Control of mean ionic radius at Ca site by Sr co-doping for Ce doped LiCaAlF₆ single crystals and the effects on optical and scintillation properties

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Abstract

Sr co-doped Ce:LiCaAlF₆ [Ce:Li(Ca,Sr)AlF₆] crystals with various Ca/Sr ratios were grown by a micro-pulling-down (μ -PD) method and effects of Sr co-doping on crystal structure, chemical composition, optical and scintillation properties for Ce:LiCaAlF₆ crystals were investigated as a neutron scintillator. High transparent Ce2%:Li(Ca,Sr)AlF₆ crystals with 2% and 5% Sr contents were obtained while Ce2%:Li(Ca,Sr)AlF₆ crystals with 10% and 20% Sr contents included milky parts in the crystals. *a*- and *c*-axis lengths of Ce:Li(Ca,Sr)AlF₆ phase systematically increased with an increase of Sr content. In addition to the emission at 284 and 308 nm from Ce³⁺ ion, emission peaks at 367 nm appeared by Sr co-doping.

Keywords : Scintillator; Crystal; LiCaAlF₆; Neutron

1. Introduction

Worldwide increase of ³He gas demand for some neutron detectors triggered energetic investigations of neutron scintillators [1-5]. Among these researches, we have developed Rare-Earth (RE) doped LiCaAlF₆ [RE:LiCaAlF₆] and LiSrAlF₆ [RE:LiSrAlF₆] scintillator crystals with the colquiriite structure [6-10]. Especially, Ce doped LiCaAlF₆ and LiSrAlF₆ crystals are one of the most expected alternatives for ³He gas due to some advantages compared to other materials. The advantages are described as follows. LiCaAlF₆ and LiSrAlF₆ crystals include ⁶Li elements with high cross-section to thermal neutron and Ce³⁺ ions in the Ce:LiCaAlF₆ and Ce:LiSrAlF₆ crystals emit photons by irradiation of α -ray which is generated by the reaction between ⁶Li and neutron. In addition, the crystals are composed of the elements with low atomic number and the densities are relatively low. This feature is important for decreasing the influence by γ -ray as a noise source. From the commercial aspect, the LiCaAlF₆ and LiSrAlF₆ are congruent composition and their bulk single crystals with a diameter of 1 ~ 3 inches can be grown from the melt by the Czochralski method [11]. Especially, Ce:LiCaAlF₆ and Ce:LiSrAlF₆ crystals indicates relatively fast decay time compared to other neutron scintillators [10,12]. However, their light yields are not sufficient compared to other alternatives and therefore we have tried to improve their light yield.

In this paper, Sr co-doped LiCaAlF₆ [Li(Ca,Sr)AlF₆] and Ce:LiCaAlF₆ [Ce:Li(Ca,Sr)AlF₆] single crystals were grown and the effects of Sr co-doping on the structure, chemical composition, optical and scintillation properties were investigated. Ce³⁺ ions are considered to substitute the Ca²⁺ site in LiCaAlF₆ and Sr²⁺ site in LiSrAlF₆ crystals. However, the ionic radius of Ca²⁺ ion (1.00 Å, CN:6) is smaller than that of Ce³⁺ ion (1.034 Å, CN:6). On the other hand, the ionic radius of Sr²⁺ ion (1.16 Å, CN:6) is larger than that of Ce³⁺ ion. Therefore, the substitution of Ce³⁺ ion on the Ca site in LiCaAlF₆ can be affected by Sr co-doping to LiCaAlF₆ crystal.

2. Experimental

2.1 Crystal growth

Sr co-doped LiCaAlF₆ and Ce:LiCaAlF₆ crystals were grown by a micro-pulling-down (μ -PD) method with a vacuum-tight chamber and a diffusion pump. Starting materials, ⁶Li-enriched LiF (⁶LiF 95%), CaF₂, SrF₂, AlF₃ and CeF₃ (> 4N purity), were mixed as nominal compositions, Li(Ca_{1-x-y}Sr_xCe_y)AlF₆ with $x = 0.02, 0.05, 0.1, 0.2$ and $y = 0.02$. Mixed powders were set in a carbon crucible with a $\phi 2$ mm hole at the bottom and the crucible was placed in the

center of the chamber. A carbon insulator and high-frequency induction coil surrounded the crucible. Inside of the chamber was vacuumed up to 10^{-4} Pa by the diffusion pump and the crucible was heated at approximately 300°C by the high-frequency induction coil during the vacuuming to remove moisture on the surface of mixed powders, crucible, insulator and equipment. After the baking process, high-purity Ar gas was introduced in the chamber and crystal growth was performed in Ar using Pt wire as a seed. Growth rate was 0.1 mm/min. Finally, as-grown crystal was obtained after cooling of grown crystal for 2 hours.

