Optical Materials 68 (2017) 70–74

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

# Growth and scintillation properties of Eu doped $LiSrI_3$/LiI eutectics

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ARTICLE INFO

*Article history:*
Received 3 October 2016
Received in revised form
25 April 2017
Accepted 4 May 2017
Available online 11 May 2017

*Keywords:*
Eutectic
Scintillator
Europium
Luminescence
$LiSrI_3$

ABSTRACT

Eu doped $LiSrI_3$/LiI eutectics were grown by the Bridgman method in a quartz ample with 4 mm inner diameter. and their directionally solidified eutectic system has been investigated. Growth rate was 0.3 mm/min. The eutectic showed well aligned eutectic structure and optically transparent. Grown Eu doped LiSrI3/LiI eutectic shows 400 nm emission ascribed to $Eu^{2+}$ 4f-5d transition under X-ray excitation. The light yield was around 26,000 photon/MeV for 662 keV gamma-ray and 35,000 photons for 5.5 MeV alpha-ray.



## 1. Introduction

Inorganic scintillators were widely used in radiation detection applications such medical imaging, security system, astrophysics, and well logging. Recently, scintillator for thermal neutron detection have been developed due to diminishing resources of $^3$He gas. Most famous thermal neutron detectors are the $^3$He gas counters now because of their high thermal neutron cross section and low background gamma-ray sensitivity. However, the demand for $^3$He gas counters have been rapidly increased and drying resource of $^3$He up because an use of neutron detectors for national security and oil logging applications increased. The research-and-development efforts in alternative neutron detection technology have been done [1,2]. This huge discrepancy between the demand and supply motivates us to develop novel thermal neutron scintillators which would replace the contemporary $^3$He based systems. In this decade, some novel single crystal scintillators for neutron detection have been reported. Among them, $LiCaAlF_6$ (LiCAF) and $Cs_2LiYCl_6$ (CLYC) based single crystal scintillator is the most promising candidate [3,4]. $LiCaAlF_6$ includes $^6$Li in the host lattice and have a function of the pulse shape discrimination between neutrons and gamma-rays. As it is single crystal, Li content is limited by the chemical formula and can't be increased. Thus, if we need higher neutron capture cross section, we have to find other way. As a candidate for novel neutron detectors, Eu activated LiF-$CaF_2$ eutectic scintillators were developed and their scintillation properties under $^{252}$Cf neutron exposure were examined [5,6]. The most important advantage of eutectic scintillators is higher Li content than that of conventional neutron single crystal scintillators such LiCAF and CLYC. Other higher Li content scintillators such Li-glass, Eu:LiI, LiF/ZnS are reported [7]. However, Li-glass and Eu:LiI showed lower light yield of 6000 and 15,000 photon/MeV than LiCAF or CLYC. LiF/ZnS is phosphor and not transparent. The interest in this study is not only to increase Li content but also the possible design for high resolution neutron imager using the directionally solidified eutectic (DSE) system coupled with high resolution photo detectors. Possibility of high resolution using DSE system is proposed by GAP-$Al_2O_3$ [8] and $SrHfO_3/Al_2O_3$ [9], $Gd_2Si_2O_7/SiO_2$ [10] system for X-ray CT application. Some eutectics containing Li are investigated for neutron detection system by LiF/$SrF_2$ [9], LiF/$CaF_2$ [10], LiF/$LiGdF_4$ [13] LiF/$CaF_2$/$LiBaF_3$ [14].

In order to find good combination of eutectic structure containing Li, choice of scintillator materials is important. Recently, Eu activated iodide scintillator such Eu:$SrI_2$ [15,16] has attracted attention due to high light yield over 70,000 photons/MeV and

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http://dx.doi.org/10.1016/j.optmat.2017.05.010
0925-3467/

decay time of ~1 μs. Most recently, Eu: $LiSr_2I_5$ single crystal scintillator is reported and it have high light yield of 60,000 photons/MeV [17]. In this study, Eu doped LiI/$LiSrI_3$ eutectics were fabricated by the Bridgeman (BZ) method. Eu was selected as emission center for $LiSrI_3$ matrix to obtain enough scintillation light and acceptable decay time around ~1 μs. Investigations of their crystal phase were performed. Luminescence and scintillation properties were also evaluated.

