



Crystal growth and optical properties of indium doped LiCaAlF₆ scintillator single crystals



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ARTICLE INFO

Article history:

Received 26 May 2016

Received in revised form

14 October 2016

Accepted 19 October 2016

Available online 28 October 2016

Keywords:

Scintillator

LiCaAlF₆

Single crystal

Indium

ABSTRACT

The In-doped LiCaAlF₆ [In:LiCAF] single crystals were grown by the micro-pulling-down (μ -PD) method, and the phases, chemical compositions, transmittance and radioluminescence spectra were investigated. All the grown crystals showed high transparency and single phase of LiCAF without visible cracks and inclusions except for the end part of In2%:LiCAF crystal which included the impurity phase. In the radioluminescence spectra of the In:LiCAF crystals under X-ray irradiation, the emission peak around 750 nm was revealed.

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1. Introduction

Neutron detectors using neutron scintillators have been developed for some applications represented e.g. by the homeland security devices [1]. The ³He gas proportional counter has been widely used as a basic detector for the thermal neutron due to the high capture cross-section to the thermal neutron and the low sensitivity to γ -ray. However, the supply crisis of ³He gas by the excessive demand became critical and the importance of the alternative neutron scintillators has increased. Therefore, novel neutron scintillator with high scintillation performance becomes required as an alternative of ³He gas. We have developed the LiCaAlF₆ (LiCAF) neutron scintillator with a large capture cross-section to neutrons by ⁶Li enrichment [2–5]. In addition, the effective atomic number and density of the LiCAF are relatively low which provides low sensitivity to γ -ray. Additional advantages include the availability of large bulk single LiCAF crystals

grown by the melt-growth technique and its non-hygroscopic character.

In our previous studies, the Eu²⁺- and Ce³⁺-doped LiCAF (Eu:LiCAF, Ce:LiCAF) single crystals were developed as the neutron scintillator and their scintillation properties were investigated [1–4]. In the reports, Eu:LiCAF showed the high light yield (~30,000 photons/neutron) and Ce:LiCAF had short decay time (~40 ns) to the thermal neutron irradiation that originated from the 5d-4f transition of the dopants, Eu²⁺ and Ce³⁺ ions. These materials are belong to strong candidates for next-generation neutron scintillator. However, the dopants, Eu and Ce ions, are the rare-earth elements and there is a possibility of supply crisis as happened in last decade.

On the other hand, ns²-type cations show luminescence originated from the s²-sp transition [6]. In our previous study, we tried to grow the Sn²⁺ and Pb²⁺ doped LiCAF single crystal to demonstrate the luminescence from the s²-sp transition of the Sn²⁺ and Pb²⁺ in the LiCAF [7]. Unfortunately, the Sn:LiCAF single crystal couldn't be obtained due to the high vaporization of the SnF₂ above 400 °C. By contrast, the Pb:LiCAF single crystal could be grown and the grown crystal showed emission peaks around 210 and 830 nm under X-ray irradiation consistently with previous reports [8,9].

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In this study, we focused on the luminescence originated from s^2 - sp transition of In^{3+} ion. There are some reports about the In doped CsI crystal and it showed high light yield and great energy resolution [10,11]. Moreover, it was used as a dopant in another promising ternary iodide host [12]. However, to our knowledge, there is no earlier study about the In doped LiCAF single crystal. Therefore, we grew the In:LiCAF single crystals with various In concentrations and studied their luminescence as an alternative to the Eu and Ce dopants in the LiCAF neutron scintillator.