2.2 Crystal structure and crystallinity, chemical composition

Powder X-ray diffractions of grown crystals were investigated to identify their phases and calculate their lattice parameters of the phases. In the measurements of lattice parameters, Ti powder was used as an internal standard. Crystallinity of the grown crystal was evaluated by the X-ray rocking curve (XRC) using in-plane X-ray diffractometer. ω scan was investigated for the reflection of (1 1 4) from the grown crystals. **Chemical compositions of grown crystals were measured by Energy Dispersive X-ray Spectroscopy (EDX). Actual Sr concentrations in the grown crystals were almost same as nominal compositions.**

2.3 Optical and scintillation properties

The transmittance spectra of the polished specimens with 1 mm thickness were measured by spectrophotometer (JASCO V530) in the wavelength region ranged from 190 to 900 nm. The emission spectra and the decay curves of the crystals under ultraviolet excitation were measured under ultraviolet excitation using spectrofluorometer (EDINBURGH INSTRUMENTS FLS920). The pulse-height spectra and the decay time of the crystals under neutron irradiation were evaluated based on the response detected from the polished specimens exposed to a source of ^{252}Cf emitting neutron with photomultiplier tube (PMT) HAMAMATSU R7600U and lead blocks. The polished specimens covered with the Teflon tape were attached to the light entrance window of the PMT with optical grease. The signal passed through the shaping amplifier (ORTEC 570) and then converted to the digital signals by a multi-channel analyzer (AMPTEK CO. Pocket MCA 8000A).

3. Results and Discussions

3.1 Crystal growth

$\text{Ce}2\%:\text{Li}(\text{Ca},\text{Sr})\text{AlF}_6$ crystals were grown by the μ -PD method and fiber crystals approximately 2 mm in diameter and several centimeters in length were obtained. As-grown and polished $\text{Ce}:\text{Li}(\text{Ca},\text{Sr})\text{AlF}_6$ crystals are shown in Fig.1. As-grown $\text{Ce}:\text{LiCaSrF}_6$ crystals with Sr2% content indicated high transparency and there were no visible crack and inclusion in

the crystals. In addition, inside of the Ce2%Sr5%:LiCaAlF₆ crystal was transparency while the surface of as-grown crystal was opaque. In contrast, milky parts were observed in the Ce:Li(Ca,Sr)AlF₆ crystals with 10% and 20%Sr contents. In particular, milky parts in the crystals increased with an increase of Sr contents.

3.2 Crystal structure and Chemical composition

Figure 2(a) is the powder XRD patterns of Ce:Li(Ca,Sr)AlF₆ crystals. All diffraction peaks in the XRD patterns could be identified by the colquiriite structure [13]. However, the diffraction peaks from secondary phases were not observed due to the small amounts of impurity phases below detection limit of powder XRD measurement. The positions of diffraction peaks from Ce:Li(Ca,Sr)AlF₆ phase systematically increased with an increase of Sr content and the result suggests that their lattice parameters varied by the Sr content. Therefore, lattice parameters, *a*- and *c*-axis lengths, of the Li(Ca,Sr)AlF₆ crystals were calculated from the XRD patterns as it is illustrated in Fig.2(b). *a*- and *c*-axis lengths systematically increased with an increase of Sr content. This result suggests that the Ca sites in LiCaAlF crystals were substituted by the Sr ions with larger ionic radius than Ca²⁺ ion.

Crystallinity of Ce2%Sr2%:LiCaAlF₆ crystal was evaluated by the XRC as it is illustrated in Fig.3. Single peak from (1 1 4) was observed in the measurement. However, the shoulder appeared on the side of the peak and the full width of half maximum (FWHM) on the peak was larger than that of Ce:LiCaAlF₆ crystal without Sr co-doping. The result suggests that the Sr co-doping introduced some lattice distortions in the Ce:LiCaAlF₆ crystal.

