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Growth and radioluminescence of metal elements doped $LiCaAlF_6$ single crystals for neutron scintillator

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HIGHLIGHTS

- Pb^{2+} doped LiCAF single crystals were grown by micro-pulling-down method.
- We measured powder XRD and transmittance of grown crystals.
- We revealed radioluminescence emission spectra under X-ray irradiation.

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ABSTRACT

The ns^2-type metal elements (Pb and Sn) doped $LiCaAlF_6$ single crystals were grown by a micro-pulling-down (μ-PD) method. Pb doped $LiCaAlF_6$ [Pb:LiCAF] crystals showed high transparency and single phase of the LiCAF structure. However, we could not obtain Sn:LiCAF crystals due to the evaporation of SnF_2 during the crystal growth. There was an absorption peak around 193 nm in the transmittance spectrum of Pb:LiCAF crystal. In the radioluminescence spectrum of the Pb:LiCAF crystal under X-ray irradiation, two emission peaks around 200 and 830 nm were observed.

1. Introduction

Neutron detectors using neutron scintillators have been investigated for some applications of the homeland security devices. ^{3}He gas proportional counter has been used widely as a basic sensor for the thermal neutron detection due to the high capture cross-section to the thermal neutron and the low sensitivity to γ-ray. However, the importance of alternative neutron scintillators has increased due to the supply crisis of ^{3}He gas by the excessive demand. Therefore, the neutron scintillator has become gradually of interest as an alternative material of ^{3}He gas. In the material research of novel neutron scintillators, we have developed a $LiCaAlF_6$ [LiCAF] scintillator crystal including ^{6}Li with the high capture cross-section to the thermal neutron. In addition, the effective atomic number and density of the LiCAF are relatively low which results in small detection efficiency for γ-ray. The large bulk single crystal of the LiCAF can be grown by the melt-growth technique and it is non-hygroscopic.

Eu^{2+} doped LiCAF [Eu:LiCAF] and Ce^{3+} doped LiCAF [Ce:LiCAF] single crystals have been developed and their scintillation properties were investigated in the previous reports (Yoshikawa et al., 2009; Yanagida et al., 2009; Yokota et al., 2011; Yanagida et al., 2011). Especially, Eu:LiCAF has the high light yield (~30,000 photons/neutron), and Ce:LiCAF showed an emission with short decay time (~40 ns). However, the Eu and Ce dopant ions are rare-earth elements and there is a possibility of their supply crisis as it

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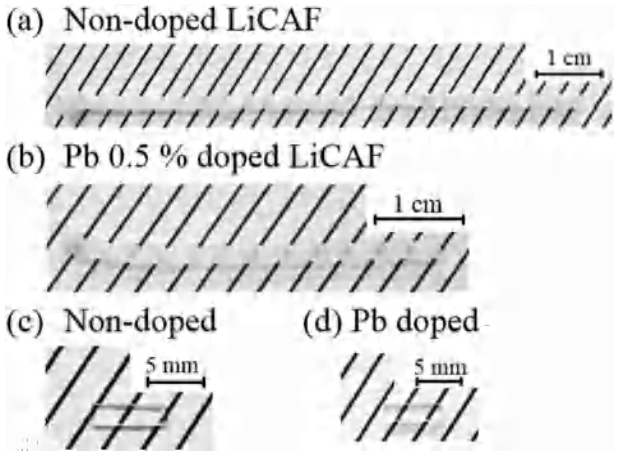

Fig. 1. (a) As-grown non-doped LiCAF and (b) Pb:LiCAF crystals grown by the μ-PD method. (c) Polished non-doped LiCAF and (d) Pb:LiCAF specimens.

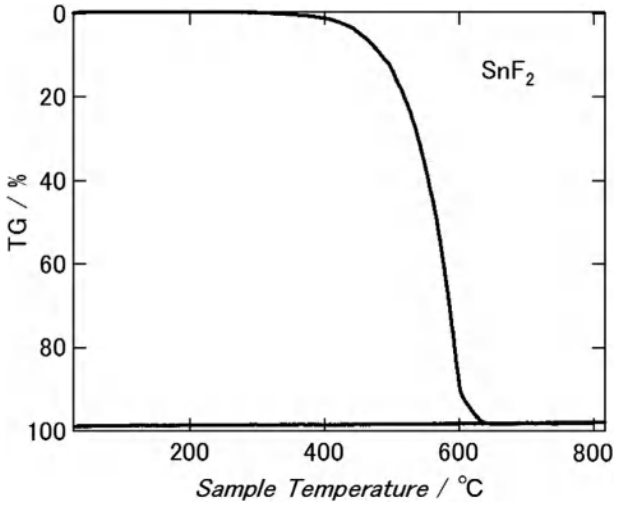

Fig. 2. Thermogravimetric analysis of SnF_2 powder.

