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Luminescence properties of Nd^{3+} doped $LiLuF_4$ single crystals with different dopant concentrations

Akihiro Yamaji [a,*], Yutaka Fujimoto [a], Takayuki Yanagida [b], Noriaki Kawaguchi [c], Kentaro Fukuda [c], Yuui Yokota [a], Akira Yoshikawa [a]

[a] IMR, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
[b] NICHe, Tohoku University, 6-6-10 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
[c] Tokuyama Corporation, Shibuya 3-chome, Shibuya, Tokyo 150-8383, Japan

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ABSTRACT

Nd-doped $LuLiF_4$ single crystalline scintillators with different Nd concentrations of 1%, 2%, 3%, and 4% were grown by the micro-pulling-down (μ-PD) method and that of Nd 1% were grown by the Czochralski method. There are some absorption bands due to Nd^{3+} 4f–4f transitions in the spectra and these lines correspond to the transitions from the ground state $^4I_{9/2}$ to the excited states. In photo- and radio-luminescence spectra, Nd^{3+} 4f–4f transition peaks were observed. The photoluminescence decay time for $^4D_{3/2} \rightarrow {}^4I_{13/2}$ transition showed approximately 0.75 μs and slow component. The highest light yield was estimated to be 700 photon/MeV for $LuLiF_4$:Nd2% crystal grown by the μ-PD method.

1. Introduction

Inorganic crystalline scintillators have been widely used for radiation detection techniques in many fields such as high energy physics, security applications and medical imaging. In recent years, we had intensely investigated 4f–4f forbidden transition of trivalent rare-earth ions in scintillation materials for signal integrated-type measurements such as X-ray CT because scintillation decays up to few μs can be sufficient. In fact, the materials, such as, $CdWO_4$, Gd_2O_2S:Pr and Eu-doped sesquioxides are proposed for the X-ray radiology system. By previous our studies, trivalent rare-earth doped oxide scintillators like YAG:Nd, LuAG:Nd, LuAG:Tm, YAP:Tm and LuAG:Er found to demonstrate interesting properties including high light yield [1–5], intense emission bands in UV–IR region and enough decay time to detect by Si photodiode based detectors in X-ray CT system. Therefore, in this study, we focused attention on another type material, the Nd^{3+} doped lutetium lithium fluoride ($LuLiF_4$:Nd). Trivalent rare-earth doped the $LuLiF_4$ crystals previously have been investigated for infrared laser host [6,7] and vacuum ultra violet (VUV) emitting phosphors in gas counters as a light detector [8,9] while, up to now, no reports to study scintillation properties of $LuLiF_4$ with 4f–4f forbidden transition of trivalent rare-earth ion as an emission center. Furthermore, 4f–4f emission lines of Nd^{3+} would show in the high quantum efficiency (QE) ranges of the conventional PMT or APD. In present work, we examined the optical and scintillation properties of Nd^{3+}-doped $LuLiF_4$ single crystals with different concentrations.

2. Experimental procedure

The stoichiometric mixture of 4 N purity LiF, LuF_3 and NdF_3 powders (Stella Chemifa Corporation) were used as starting materials. Concentrations of Nd^{3+} ions in $LuLiF_4$ were 1%, 2%, 3%, and 4%. The concentration is described by the atomic percentage of Nd referred to Lu. In the micro-pulling-down (μ-PD) method [10], the mixture was load into the graphite crucible and baked for 1 h in the vacuumed chamber to remove the oxygen traces from the raw materials and adsorbates on the chamber surface. After the evacuation, the chamber was filled with high purity Ar and CF_4 mixed gas and the crystal growth was performed with typical pulling rate of 0.10 mm/min. On the other hand, $LuLiF_4$:Nd1% was also prepared by the Czochralski (Cz) method as comparison. In the Cz method, the Nd 1 mol% doped $LuLiF_4$ crystals was grown by a vacuum tight Cz system equipped with a radio frequency induction heater and automatic diameter control system. The crucible and the thermal insulators were made of high-purity graphite. The starting materials were melted and the crystal was pulled upon along c-axis with undoped $LuLiF_4$ crystal as a seed. The grown crystals were fabricated the measurements samples which were $1 \times 2 \times (10–15)$ mm^3 and $5 \times 5 \times 5$ mm^3, respectively.