## 2. Experimental procedure

### 2.1. Crystal growth

The starting powders (4N) of LiI, $SrI_2$ and $EuI_2$. was weighed and mixed according to the eutectic composition were $EuI_2$:LiI:$SrI_2$ = 0.25:50:24.75. Crystal growth was performed by the BZ method in a quartz ample with 4 mm inner diameter. The detail of crystal growth by the BZ method was described in Fig. 1. In the unidirectional solidification processes, $LiSrI_3$ and LiI phases deposit from the melt on their own formed solid phases. Mixed powders were set in the quartz ample in 9N purity Ar gas after baking process at 250 °C under high vacuum (~$10^{-5}$ Pa) to eliminate water and oxygen. The ample was heated by a platinum heater with the high-frequency induction coil after sealed cutting. The ample was pulled down at seed of 0.3 mm/min. Mirror polished circular samples with 1-mm thickness were obtained from the grown eutectic for BEI investigation, luminescence and scintillation properties measurements.

### 2.2. Structural evaluation of eutectic composites

Circular and rectangular samples and with 1 mm thickness were obtained from the grown crystal. The cut surface was optically polished and the eutectic phase structure was observed by back scattered electron image (BEI) using Hitachi S3400N. The eutectic structures on transverse and vertical cross-section were observed. The obtained phases in the eutectics were investigated by X-ray radiation (XRD) using RIGAKU RINT-2000.

### 2.3. Measurements of luminescence properties and scintillation properties

Photoluminescence properties were investigated by a spectrometer (Edinburgh FLS920) using optical source (Edinburgh Xe 900). At the SR-163 spectrometer (ANDOR TECHNOLOGY) equipped with the CCD detector DU920P (ANDOR TECHNOLOGY) the radioluminescence spectra were measured under an α-ray from a $^{241}Am$ source. Light output measurements were performed by using photomultiplier tube (PMT Hamamatsu R7600U-200). The samples were coupled by the PMT using silicone grease (OKEN, 6262A). To determine the light yield, the energy spectra were collected under γ-ray and α−ray excitation by using a PMT (Hamamatsu H7600, bialkali photocathode, quartz window). The signal was fed into a shaping amplifier (ORTEC 572A), a multichannel analyzer (MCA) (ORTEC 926), and finally to a personal computer. The shaping time was set as 10 μs. The bias for the PMT was supplied by an ORTEC 556. For the decay time measurement the same setup with the PMT and digital oscilloscope TD5032B were used.

## 3. Results and discussion

Eu doped LiI/$LiSrI_3$eutectic were prepared by the BZ method. White rod with 4 mm diameter and 20 mm length was obtained by the BZ method. As grown eutectic and 1 mm thick plate after polishing were shown in Fig. 2. The $LiSrI_3$/LiI eutectic samples also showed optical transparency like bundle optical fibers and the background images are visible on the surface through the transparent rods grown in the material. Results of powder XRD of the grown eutectic with a $LiSrI_3$ crystal reference are shown in Fig. 3. The grown eutectic showed mixture of tricrynic $LiSrI_3$ phase and cubic LiI phases with trace of hydroxyl Iodide coming from hygroscopic characteristic of LiI and $LiSrI_3$ during the crushing. The BEI of the grown crystals in vertical and transverse cross-section are shown in Fig. 4. The grown eutectic structure showed mixture of rods and plates shape of LiI phase surrounded by $LiSrI_3$ matrix. The average rod size was about 3.6 μm in Fig. 5-b and the fiber density was about 16,800 fibers/$mm^2$. This mixed structure of LiI was aligned with length of around 50 μm. Up to now, some groups investigated transformation between rod-like shape and lamellar shape in eutectic structure [18–21]. They conclude that