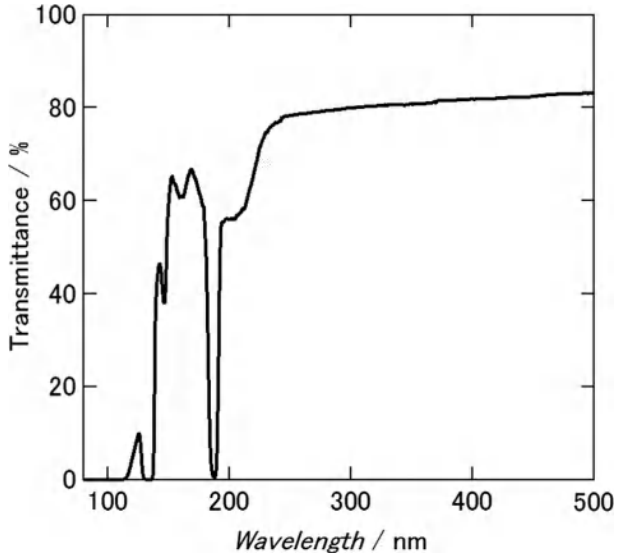

Fig. 4. Transmittance spectra of the polished Pb:LiCAF specimens.

happened in last decade.

The ns^2-type cations, Sn^{2+} and Pb^{2+}, are expected to show luminescence originated from s^2-sp transition. In previous reports (Wang and Gan, 2014; Donker et al., 1988, 2006), Sn^{2+} in various host materials as $46P_2O_5$–$38Li_2O$–16ZnO glasses, CaO and CaCO exhibits broad emission around 400 nm. However, there is no report about the luminescence of Sn^{2+} in a fluoride host material. On the other hand, there is a report about Pb doped LiCAF crystal and an emission peak around 209 nm was observed (Novoselov et al., 2007; Pejchal et al., 2009). However, there is no research about the luminescence in the longer wavelength region.

On these backgrounds, we grew ns^2-type metal elements doped LiCAF crystals and investigated their properties to obtain a novel dopant candidate for the LiCAF crystal.

2. Experimental procedure

Non-doped and ns^2 ion doped $LiCaAlF_6$ single crystals were grown by a micro-pulling-down (μ-PD) method with a high-vacuum chamber for fluorides. Starting materials, LiF (4N), CaF_2 (4N), AlF_3 (4N), SnF_2 (3N) and PbF_2 (3N) powders, were mixed as

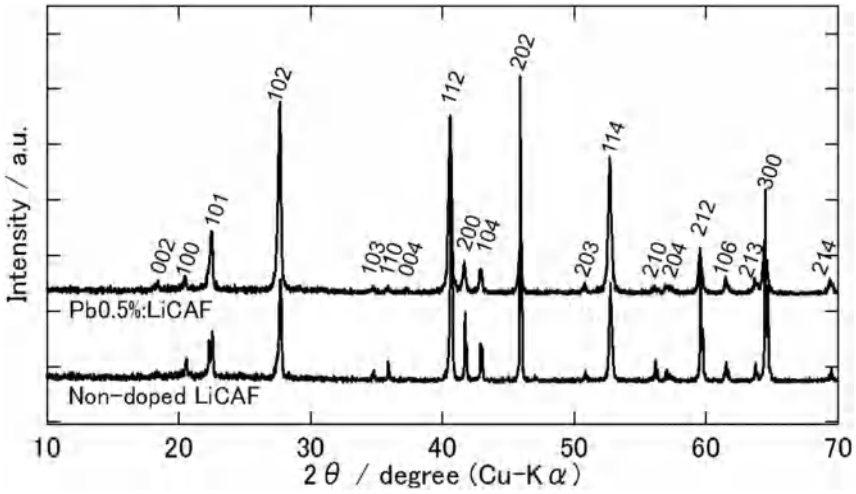

Fig. 3. Powder XRD patterns of the grown non-doped LiCAF, and Pb:LiCAF crystals.

