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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.

## ARTICLE INFO

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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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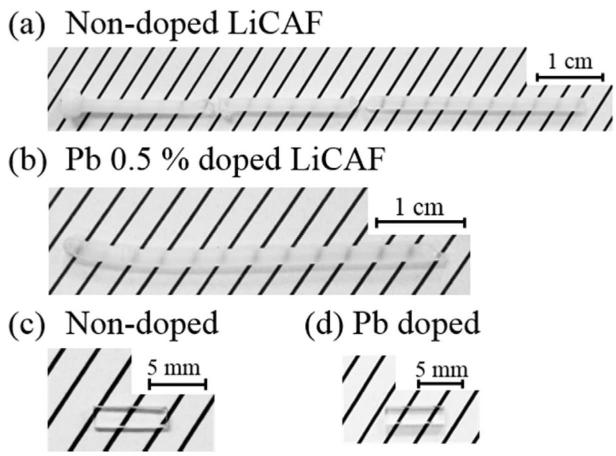


**Fig. 1.** (a) As-grown non-doped LiCAF and (b) Pb:LiCAF crystals grown by the μ-PD method. (c) Polished non-doped LiCAF and (d) Pb:LiCAF specimens.

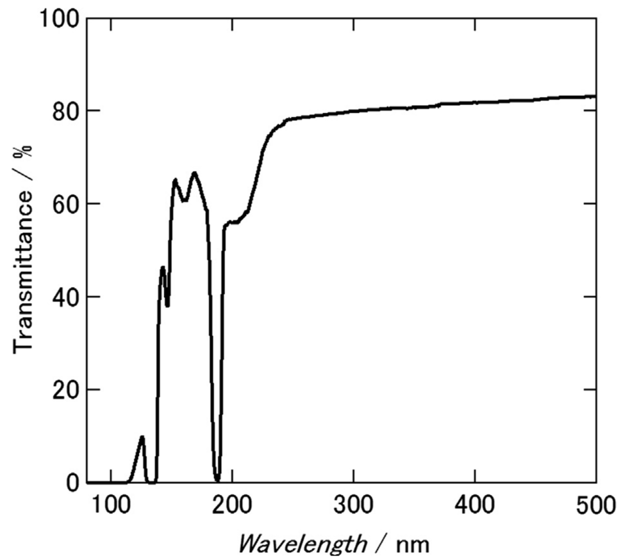


**Fig. 4.** Transmittance spectra of the polished Pb:LiCAF specimens.

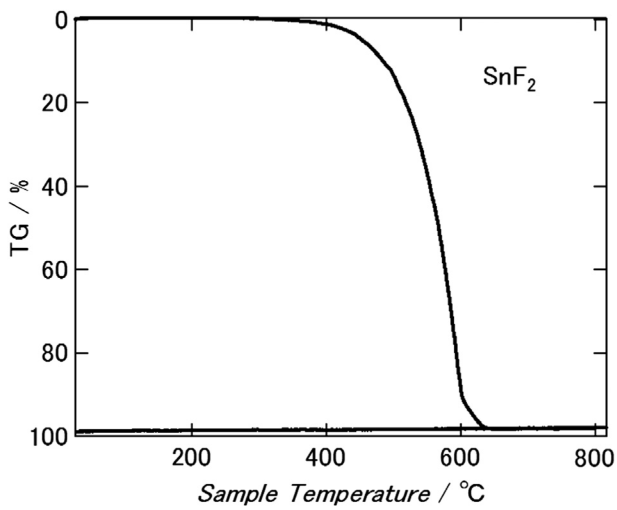


**Fig. 2.** Thermogravimetric analysis of $SnF_2$ powder.

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

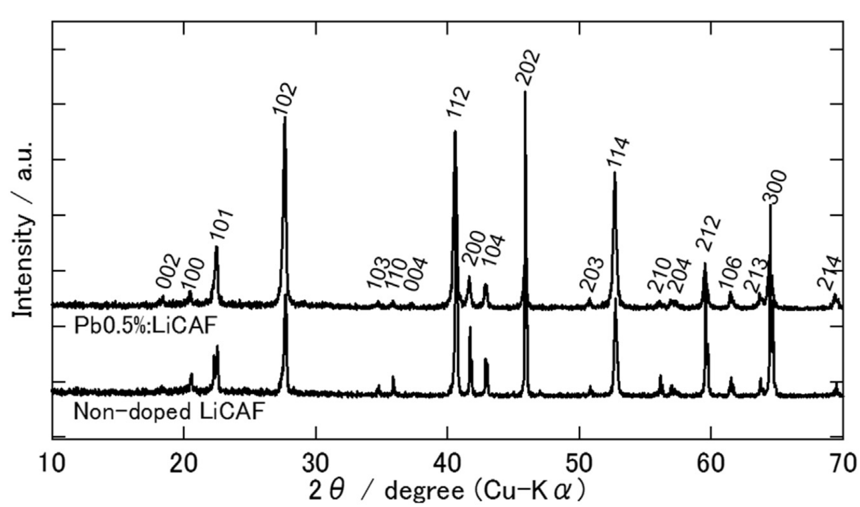


**Fig. 3.** Powder XRD patterns of the grown non-doped LiCAF, and Pb:LiCAF crystals.