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# Observation of new excitation channel of cerium ion through highly vacuum ultraviolet transparent LiCAF host crystal

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## Abstract

The transmission spectra of LiCaAlF<sub>6</sub> (LiCAF) and LiSrAlF<sub>6</sub> (LiSAF) are investigated in the ultraviolet (UV) and the vacuum ultraviolet (VUV) region. The transmission edge of LiCAF (112 nm) shows almost the same value as that of LiF. Taking into account difficulties of material processing and polishing due to the cleavage or the hydroscopic nature of LiF, LiCAF is regarded as a more suitable optical material in the UV and the VUV region. Moreover, the new excitation channel around 112 nm is discovered for Ce:LiCAF crystal. This excitation is originated not from absorption of Cerium ions but from absorption around the bandgap of the host crystal. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Recently, various new fluoride crystals have been developed as the host crystals for new solid-state tunable ultraviolet (UV) and infrared laser materials. Among them, LiCaAlF<sub>6</sub> (LiCAF) and

LiSrAlF<sub>6</sub> (LiSAF) are the successful materials for Chromium [1,2] or Cerium [3–7] doping. For Cerium doping in particular, Ce<sup>3+</sup>:LiCaAlF<sub>6</sub> (Ce:LiCAF) and Ce<sup>3+</sup>:LiSrAlF<sub>6</sub> (Ce:LiSAF) are attractive solid-state lasers with their practical tuning region from 280 to 315 nm and capability of the fourth harmonic of an Nd:YAG laser pumping [8]. 60 mJ output from Ce:LiCAF was already demonstrated with large-sized Czochralski (CZ) grown crystal. In spite of the similar tunability and laser efficiency, LiCAF is even more attractive than LiSAF because the solarization effect of LiCAF was much smaller than that of LiSAF

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[3–7]. In order to improve the laser performance, it is necessary to investigate these materials from the spectroscopic point of view. In addition, there is a possibility that these materials will be used as an optical material in the UV and the vacuum ultraviolet (VUV) region. These kinds of materials have become much important for the deep ultraviolet lithographic technology for the semiconductor processing technology of the next century and the UV and the VUV spectroscopy. In this paper, the transmission characteristics of LiCAF and LiSAF are reported by using synchrotron orbital radiation. LiCAF shows almost the same transmission characteristics compared with LiF [9]. Moreover, if other pumping schemes were available for this crystal, it will also expand the applicability of this laser medium. Observation of new excitation channel of  $\text{Ce}^{3+}$  ions through LiCAF host crystal was also found.

## 2. Experimental procedure

Crystals of LiCAF and LiSAF were grown in a CZ system driven by a 30 kW RF generator. Commercially available  $\text{AlF}_3$ ,  $\text{CaF}_2$ ,  $\text{SrF}_2$  and LiF powders of high purity (>99.99%) were used as the starting material. Growth orientation was controlled by using *a*-axis oriented seed crystals. The pulling rate was 1 mm/h and the rotation rate was 10 rpm. The growth was carried out in the Ar gas atmosphere and the starting material was melted at 1120 K [10]. Na<sup>+</sup> was co-doped for the charge compensation. The all fluoride samples for spectroscopy were cut about 1-mm thick. The experiment was performed at the ultraviolet synchrotron orbital radiation facility (UVSOR) in Institute for Molecular Science (IMS) using a 1-m focal-length Seya–Namioka monochromator [11] at room temperature. The beam flux at the sample position was about  $10^{10}$  photons/s around 200 nm with 0.1 mm slit. To obtain transmission spectra, the Seya–Namioka monochromator was used to select the excitation wavelength and the transmitted signal was detected by a photo multiplier. These apparatuses were aligned collinearly

and were placed in a chamber that is evacuated to better than  $1 \times 10^{-9}$  Torr by an ion pump.

Fig. 1 indicates the transmission spectrum of various fluoride samples. In this experiment, 1% transmission point was defined as the transmission edge, because the 1% transmission is dark enough to use these materials for not only a laser crystal but also a practical window in the UV and the VUV region. The transmission edge of LiCAF and LiSAF were located at 112 and 116 nm, respectively. In particular, the transmission edge of LiCAF is very close to that of LiF reported in Ref. [9]. The difference of the transmission edge between LiCAF and LiSAF may be due to the solarization free nature of LiCAF. The absorption dip at around 130 nm in the LiCAF and the LiSAF transmission spectra might be attributed to the color center or impurity. Therefore, after improving the crystal quality, this absorption should be disappeared. Certainly LiF is a good window material because it has wide transmission wavelength down to about 110 nm. However, in the UV and the VUV region, the problems of the commonly used optical materials such as LiF are the limitation of transmission wavelength, the solarization of the material with irradiation of high power UV light, and the difficulty of material

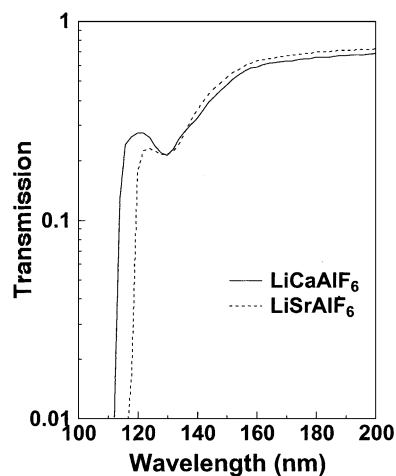


Fig. 1. Transmission characteristics of LiCAF and LiSAF at room temperature. The transmission edge of LiCAF and LiSAF are 112, 116 nm, respectively. The definition of the transmission edge is written in the text.