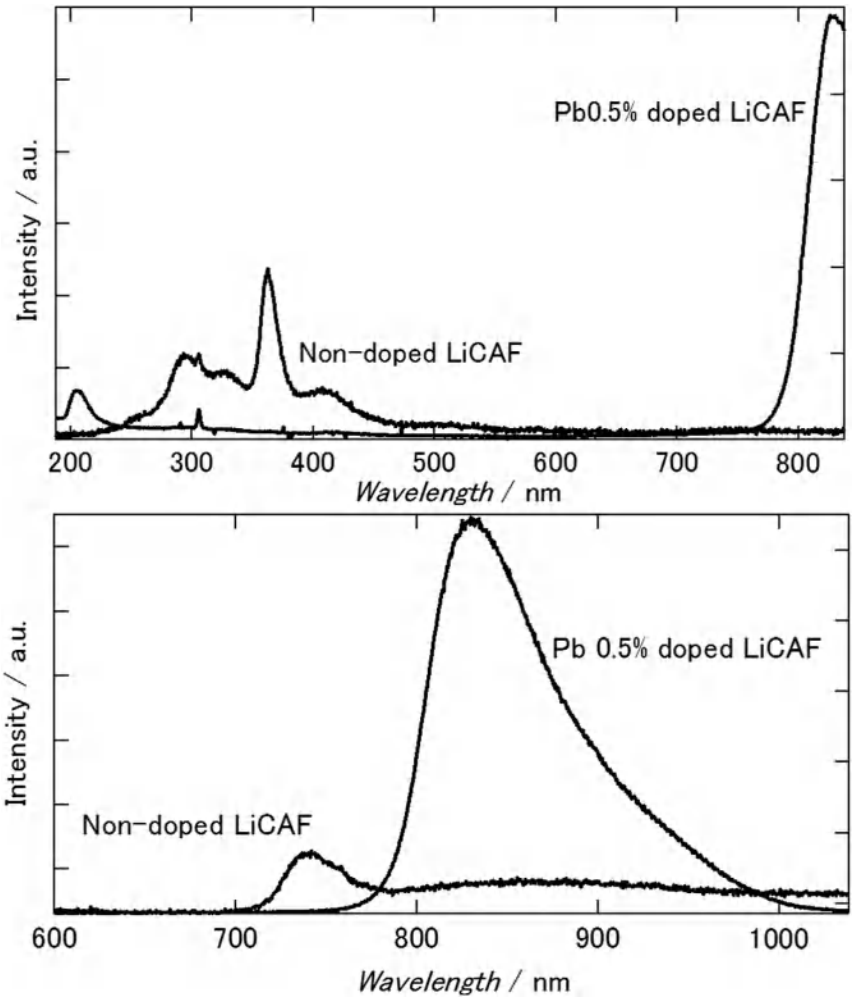

Fig. 5. Radioluminescence spectra of the polished non-doped LiCAF and Pb:LiCAF specimens under X-ray irradiation.

nominal compositions of $Li(Ca_{1-x}M_x)AlF_6$ ($x = 0.005$, M = Sn or Pb). The mixed powder was loaded into a carbon crucible with a ϕ2 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 chamber was evacuated up to ~10^{-4} Pa and the crucible was heated at ~300 °C to remove moisture on the surfaces of the powders, crucible, insulator and all the equipment. After the baking process, the chamber was filled with high purity Ar/CF_4 mixed gas (Ar: $CF_4 = 9$: 1) up to the ambient pressure. The crucible was heated up to the melting point of LiCAF (about 820 °C), and crystal growth was performed at 0.1 mm/min growth rate using a platinum wire as a seed. Grown crystals were cut and polished for measurements of their properties. The dimensions of the polished specimens were $7 \times 2 \times 1^t$ mm.