Optical transmittance spectra were measured by UV–VIS double beam spectrophotometer (JASCO V-550) in the spectral range from 200 to 900 nm. The wavelength resolution was set to 1 nm. Photoluminescence spectra measurements were performed by using the

* Corresponding author. Tel.: +81 022 215 2214.
E-mail address: yamaji-a@imr.tohoku.ac.jp (A. Yamaji).

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spectrofluorometer FLS920 (Edinburgh Instruments) equipped with a steady state xenon arc lamp as a excitation source. In the similar setup, photoluminescence decay profiles were recorded under excitation with a hydrogen steady state nanosecond pulse flash lamp by using the method of time-correlated single photon counting. 5.5 MeV alpha-ray irradiated radioluminescence spectra were measured with the similar spectrofluorometer in spectral range from 350 to 650 nm. Furthermore, those in spectral range 850–1500 nm were measured by using an X-ray tube (Mini-X, Amptek) with accelerating voltage of 40 kV, a vacuum monochromator (VM-504, ACTON) and an InGaAs photomultiplier (G6126, Hamamatsu).

^{137}Cs gamma-ray irradiated pulse height spectra were demonstrated to determine the scintillation light yield. The sample crystals were wrapped with several layers of Teflon tape and were coupled to the optical window of the PMT with silicon grease (6262A, OKEN). The high voltage of 700 V was supplied by power unit (ORTEC 556), and the signals were then read out from the anode of the PMT. Thereafter, the signals passed a pre-amplifier (ORTEC 113) a shaping amplifier (ORTEC 570) with 10 μs shaping time and were converted to digital signals by a multi channel analyzer (Pocket MCA 8000A, Amptek). At the same time, $Bi_4Ge_3O_{12}$ (BGO) crystal was measured as a reference [11]. All the experiments were conducted at room temperature.

3. Results and discussion

The Nd 1%, 2%, 3% and 4% doped $LuLiF_4$ crystals which had 2 mm in diameters and several mm in lengths were succeed to grown by the μ-PD method. In fact, the Nd concentrations in the crystals were different with the nominal concentrations due to the segregation.

Transmission spectra of $LuLiF_4$:Nd are shown in Fig. 1. Some absorption bands corresponding to 4f–4f transitions of Nd^{3+} were observed [11,12], except for $LuLiF_4$:Nd1% due to the instrumental detection limit.

Photoluminescence spectra of $LuLiF_4$:Nd under excitation at 349 nm exhibited the intense peak at 382, 421and 450 nm, as shown in Fig. 2. These lines were identified as transition from the $^4D_{3/2}$ level to the $^4I_{11/2}$, $^4I_{13/2}$ and $^4I_{15/2}$ levels, respectively [13]. The photoluminescence decay curve of $LuLiF_4$:Nd1% crystal grown by the Cz method for $^4D_{3/2} \rightarrow {}^4I_{11/2}$ transition is presented in Fig. 3. The decay time is calculated from the double exponential fitting and the values found to be about 0.81 μs and several tens μs. Thus, those of $LuLiF_4$:Nd 1.0%, 2.0%, 3.0%, and 4.0% crystals by the μ-PD method were determined 0.70, 0.78, 0.64 and 0.68, respectively.

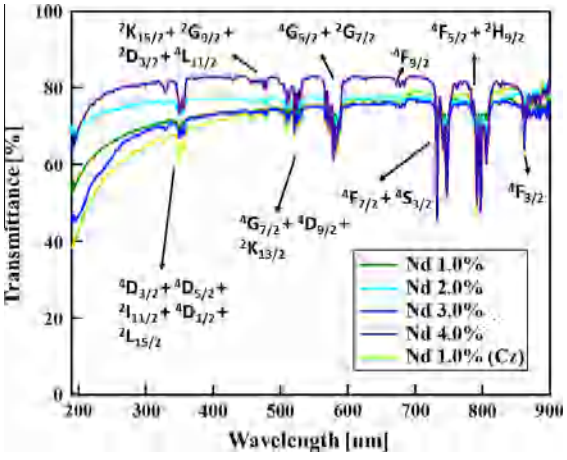

Fig. 1. Transmittance spectra of $LuLiF_4$:Nd.