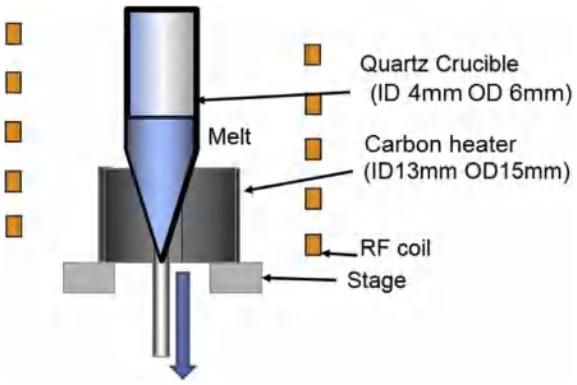


**Fig. 1.** Schematic of the arrangement for growth of the eutectic scintillator.

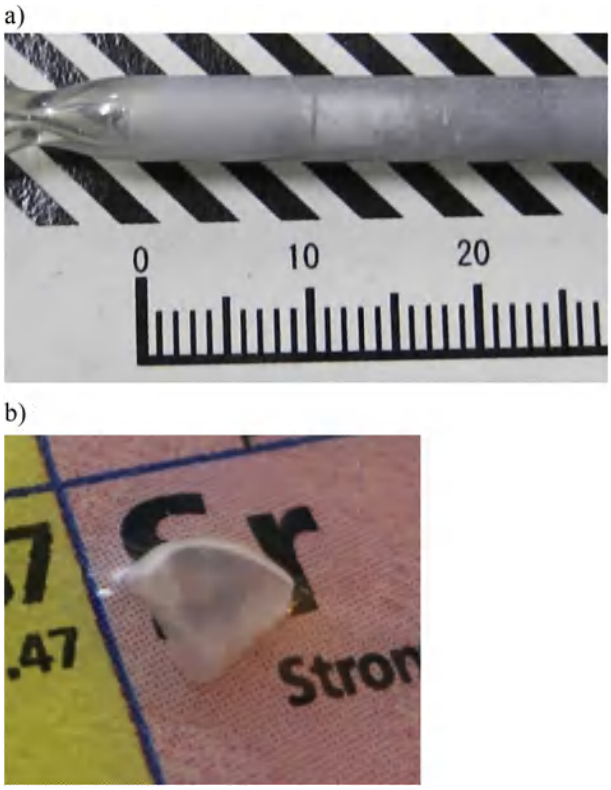


**Fig. 2.** Photograph of the a) as grown Eu LiI/$LiSrI_3$ eutectic and b) polished sample.

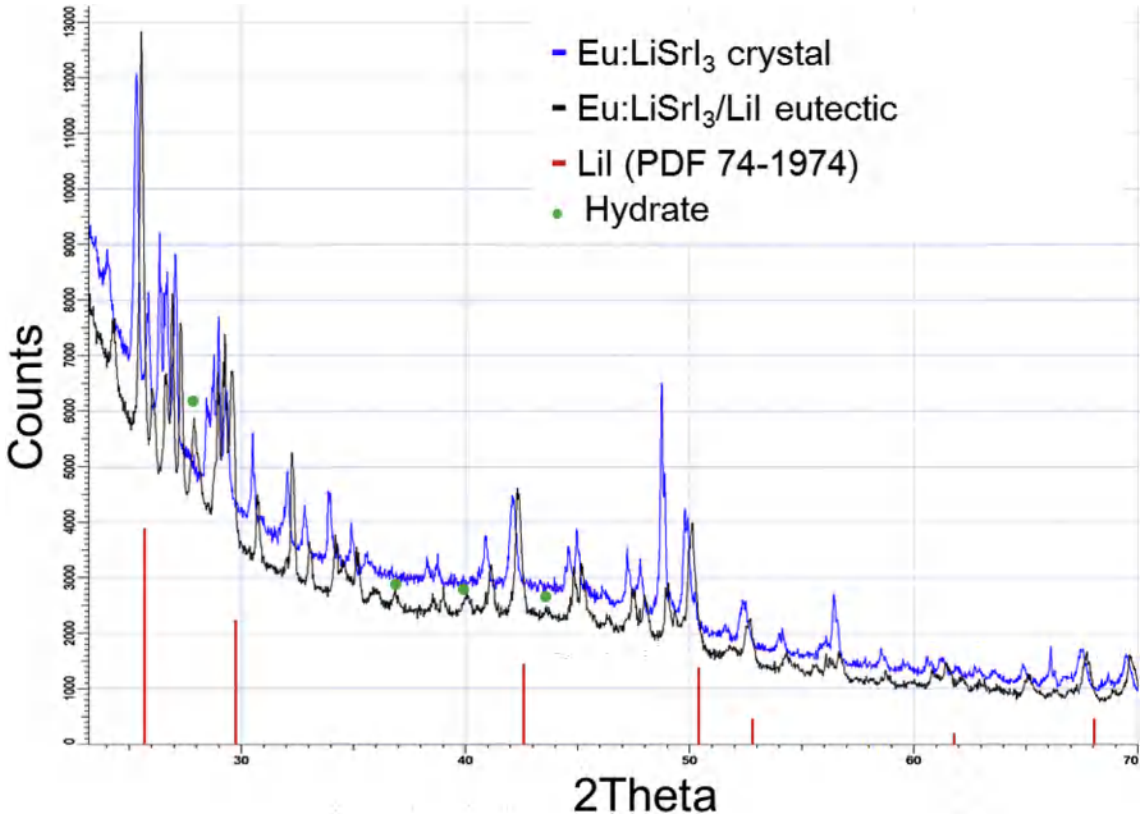


**Fig. 3.** Powder X-ray diffraction pattern for the LiI/$LiSrI_3$ eutectic and $LiSrI_3$ crystal reference.

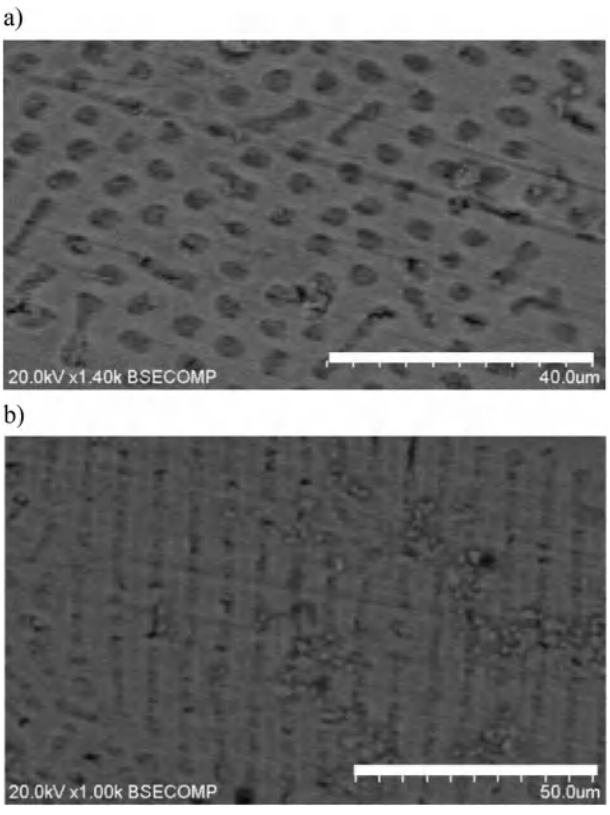


**Fig. 4.** BEI of the polished LiI/$LiSrI_3$ eutectic a) transverse cross-section and b) vertical cross-section along growth direction.

transformation of the eutectic depended on the volume ratio of components and the relative interface energy. Rod-like shape can be obtained at volume ratio around 30–40% [22]. Density of $LiSrI_3$ was not reported and it is difficult to measure because of its hygroscopisity. It is thought that volume ratio of LiI:$LiSrI_3$ in this system is in 30–40% range.