2. Experimental procedure

Non-doped and In doped LiCaAlF_6 (LiCAF and In:LiCAF) single crystals were grown by the micro-pulling-down (μ -PD) method with a tight-vacuum chamber and a diffusion pump. Starting materials, LiF (4N), CaF_2 (4N), AlF_3 (4N) and InF_3 (2N up) powders, were mixed as nominal compositions of $\text{Li}(\text{Ca}_{1-x}\text{In}_x)\text{AlF}_6$ ($x = 0, 0.005, 0.01$ and 0.02). The mixed powder was melted at higher temperature than the melting point of the LiCAF and we confirmed that the mixed powder was completely melted. The molten material was set into a carbon crucible with a $\varnothing 2$ mm hole at the bottom. After the crucible and an insulator were placed in the center of a high-frequency induction coil in the chamber, the inside of the chamber was evacuated up to $\sim 10^{-4}$ Pa on heating the crucible at ~ 300 °C to remove moisture adsorbed on the surfaces of the powders, crucible, insulator and equipment. After the baking process, the chamber was filled with high purity Ar/ CF_4 mixed gas (Ar: $\text{CF}_4 = 9:1$) up to the ambient pressure. The crucible was heated up to the melting point of LiCAF or In:LiCAF and crystal growth was performed at 0.1 mm/min growth rate by pulling-down the melt from the hole of the crucible using a platinum wire as a seed. Grown crystals were cut and polished to 1 mm thickness for measurements of optical and scintillation properties.

Chemical compositions of the grown crystals were evaluated by an electron probe micro-analyzer [EPMA] (JEOL JXA-8530F). Transmittance spectra of the polished specimens were measured by the Si-Photodetector at the UVSOR Facility of the Institute for Molecular Science BL3B (IRD AXUV 100) in the wavelength range from 80 to 300 nm. After the as-grown crystals were ground perfectly, the powder X-ray diffraction (XRD) measurements of the powders were performed to identify the phases of the grown crystals (RIGAKU RINT2000). Local surface of the polished specimen was observed by the scanning electron microscope (SEM) (HITACHI S-3400N) and chemical composition of each phase was evaluated by the Energy Dispersive X-ray Spectroscopy (EDX) (HORIBA EMAX X-act). X-ray excited radioluminescence spectra of the polished specimens were measured by a Charge Coupled Device (CCD) detector (ANDOR DU420-OE) using $\text{Cu-K}\alpha$ X-ray source (40 kV, 40 mA).

3. Results and discussion

Non-doped LiCAF and In:LiCAF single crystals were grown by the μ -PD method and as-grown crystals were shown in Fig. 1(a). The diameter of the grown single crystals was limited to 2 mm by the hole of the crucible during the crystal growth. All the as-grown crystals had no cracks and visible inclusions in the front part, they were colorless with high transparency. However, the end parts of In2%:LiCAF single crystals included milky parts. It is considered to be due to the segregation of the In ion along the growth direction. Polished specimens were obtained from the front and end parts of the as-grown crystals (Fig. 1(b)). The polished specimen of the front part with rectangular shape and 1 mm thickness showed high

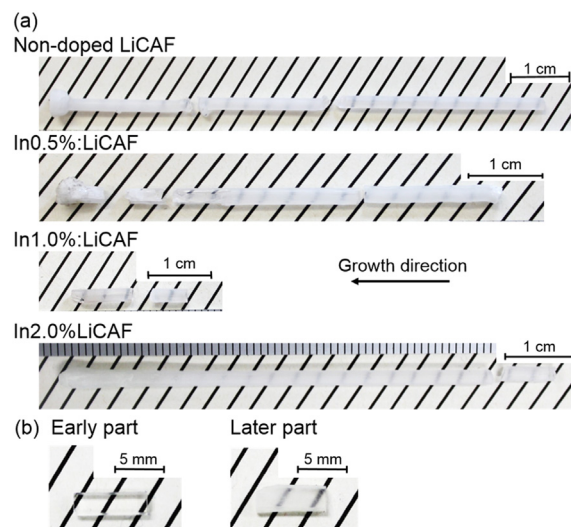


Fig. 1. (a) As-grown LiCAF and In:LiCAF crystals grown by the μ -PD method and (b) polished In2%:LiCAF specimens obtained from early and later parts.

transparency. On the other hand, there are some milky parts in the polished specimen of the end part of In2%:LiCAF.