Chemical compositions of the grown crystals were evaluated by an electron probe micro-analyzer [EPMA] (JEOL JXA-8530F). Transmittance spectra of the polished specimens of non-doped and Pb doped LiCAF were measured by the SI-Photodetector (AXUV 100 (IRD)) and a spectrophotometer (JASCO V-550) in the wavelength range from 80 to 300 nm and 300–500 nm, respectively. After the as-grown crystals were ground perfectly, powder X-ray diffraction [XRD] measurements of the powders were performed to identify the phases of the grown crystals (RIGAKU RINT2000). X-ray excited radioluminescence spectra of the polished samples were measured by Charge Coupled Device [CCD] detector (ANDOR SR163 for short wavelength and ANDOR DU420-OE for long wavelength) using Cu-K_α X-ray source (40 kV, 40 mA). Volatility characteristics of SnF_2 powder was analyzed by a thermogravimetry (SETARAM SETSYS24).

3. Results and discussion

Non-doped and ns^2-type metal elements doped LiCAF crystals with the diameter of 2 mm were grown by the μ-PD method as shown in Fig. 1. The as-grown non-doped LiCAF is shown in Fig. 1(a) and the Pb:LiCAF crystal obtained from the Pb0.5%:LiCAF starting material is shown in Fig. 1(b). The all grown crystals did not show any cracks and visible inclusions and were colorless. The polished samples obtained from the grown crystals show high transparency (Fig. 1(c) and (d)).

The actual concentrations of the dopants in the grown crystals were evaluated by the EPMA. The actual Sn concentrations in the Sn:LiCAF crystals were less than the limit of detection. In addition, the thermogravimetric analysis revealed that the almost all SnF_2 powders were vaporized in the temperature range of 400–600 °C as it is shown in Fig. 2. The results suggest that SnF_2 starting material in the mixed powders was vaporized during the crystal growth and therefore Sn^{2+} ions could not be doped in the grown crystals. On the other hand, the actual Pb concentration in the Pb:LiCAF crystal was approximately 0.03%.

PowderXRDmeasurementsofthegrowncrystalswereperformedto investigate the phases and Fig. 3 shows the powder XRD patterns. All

diffraction peaks of the all grown crystals were identified with the LiCAF crystal structure (trigonal, space group: $P\bar{3}1c$) and there was no secondary phase in the XRD patterns. Any shift of the diffraction peaks for the Pb:LiCAF crystals was not observed by the Pb doping compared to the non-doped LiCAF crystal.

Transmittance spectra of the polished Pb:LiCAF specimen was measured in the wavelength range from 80 to 500 nm as it is illustrated in Fig. 4. The transmittance of the LiCAF specimen was more than 70% and there was no absorption peak in the measured wavelength range. On the other hand, in the transmittance spectra of Pb:LiCAF specimen an intense absorption peak was observed at 196 nm followed by another absorption peaks at shorter wavelengths and band edge of LiCAF host at about 115 nm. Absorption peaks at 196 nm and 135 nm could be ascribed to the so called A and C absorption bands of the Pb^{2+} center (Jacobs, 1991).

Fig. 5 shows the radioluminescence spectra of non-doped and Pb:LiCAF crystals under X-ray irradiation. The emission peaks around 290, 380 and 510 nm were observed for non-doped LiCAF crystal, and these peaks would be originated from self-trapped and trapped exciton (True et al., 2007). In the short wavelength region, an emission peak around 205–210 nm was observed and ascribed to Pb^{2+} center consistently with the previous report about the Pb:LiCAF crystal (Novoselov et al., 2007). In addition, we revealed that there was another emission peak around 830 nm in the long wavelength region. Its origin is in question, such an emission can arise due to a defect in the structure arising due to non-stoichiometry of LiCAF lattice due to Pb evaporation. Alternatively, it can be also due to Pb^{+} center which emits at about 880 nm in $LiBaF_3$ lattice (Prado et al., 1996).

4. Conclusion

Sn^{2+} or Pb^{2+} doped LiCAF single crystals were grown by the μ-PD method and their phases, chemical compositions, and optical and scintillation properties were investigated. However, the results of EPMA and thermogravimetric analysis revealed that SnF_2 powder vaporized during the crystal growth and Sn:LiCAF crystals could not be obtained while Pb could be doped in the LiCAF crystal. All the grown crystals showed high transparency without visible cracks and inclusions. The powder XRD patterns showed that all the grown crystals were single phase of LiCAF crystal structure. In the radioluminescence spectrum of the Pb:LiCAF crystal under X-ray irradiation, there was an emission peak around 830 nm in addition to the emission peak at 210 nm. While the latter originates from s^2-sp transition of Pb^{2+}, the former can be due to a defect or Pb^{+} center and further studies are necessary to explain its origin.

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