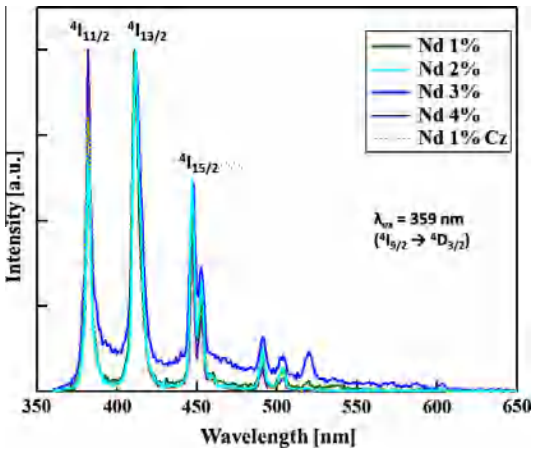

Fig. 2. Photoluminescence spectra of $LuLiF_4$:Nd under 359 nm excitation.

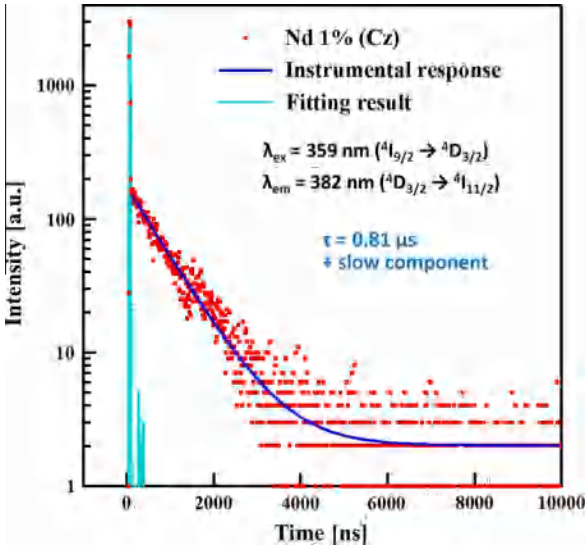

Fig. 3. Photoluminescence decay curve of $LuLiF_4$:Nd1% by the Cz method for $^4D_{3/2} \rightarrow {}^4I_{11/2}$ transition.

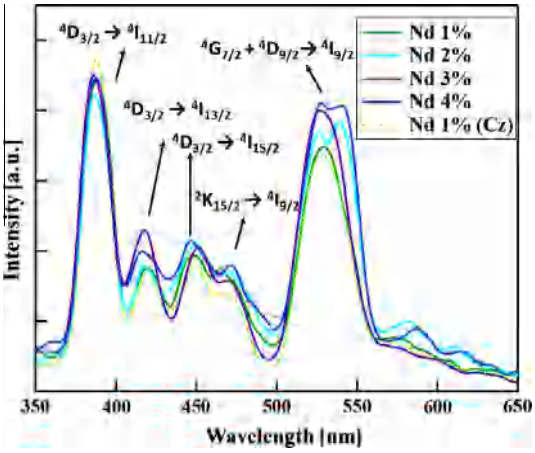

Fig. 4. Radioluminescence spectra in spectral range 350–650 nm of $LuLiF_4$:Nd under 5.5 MeV alpha-ray irradiation.

The results of radioluminescence spectra in spectral range from 350 to 650 nm of $LuLiF_4$:Nd under 5.5 MeV alpha-ray excitation are presented in Fig. 4. Two intense peaks are observed at 385 and

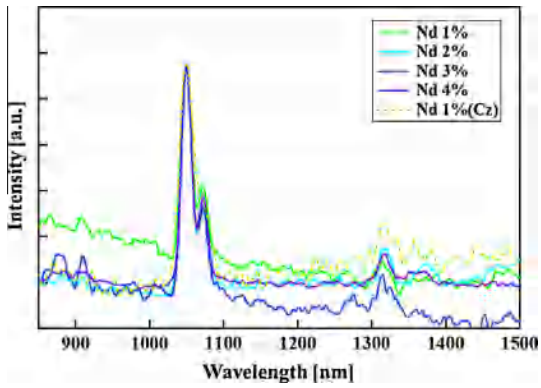

Fig. 5. Radioluminescence spectra in spectral range 850–1500 nm of $LuLiF_4$:Nd under X-ray irradiation.