Powder XRD measurements of the grown crystals were performed to investigate the phases. Fig. 2(a) shows the powder XRD patterns. All the diffraction peaks of all the as-grown crystals with high transparency were identified with the LiCAF crystal structure (trigonal, space group: P31c) and there was no secondary phase in the XRD patterns. On the other hand, the end part of the In2%:LiCAF crystal included impurity phase of CaF_2 in addition to the LiCAF phase. The milky part in the crystal is most probably due to an impurity phase. The local surface of the polished specimen for the later part of the In2%:LiCAF crystal was observed by the EDX (Fig. 2(b)). The impurity phase was included in the matrix phase and the results of the EDX analysis revealed that the impurity phase included highly concentrated In as it is illustrated in Fig. 2(c). The impurity is considered to be the InF_3 . According to the analysis of the chemical compositions for the In:LiCAF single crystals by the EPMA, the spectra from the In could be detected in the LiCAF phase. However, the In concentration in the LiCAF phase were too small to fix the value of the concentration in LiCAF phase. The results suggest that the In ion in the grown crystals exists as In^{3+} ion which is not incorporated into the LiCAF lattice due to the differences of the ionic radius and the valence of the ions between In^{3+} and Ca^{2+} because the InF_3 was used as the starting material without any reduction treatments. Transmittance spectra of the polished In:LiCAF specimens were measured in the wavelength range from 80 to 300 nm and from 200 to 800 nm (Fig. 3(a) and (b)). The transmittance of the non-doped LiCAF was slightly lower than that of the In:LiCAF. Transmittance of the non-doped LiCAF and In:LiCAF specimens was higher than 70% in the wavelength range of 200–800 nm with no clear absorption peaks (Fig. 3(a)). On the other hand, the edge of transmittance was observed for non-doped LiCAF and In:LiCAF specimens in the wavelength range of 50–300 nm (Fig. 3(b)). The edge of transmittance was shifted to longer wavelength by the In doping. In addition, small absorption peak around 200 nm was observed for non-doped LiCAF and In:LiCAF specimens and it is considered to be attributable to the LiCAF host material.

Fig. 4 shows the radioluminescence spectra of the non-doped LiCAF and In:LiCAF specimens under X-ray irradiation. Broad