### 3.1. Luminescence and scintillation properties

Emission and excitation spectra of the grown Eu doped LiI/$LiSrI_3$ eutectic were measured in reflection mode at 360 nm excitation

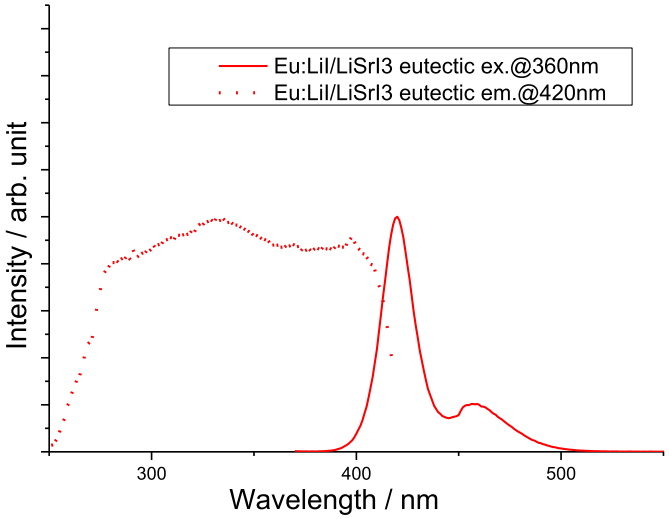


**Fig. 5.** Emission and excitation spectra of the grown Eu doped LiI/$LiSrI_3$ eutectic.

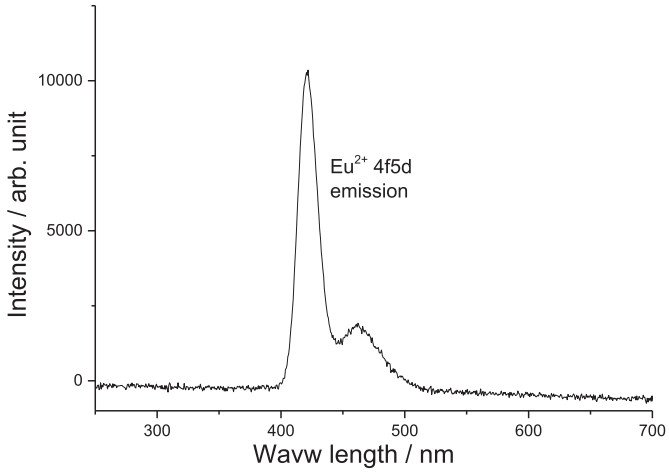


**Fig. 6.** Radioluminescence spectra of the grown Eu doped LiI/$LiSrI_3$ eutectic measured under an α-ray from a $^{241}$Am source.

excitation of $Eu^{2+}$ 4f5d transition similar to the Eu:$SrI_2$ [15,16] have been observed. Small stokes shift of around 20 nm (400–420 nm) was observed. The Pulse height spectra of the eutectic sample excited by 662 keV gamma-ray of $^{137}$Cs at room temperature and measured using the PMT are shown in Fig. 7. Light outputs of the sample was around 26,000 photon/MeV and 80% of the commercially available LYSO standard with 34,000 photon/MeV. The Pulse height spectra of the Eu:$LiSrI_3$ excited by 5.5 MeV alpha-ray of $^{241}$Am was also obtained to simulate $^{6}$Li(n,a)$^{3}$H reaction as a thermal neutron scintillator. Light output was around 35,000 photon/5.5 MeV alpha-ray. The scintillation decay curves of the sample excited by 662 keV gamma-ray are shown in Fig. 8. Scintillation decay time was 510 ns and obtained decay time was comparable value for other $Eu^{2+}$ doped scintillators [11,12,14–16].

