak shift was observed within accuracy of the used XRD apparatus; therefore, Ce was possibly doped as an interstitial.

Figure 2 shows the diffuse transmittance spectra of the undoped and Ce-doped LiAlO₂ crystals. The difference of transmittance among the samples is considered to be due to some cracks generated during crystal growth and impurity phase of LiAl₅O₈ owing to doping Ce. Particularly, the 0.1% Ce-doped LiAlO₂ crystal had more cracks than the 0.5% one, and transmittance decreased. No absorption edge was observed in measurement range. The reported band gap of LiAlO₂ was 6.5 eV (191 nm), and the band gap of synthesized crystal seemed to be consistent with this report. In addition, Ce-doped LiAlO₂ crystals showed another absorption band at around 315 nm. Because the depth of this absorption increased with concentration of Ce, this absorption caused by doping of Ce.

Figure 3 shows the PL excitation and emission spectra of Ce-doped LiAlO₂ crystals. When excited at 315 nm, a broad emission band at 450–550 nm was observed. The excitation and emission wavelengths were coincided with Ce-doped LiAlO₂ reported in sintered ceramic form. The absorption band of Ce-doped LiAlO₂ crystals shown in Fig. 2 overlapped with emission spectra, and the red-shift occurred because of self-absorption. No emission was detected from the undoped LiAlO₂ crystals although various excitation wavelengths were investigated.

Figure 4 shows the PL decay curves of the Ce-doped LiAlO₂ crystals, and the obtained decay time constants are also presented in the figure. Excitation and monitored wavelengths were 340 and 400 nm, respectively. Excluding an instrumental response component at time range
shorter than 50 ns in Fig. 4, decay curves were approximated by a single exponential decay component. The decay time constants of Ce-doped LiAlO₂ crystals were approximately 30 ns. This value was typical for the 5d–4f transition of Ce³⁺.

Judged from the PL spectra and the decay time constants, the origin of luminescence of Ce-doped LiAlO₂ crystals is the 5d–4f transition of Ce³⁺.

Figure 5 shows the X-ray-induced scintillation spectra of the undoped and Ce-doped LiAlO₂ crystals. The undoped LiAlO₂ crystal showed luminescence peaking at 340 nm which agreed with the previous report. The Ce-doped LiAlO₂ crystals showed luminescence at 340 and 400 nm. As the concentration of Ce increased, luminescence at 340 nm decreased, while luminescence at 400 nm increased.

Figure 6 shows the X-ray-induced scintillation decay curves of the undoped and Ce-doped LiAlO₂ crystals, and the obtained decay time constants are also presented in the figure. The decay curves of the undoped and Ce-doped LiAlO₂ crystals were approximated by a sum of two and three exponential functions, respectively. The first component of the Ce-doped LiAlO₂ crystals was approximately 40 ns, which was close to PL decay and ascribed to the 5d–4f transition of Ce³⁺. Additionally, all the crystals showed decay times of 250 ns and 2 μs which were slower than that of the 5d–4f transition of Ce³⁺. The decay time constants are considered to be due to oxygen vacancies in the host. Taking the comprehensive results of scintillation spectra and decay time into account, the luminescence at 400 nm was ascribed to the 5d–4f transition of Ce³⁺ with decay time of 40 ns, and the luminescence at 340 nm was attributed to oxygen vacancies with decay times of 250 ns and 2 μs.

Figure 7 shows the ²⁵²Cf-irradiated pulse height spectra of the undoped and Ce-doped LiAlO₂ crystals. The shaping times for the undoped and Ce-doped LiAlO₂ crystals were 10 and 0.5 μs, respectively. A clear thermal neutron peak was observed in all the samples, and the channels of the undoped, 0.1, 0.5, and 1% Ce-doped LiAlO₂ crystals were 96, 105, 316, and 449 channel, respectively.
Considered by quantum efficiency of PMT and the observed peak channels, the scintillation $LY$ of the undoped, 0.1, 0.5, and 1% Ce-doped LiAlO$_2$ crystals were estimated to be 440, 510, 1540, and 2190 ph/n, respectively. The $LY$ of the Ce-doped LiAlO$_2$ crystals increased with Ce concentration. However, these $LY$ were quite low compared with previous works. The previous works used Czochralski or Micro-pulling down method under inert gas for preparations of crystals, while our samples were synthesized by the FZ method in air. This difference of growth condition possibly reduced oxygen vacancies which act as a luminescence center.

**Figure 8** (left) represents two dimensional histograms of 0.5 and 1% Ce-doped LiAlO$_2$ crystals integrated by different time windows (fast and slow). The lines plotted in the two dimensional planes suggest gamma-ray branch which shows events induced by gamma-rays. Events shifted from the gamma-ray branch toward upper side in the plane are caused by neutrons. Thus, we can separate gamma-ray and neutron induced events by the PSD technique, while the separation was not better than Czochralski grown undoped LiAlO$_2$. The fast component due to Ce$^{3+}$ can be clearly observed in gamma-ray induced decay, and difference of this fast component would enable us to use the PSD technique for these samples. Although we confirm that Ce-doped LiAlO$_2$ can show PSD capability, Czochralski grown undoped LiAlO$_2$ will be better for PSD. In a future plan, examination of Czochralski grown Ce-doped LiAlO$_2$ will be interesting, and we would like to challenge it elsewhere.

### 4. Conclusion

We developed undoped and Ce-doped LiAlO$_2$ single crystals by the FZ method and investigated the PL, and scintillation properties. Under X-ray irradiation, the Ce-doped crystals showed luminescence due to oxygen vacancies and the 5d–4f transition of Ce$^{3+}$. In the pulse height spectra under neutron irradiation from $^{252}$Cf, the synthesized crystals exhibited thermal neutron peak, and scintillation $LY$ increased by doping of Ce. The scintillation $LY$s of the undoped, 0.1, 0.5, and 1% Ce-doped LiAlO$_2$ crystals were estimated to be 460, 540, 1630, and 2320 ph/n, respectively. In 0.5 and 1% Ce-doped LiAlO$_2$ crystals, PSD capability was confirmed, and the origin of PSD was the ratio of the fast decay component to the slow component. The fast decay time constants of Ce-doped LiAlO$_2$ crystals are effective for practical application although the improvement of $LY$s is required.
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