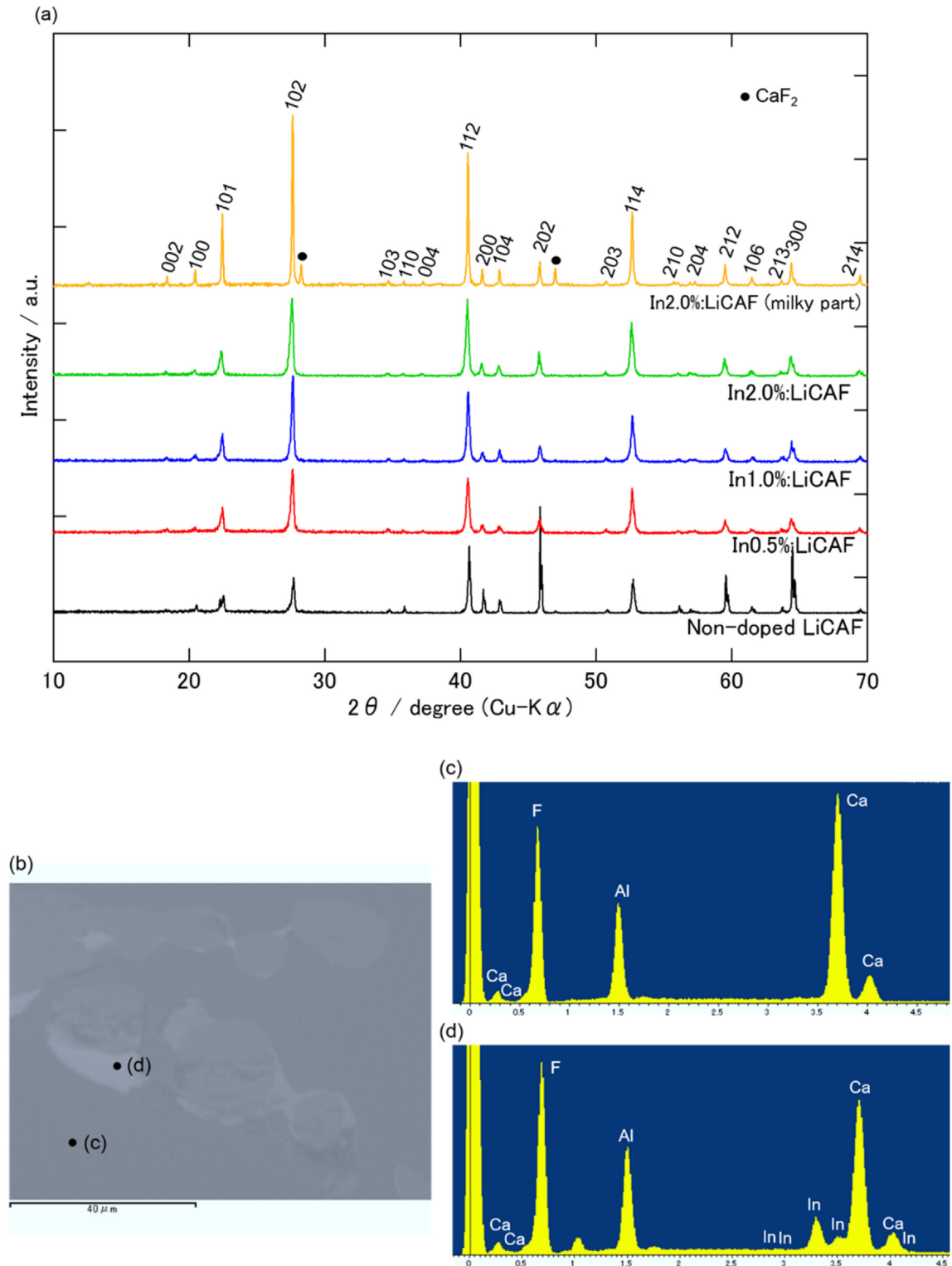


Fig. 2. (a) Powder XRD patterns of non-doped and In doped LiCAF crystals. (b) SEM image and (c), (d)EDX spectra of the later part of In2%:LiCAF crystal.

emission peak from 650 to 900 nm was observed for the all the In:LiCAF specimens while non-doped LiCAF specimen showed sharp emission peak around 740 nm which has been ascribed to the self-trapped or trapped exciton [5]. The In0.5%:LiCAF specimen showed the highest intensity of the broad emission peak. In fact, given the literature data for In⁺ dopant in several alkali halide

hosts, and considering the octahedral Li site where In⁺ should be embedded, the lowest absorption band of In⁺ in LiCAF is supposed to peak around 4.3–4.5 eV. With the estimated Stokes shift of about 1.4 eV [13] the emission peak could be placed around 3 eV (413 nm) which is consistent with the peak of In⁺ emission at 540–550 nm in CsBa₂I₅ and CsI [10,12] as the crystal field strength