3.3 Optical properties

The transmittance spectra of the polished Ce:Li(Ca,Sr)AlF₆ crystals were measured in the wavelength range from 200 nm to 900 nm (Fig.4(a)). Absorption peaks around 270 nm which originated from 4f-5d transition of Ce³⁺ ion were observed for all crystals. Transmittances above 300 nm for Ce2%Sr10% and Ce2%Sr20%:LiCaAlF₆ crystals decreased compared to the Ce2%Sr5%:LiCaAlF₆ crystal and the result is considered to be due to the generation of milky parts.

Photoluminescence spectra of Ce:Li(Ca,Sr)AlF₆ crystals under 270 nm excitation are shown in Fig.4(b). All crystals indicated emission peaks at 284 and 308 nm which originated from 5d-4f transition of Ce³⁺ ion. In addition, emission peaks around 367 nm were also observed for all crystals while there is no peak around the wavelength in the Ce:LiCaAlF₆ crystals without Sr co-doping [14]. The relative intensity of additional emission peak at 367 nm for Ce2%Sr10%:LiCaAlF₆ crystal indicated the maximum. The result suggests that Sr co-doping generated the additional energy level which contributed to the emission around 367 nm.

3.4 Scintillation properties

Pulse-height spectra of Ce:Li(Ca,Sr)AlF₆ crystals under α -ray irradiation from ²⁴¹Am radiation source are shown in Fig.5(a). All crystals indicated alpha-peaks in the pulse-height spectra. The positions of the alpha-peaks slightly decreased with an increase of Sr content. The results are considered to be attributable to the decrease of transmittance by Sr co-doping.

4. Conclusions

We grew Sr co-doped Ce:LiCaAlF₆ crystals by the μ -PD method and investigated their structures, crystallinity, optical and scintillation properties. Ce2%:Li(Ca,Sr)AlF₆ crystals with Sr 2%, 5%, 10% and 20% concentrations were obtained and Ce2%Sr2% and Ce2%Sr5%:Li(Ca,Sr)AlF₆ crystals indicated high transparency while Ce2%Sr10% and Ce2%Sr20%:Li(Ca,Sr)AlF₆ crystals included milky parts in the crystals. Lattice parameters of the grown crystals systematically increased with an increase of Sr content. On the other hand, transmittance decreased with an increase of Sr content due to the generation of milky parts. In the photoluminescence spectra, all crystals indicated emission peaks at 284 and 308 nm which originated from 5d-4f transition of Ce³⁺ ion. In addition, emission peaks around 367 nm were also observed and the emission are considered to be due to the generation of additional energy level by Sr co-doping. The positions of the alpha-peaks in the pulse-height spectra slightly decreased with an increase of Sr content. Ce2%Sr10% and Ce2%Sr20%:LiCaSrAlF₆ crystals indicated stronger additional emission at 367 nm than Ce2%5%:LiCaSrAlF₆ crystal and their light yields are expected to be improved by an increase of transmittance.

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Figure Captions

Figure 1 (a) $\text{Li}(\text{Ca},\text{Sr})\text{AlF}_6$ and (b) $\text{Ce}:\text{Li}(\text{Ca},\text{Sr})\text{AlF}_6$ crystals grown by the μ -PD method.

Figure 2 (a) Powder XRD patterns and (b) lattice parameters of $\text{Li}(\text{Ca},\text{Sr})\text{AlF}_6$ crystals.

Figure 3 (a) Transmittance spectra of $\text{Ce}:\text{Li}(\text{Ca},\text{Sr})\text{AlF}_6$ crystals. (b) BSE images of $\text{Ce}:\text{Li}(\text{Ca},\text{Sr})\text{AlF}_6$ crystals.

Figure 4 (a) Transmittance and (b) Photoluminescence spectra of $\text{Ce}:\text{Li}(\text{Ca},\text{Sr})\text{AlF}_6$ crystals.

Figure 5 Pulse-height spectra of $\text{Ce}:\text{Li}(\text{Ca},\text{Sr})\text{AlF}_6$ crystals under α -ray excitation.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5