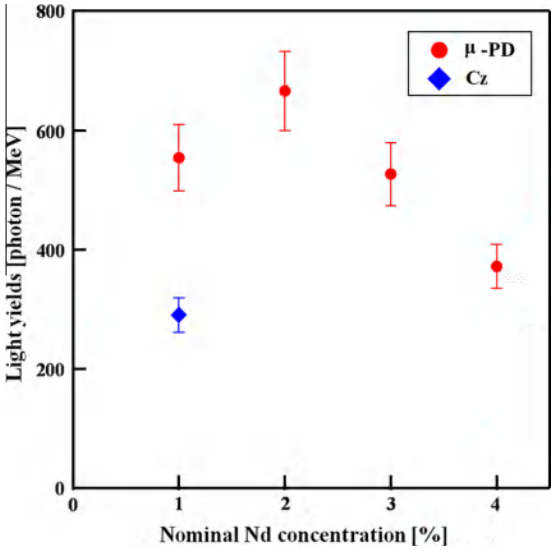

Fig. 6. Light yields of $LuLiF_4$:Nd under 662 keV gamma-ray (^{137}Cs) irradiation plotted against the nominal Nd concentration.

530 nm. By comparing the results of previous study [14], these peaks can be assigned to the $^4D_{3/2} \rightarrow {}^4I_{11/2}$ and $^4G_{7/2} \rightarrow {}^4I_{9/2}$, respectively. In the radoluminesence spectra, the transitions from several 4f level of Nd were overlapped. The results of radioluminescence spectra in spectral range from 850 to 1500 nm of $LuLiF_4$:Nd under X-ray excitation are shown in Fig. 5. There are intense and weak peaks at 1050 nm and 1315 nm, which are ascribed to the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ transition [15], respectively.

The light yields of $LuLiF_4$:Nd under 662 keV gamma-ray (^{137}Cs) irradiation is recorded in Fig. 6 and are calculated by comparing the ^{137}Cs 662 keV photoabsorption peak channels of $LuLiF_4$:Nd with that of BGO (LY = 8200 photon/MeV [16]), emission wavelength: 480 nm. The QE of the PMT are 42% at 385 nm, 27% at 480 nm and 12% at 530 nm, respectively. Then, the peak channels of $LuLiF_4$:Nd are dominated by the emission at 480 nm and the light yields are estimated taking into account the QE at 385 nm and 530 nm. The light yield of $LuLiF_4$:Nd2% crystal is determined to be about 700 photon/MeV. The light yield of the crystal prepared by the μ-PD method was higher than that of the crystal prepared by Cz method the nominal Nd concentration of which was equivalent due to the different Nd concentrations in the crystals with the different crystal growth methods.

4. Conclusions

We grew nominally Nd 1.0%, 2.0%, 3.0%, and 4.0% doped $LuLiF_4$ single crystals by the μ-PD method and that of Nd 1.0% by the Cz method. There are some absorption bands due to Nd^{3+} 4f–4f transitions in the spectra and these lines correspond to the transitions from the ground state $^4I_{9/2}$ to the excited states. In photo- and radio-luminescence spectra, Nd^{3+} 4f–4f transition peaks were observed. The photoluminescence decay time for $^4D_{3/2} \rightarrow {}^4I_{13/2}$ transition showed approximately 0.75 μs and slow component. The highest light yield was estimated to be 700 photon/MeV for $LuLiF_4$:Nd2% crystal grown by the μ-PD method. However, the PMT were not suitable for the other intense peak in IR wavelength region due to transitions such as $^4G_{7/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{11/2}$. For the future work, we attempt to evaluate the light yield arisen from these transition. Particularly, the near infrared scintillation is expected to use for the radiation therapy as a real-time dose monitor.

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