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Scintillation properties of LiF–SrF_2 and LiF–CaF_2 eutectic

Takayuki Yanagida [a,*], Noriaki Kawaguchi [b], Yutaka Fujimoto [a], Kentaro Fukuda [b], Kenichi Watanabe [c], Atsushi Yamazaki [c], Akira Uritani [c]

[a] Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu-ku, Kitakyushu 808-0196, Japan
[b] Tokuyama Corporation, 1-1 Mikage-cho, Shunan-shi, Yamaguchi 745-8648, Japan
[c] Quantum Science and Energy Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

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ABSTRACT

Dopant free eutectic scintillators ^{6}LiF–SrF_2 and ^{6}LiF–CaF_2 were developed by the vertical Bridgeman method for the purpose of thermal neutron detection. The molar ratio of LiF and Ca/SrF_2 was 4:1 on its eutectic composition. The α-ray induced radioluminescence spectra of the scintillators showed intense emission peak at 300 nm due to the emission from the self-trapped exciton in Ca/SrF_2 layers. When the samples were irradiated with ^{252}Cf neutrons, ^{6}LiF–SrF_2 and ^{6}LiF–CaF_2 exhibited the light yields of 4700 and 9400 ph/n, respectively. Scintillation decay times of ^{6}LiF–SrF_2 and ^{6}LiF–CaF_2 were accepted for scintillation detectors, 90 and 250 ns, respectively.

1. Introduction

Scintillation detectors, which convert a single photon (X- and γ-ray) or other high-energy particles (charged particles and neutrons) into hundreds of visible–ultraviolet photons [1], have been playing a major role in many fields of radiation detection, including medical imaging [2], security [3], astrophysics [4], particle physics [5] and well logging [6]. In these applications, scintillators for thermal neutron detection have recently attracted much attention because of deficit of ^{3}He gas [7,8]. Up to now, most of the thermal neutron detectors were ^{3}He gas proportional counters, because ^{3}He has high cross section to thermal neutrons and low background γ-ray sensitivity [9]. The natural abundance of ^{3}He is approximately 10^{-6} to ^{4}He, and it can be generated by the decay of tritium which is no longer generated by nuclear experiments. The huge disproportion between the demand and the supply of the ^{3}He gas highly motivates academia and industry to develop novel inorganic scintillators suitable for the thermal neutron detectors to replace existing ^{3}He based systems.

One of the candidates for such application is ^{6}Li containing material, because ^{6}Li has a high probability (940 barn at 25 meV) of interaction with neutrons based on ^{6}Li(n, α)^{3}H reaction with high Q-value of 4.8 MeV [10]. In the recent past, ^{6}Li based scintillators, including Ce^{3+} and Eu^{2+} doped ^{6}LiCaAlF$_6$ were developed, and they demonstrated acceptable scintillation responses under ^{252}Cf neutron irradiation [11–15]. Elpasolite scintillators which have a chemical composition of A_2LiMX_6:Ce (A==Cs, Rb; M==Y, La, Sc; X==Cl, Br, I) have been also studied extensively recently [16–18]. Although elpasolites show good scintillation efficiency, huge hygroscopicity is a big problem for practical applications.

In addition to LiCaAlF$_6$ and elpasolite scintillators, ^{6}Li-based eutectics are now considered as appropriate materials for neutron detectors. LiF-containing eutectics are examples of such materials, and LiF–CaF_2 eutectic composite doped with Mn was first proposed for dosimeter applications [19]. Then, Eu-doped LiF–CaF_2 was recently studied for neutron scintillator [20]. Following these reports, evaluation of the neutron responses of ^{6}LiF–CaF_2:Eu [21] and ^{6}LiF–SrF_2:Eu [22] with different Eu concentrations was also performed. This eutectic system is especially promising, because molar ratio at the eutectic composition is 81.5:18.5 [23] that results nearly identical volumetric fraction of 56:44. Compared to conventional neutron scintillators, such as Li-glass [24], single crystal Eu:LiI [25], and LiF–ZnS powder sintered ceramic [26], the macroscopic cross section to thermal neutrons of the above eutectics is considerably high (see Fig. 1 in Ref. [20]). In addition, low sensitivity to background γ-rays due to low density is another advantage of this system.

In the present work, non-doped LiF–CaF_2 and LiF–SrF_2 eutectic scintillators are fabricated and evaluated on their scintillation responses. Unlike other eutectics scintillators, our aim is to examine dopant-free neutron scintillators. Although most of scintillators use rare earth elements as the emission center, the price of rare earth elements increases and the suppression of the usage amount of rare

* Corresponding author. Tel./fax: +81 93 695 6049.
E-mail address: yanagida@lsse.kyutech.ac.jp (T. Yanagida).

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earth is highly required. In addition, dopant-free materials are free from non-uniformity of emission properties in bulk form because the dopant segregation cannot be avoided in the melt growth. Generally, manufacturers pay their effort to fabricate uniform materials and such dopant-free scintillators are ideal for mass production. Through this study, optical transmittance, α-ray and X-ray induced radio luminescence, neutron induced light yield, and scintillation decay lifetimes under neutron and X-ray excitation were systematically studied.