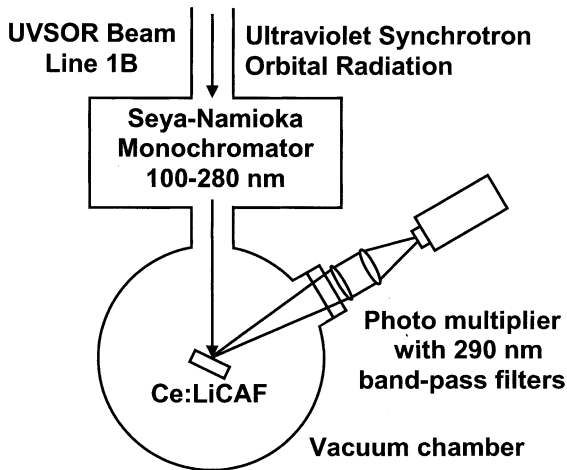


Fig. 2. The experimental setup for observation of excitation channel.

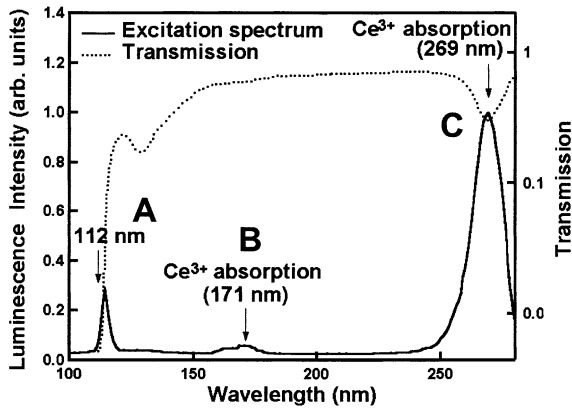


Fig. 3. The excitation spectrum and transmission curve for the Ce:LiCAF crystal. The transmission edge 112 nm corresponded to the peak of excitation spectrum.

processing and polishing due to the cleavage and the hydroscopic nature. LiCAF does not have cleavage or hydroscopic characteristics [12]. Therefore, LiCAF is regarded as a suitable optical material for UV and VUV region. Although further spectroscopic experiments are indispensable, the transmission edge of LiCAF (112 nm) is very remarkable. This material will be more important for the next generation lithographic

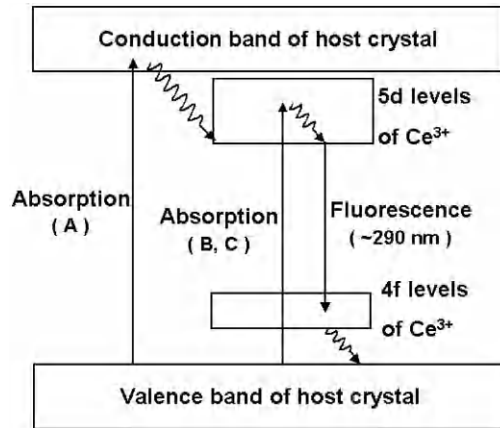


Fig. 4. Schematic of energy levels and possible decay channel in Ce:LiCAF crystal.

technology [13]. For confirming the large bandgap, the excitation characteristics of LiCAF with  $\text{Ce}^{3+}$  ion doping crystal were measured using the same apparatus as shown in Fig. 2. It was already known that the luminescence spectrum of Ce:LiCAF is around 290 nm. Therefore, the excitation characteristics of Ce:LiCAF was examined by detecting fluorescence emission with photo multiplier through 290 nm band-pass filter as shown in Fig. 3.

### 3. Results and discussion

The two peaks in the excitation spectrum corresponded to the absorption of  $\text{Ce}^{3+}$  ions. Moreover, new excitation channel at around 112 nm was found. Fig. 4 shows schematic of energy levels and possible decay channel in Ce:LiCAF crystal. The transmission edge of the crystal is known to be about 112 nm. That completely coincided with the peak of excitation spectrum. Therefore, this excitation can be considered as electron transfer from host crystal to the active  $\text{Ce}^{3+}$  ions. This experiment shows that such excitation spectrum measurement of  $\text{Ce}^{3+}$  ions will also be useful for the spectroscopy or bandgap estimation of the host crystal itself.

#### 4. Summary

In conclusion, we have presented transmission spectra of LiCAF and LiSAF by using synchrotron radiation. The transmission edge of LiCAF and LiSAF are, respectively, 112 and 116 nm were found, respectively. Compared with LiF, LiCAF is an ideal optical material in the UV and the VUV region because of the non-hygroscopic nature and the better mechanical processing properties. Additionally new excitation channel of  $Ce^{3+}$  ions through LiCAF host crystal was discovered. It is interesting that this excitation channel indicates the bandgap of the crystal. This excitation channel will be used as a potential pumping channel including electron-beam pumping or VUV pumping. For future scaling of high power Ce:LiCAF lasers [14,15].

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