## 4. Conclusion

Eu doped $LiSrI_3$/LiI eutectics were grown by the BZ method in a quartz ample with 4 mm inner diameter. The eutectic showed well aligned eutectic structure and optically transparent. Grown eutectic shows 420 nm emission ascribed to $Eu^{2+}$ 4f-5d transition under alpha-ray excitation. The light yield was around 80% of Ce: LYSO standard and 34,000 photon/MeV. Scintillation decay time under 662 keV ramma-ray was 510 ns We are planning to grow Eu doped $LiSrI_3$/LiI eutectics using $^{6}$LiI as the starting material and evaluate neutron response.

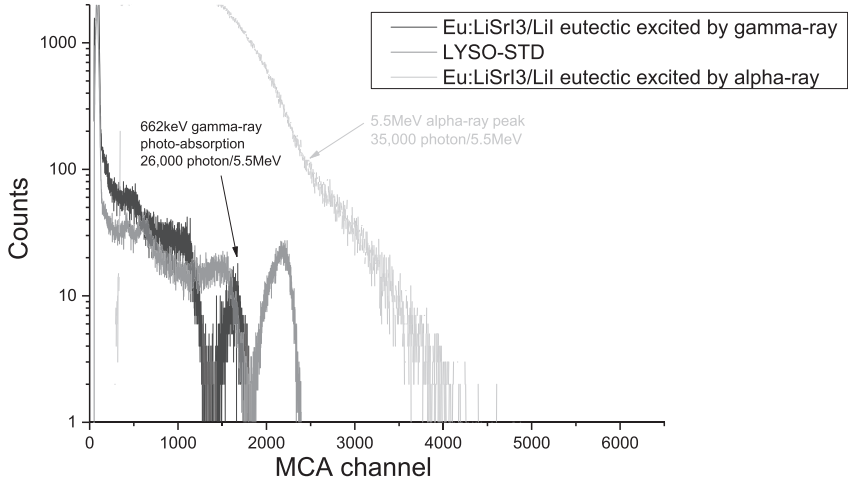


**Fig. 7.** Energy spectra of the eutectic sample and LYSO standard. Excitation by $^{137}$Cs radioisotope (662 keV gamma-ray) and $^{241}$Am (5.5 MeV alpha-ray).

and 420 nm emission, respectively (Fig. 5). Radioluminescence spectra of the grown eutectic measured under α-ray irradiation was shown in Fig. 6. The expected 420 nm emission and 280–400 nm

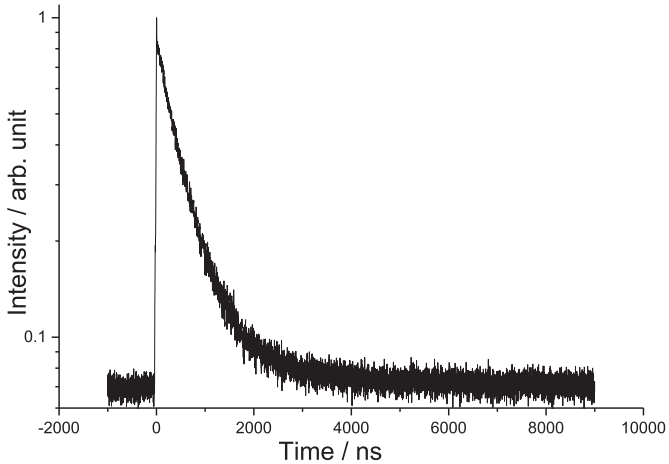


**Fig. 8.** Scintillation decay curves of the of the eutectic sample. Excitation by $^{137}$Cs radioisotope (662 keV).

## Acknowledgement

This work is partially supported by 16H05986, Grant-in-Aid for Young Scientists(A), Japan Society for the Promotion of Science. In addition, we would like to thank following persons for their support: Mr. Yoshihiro Nakamura in Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University and Mr. Hiroshi Uemura, Ms. Keiko Toguchi and Ms. Megumi Sasaki, Ms. Yuka Takeda in IMR.

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