2. Experimental procedure

High-purity (99.99%) fluoride powders of ^{6}LiF (95% enriched), CaF_2, and SrF_2, (Stella Chemifa Corporation) were used as starting materials. The LiF and Ca/SrF_2 powders were mixed in 80:20 M ratio that correspond to the eutectic composition. The mixtures were put into graphite crucibles, and the micro-Bridgman method [27] was used to produce LiF–CaF_2 and LiF–SrF_2 eutectics. The crucibles were set in the stainless chamber and enclosed by the carbon resist heater. Most parts of hot zone were made of high purity carbon. After the setting of crucibles and hot zone, the chamber was evacuated up to 10^{-4} Torr. Then, the crucible was heated up to 400 °C and kept for about 8 h at this temperature in order to remove water and oxygen traces. After the baking, the chamber was filled with high purity Ar gas (99.999%) and CF_4 gas (99.999%) until ambient pressure. The ratio of Ar and CF_4 was 9:1. Then, the crucible was heated up to 800 °C and kept for 30 min. Finally, the furnace was cooled to the room temperature with a cooling rate of 5 °C/min. After the fabrication of eutectics, they were cut and polished to the sizes of $1\times2-4\times8$ mm^3 to investigate optical and scintillation properties. Backscattered electron images were observed by using scanning electron microscope (SEM) to observe lamellar structures.

Transmittance spectra were recorded by using JASCO V670 spectrometer. If undesirable impurities are contaminated, sharp (due to rare earth) or broad (due to transitional metal) absorption bands will be observed. In addition, if the water is contaminated, absorption bands around 2700 nm will appear. Practically, the scintillators are excited by the neutron irradiation with charged particles produced from the ^{6}Li(n,α)^{3}H nuclear reaction. To simulate this process in laboratory conditions, the ^{241}Am 5.5 MeV α-ray induced radio luminescence spectra were recorded using JASCO FP8600 fluorescence spectrometer at room temperature. The main purpose of the radio luminescence measurements was to detect emission wavelength under α-ray excitation. Because the emission intensity of this kind of integrated type measurement is not a quantitative value, we cannot discuss the light yield of scintillators by radio luminescence intensities. The detailed description and geometry of the α-ray induced radio luminescence measurements were reported previously [28]. Then, X-ray-induced radioluminescence spectra were also measured to be compared with the α-ray-excited ones. The excitation source was our original instrument fabricated by OURSTEX Corporation. The X-ray tube (W target) was supplied with 70 kV and 1 mA. The emission spectra were recorded using Andor DU-420-BU2 CCD spectrometer. Its CCD-based detector (cooled down to 188 K by a Peltier module) was coupled with a monochromator SR163 (Andor, 1200 grooves/mm, 300 nm blaze wavelength). The geometry of the set-up was described previously [29].

In order to evaluate neutron induced absolute light yield, the pulse height measurements were performed. The eutectic samples wrapped with several layers of Teflon tape to collect scintillation photons were coupled with photomultiplier tube (PMT) R7600-200 produced by Hamamatsu with optical grease (OKEN 6262A). The high voltage of −700 V was supplied (ORTEC 556), and the signals were read out from the anode of the PMT. The neutron source of ^{252}Cf was enclosed in a polyethylene container of 43 mm thickness for thermalization of fast neutrons. In order to cut the background γ-rays, the samples were surrounded by 5 cm thick Pb blocks. Once a neutron from the ^{252}Cf was detected, the signals were fed into the pre-amplifier (ORTEC 113) and then to the shaping amplifier (ORTEC 572) with 2 μs shaping time. After converting to digital signals by a multi channel analyzer (Amptek, Pocket MCA 8000A), they were recorded to a computer. To evaluate the absolute light yield, Li glass scintillator GS20 (7200 ph/n [24]) was used as a standard.

Neutron induced decay lifetime profiles were recorded by TDS3052C digital oscilloscope (500 MHz and 5 Gs/s, Tektronix). As same as the radioluminescense spectra, decay time profiles under X-ray excitation were investigated by pulse X-ray streak camera system [30–31]. Because scintillation decay times under high energy photon (X- and γ-rays) and charged particles sometimes differ due to the difference of the excitation density, to compare neutron and X-ray induced decay times is important.

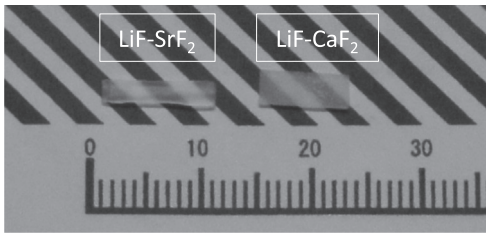

Fig. 1. Photograph of LiF–SrF_2 (left) and LiF–CaF_2 (right).

3. Results and discussion

The cut and polished LiF–CaF_2 and LiF–SrF_2 eutectic specimens had typical dimensions of $1\times2-4\times8$ mm^3. Fig. 1 illustrates view of the specimens ready for the characterizations. Their appearances looked semi-transparent due to the eutectic structure.

To observe details of the lamellar structure of the eutectic, the microscopic images were taken using SEM. Fig. 2 demonstrates such images made for LiF–CaF_2 and LiF–SrF_2. Bright fractions of the

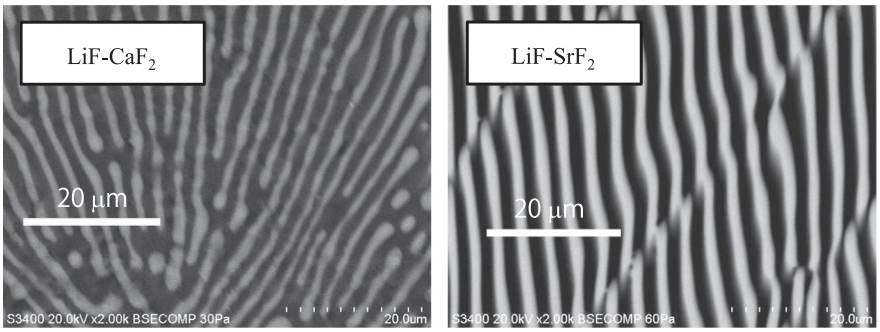

Fig. 2. SEM images of LiF–CaF_2 (left) and LiF–SrF_2 (right).