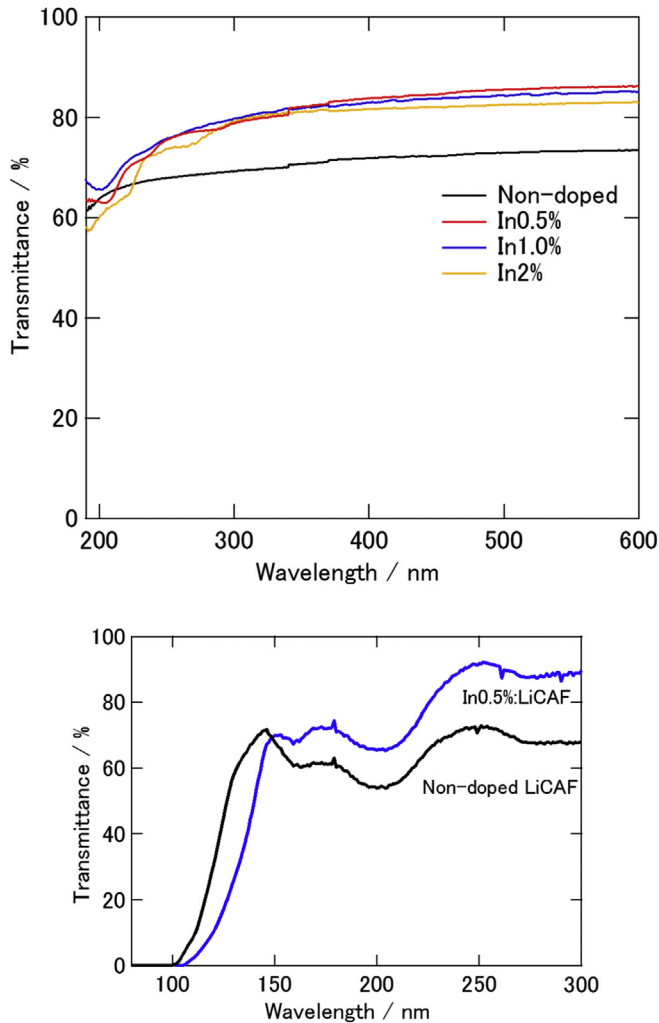


Fig. 3. Transmittance spectra of non-doped and In doped LiCAF crystals in the wavelength range of (a) 190–600 and (b) 80–300 nm.

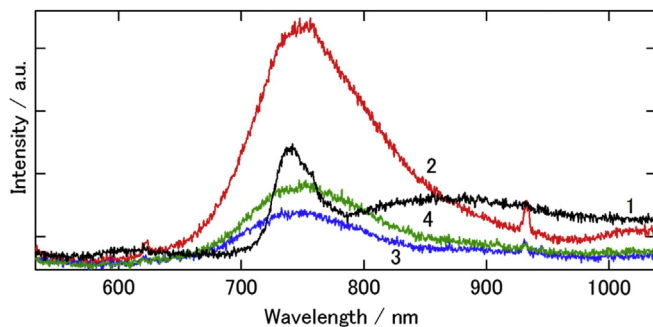


Fig. 4. Radioluminescence spectra of non-doped and In doped LiCAF crystals. (1) non-doped, (2) In0.5%, (3) In1.0%, and (4) In2.0%:LiCAF.

at the Cs site in these iodides is surely stronger compared to that at Li site of LiCAF fluoride host. Thus the observed emission in Fig. 4 can hardly be ascribed to the s^2 - sp transition of the In^+ ion itself and is rather due to a defect. Moreover, the charge state of the In ion

in the In:LiCAF crystals is not clear and further studies are necessary to explain the origin of the observed broad emission peaks.

4. Conclusion

Indium doped LiCAF single crystals were grown by the μ -PD method and their phases, chemical compositions, transmittance and radioluminescence spectra were investigated. All the grown crystals showed high transparency without visible cracks and inclusions except the end part of the In2%:LiCAF crystal which showed the milky appearance. The powder XRD patterns revealed that all the grown crystals were single phase of the LiCAF structure except for the end part of the In2%:LiCAF crystal which included the CaF_2 impurity phase. SEM image of the end part showed the impurity inclusions in the LiCAF phase in which rather high concentration of In was found. In the radioluminescence spectra of the In:LiCAF crystal under X-ray irradiation, the emission peak around 750 nm was observed. It can hardly be due to s^2 - sp transition of In^+ and its origin needs further study.

Acknowledgements

This work is partially supported by the New Energy and Industrial Technology Development Organization (NEDO), the Japan Society for the Promotion of Science (JSPS) Research Fellowships for Grant-in-Aid for Young Scientists, Japan Science and Technology Agency (JST) Adaptable & Seamless Technology Transfer Program through Target-driven R&D (A-STEP). Partial support of Bilateral AS CR-JSPS Joint Research Project, MEYS, KONTAKT II, no. LH14266 supporting Czech-Japanese collaboration is also acknowledged.

In addition, we appreciate the support by the UVSOR Facility of the Institute for Molecular Science and following persons: Mr. Takahiko Horiai, Mr. Hiroyuki Chiba, Mr. Hiroshi Uemura, Ms. Keiko Toguchi, Ms. Megumi Sasaki, Ms. Yuka Takeda and Ms. Kuniko Kawaguchi of Institute for Materials Research, Tohoku University.

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