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Crystal growth and scintillation characteristics of the Nd^{3+} doped $LiLuF_4$ single crystals

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ABSTRACT

Sixty millimeter diameter single crystal of Nd^{3+} doped $LiLuF_4$ was successfully grown by the Czochralski technique. No remarkable absorption due to unfavorable impurities was observed from optical absorption measurements in the vacuum ultra-violet spectral region. The high crystallinity and homogeneous luminescence characteristics were found from X-ray rocking curve and cathode-ray luminescence respectively. X-ray excited luminescence spectrum was measured and the significant $4f^2 5d$–$4f^3$ luminescence at 182 nm was observed in the grown crystal. The pulse height spectrum was taken upon γ-ray irradiation. As a result, the grown crystals demonstrated sufficient response to the γ-ray showing the light yield of 420 ± 30 photons/MeV. The decay curve under α-ray irradiation was also investigated and described by two component decay kinetics which consists of the decay constants of 34 and 450 ns.

1. Introduction

The micropattern gaseous detectors (MPGDs) are attractive radiation detectors because they can realize the large area detector with excellent spatial resolution in low cost. However, due to the poor detection efficiency for high energy photons, MPGDs are difficult to use in medical application such as PET or X-ray CT.

In order to compensate the detection efficiency, the combination of VUV luminescent scintillator [1–7] and MPGDs has been studied. The VUV-sensitive MPGDs including MWPC with TMAE gas [8,9], MGPM with CsI photocathode [10,11] and PPAC with CsI photocathode [12] have been developed in last decades. On the other hand, as an candidate for VUV scintillator, Nd^{3+} doped LaF_3 ($Nd:LaF_3$) was intensely studied [1,2] because $Nd:LaF_3$ can emit a sufficient VUV scintillation from the 5d–4f transition of Nd^{3+} ion. Recently, the VUV-sensitive MPGD consisting of gas electron multiplier (GEM) and micro pixel chamber (μPIC) was developed and demonstrated the capability of radiation imaging detectors in the combination with $Nd:LaF_3$ scintillator [13].

However, $Nd:LaF_3$ has potential problem to obtain the high light yield due to the energy loss via intrinsic trap level of LaF_3 to the 4f–4f transition [14]. Therefore, we have surveyed several Nd doped fluoride crystals grown by micro-pulling down technique and found that $Nd:LiLuF_4$ showed the higher light yield than that of $Nd:LaF_3$ [3]. Furthermore, the large atomic number and high density of $LiLuF_4$ crystal is preferable for high energy γ-ray detection.

Even though, as reported in the case of $Nd:LaF_3$ [9], the large size crystal with good optical properties is hardly obtained because the optical properties tends to be critically degraded by slight contamination with unfavorable impurities.

In the present work, large size single crystal of $Nd:LiLuF_4$ was grown by improved Czochralski technique. The crystal quality, optical and scintillation properties are presented and compared with those of $Nd:LaF_3$.

2. Experimental procedure

Crystal growth was performed in a vacuum-tight Czochralski system equipped with radio frequency induction heater and automatic diameter control system (Fig. 1). The crucible and thermal insulators were made of high-purity graphite. The starting material was prepared from commercially available fluoride powders of LiF, LuF_3 and NdF_3 (>99.99%) and loaded into a graphite crucible. The

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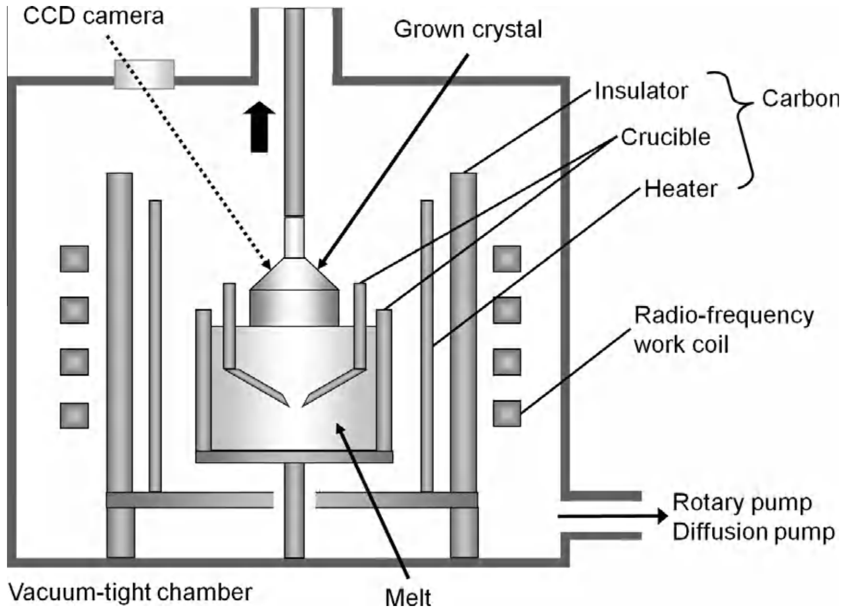

Fig. 1. Schematic view of vacuum-tight Czochralski apparatus equipped with precise atmosphere control.

Fig. 2. View of as-grown Nd:$LiLuF_4$ single crystal (a) and disk cut from the crystal (b).

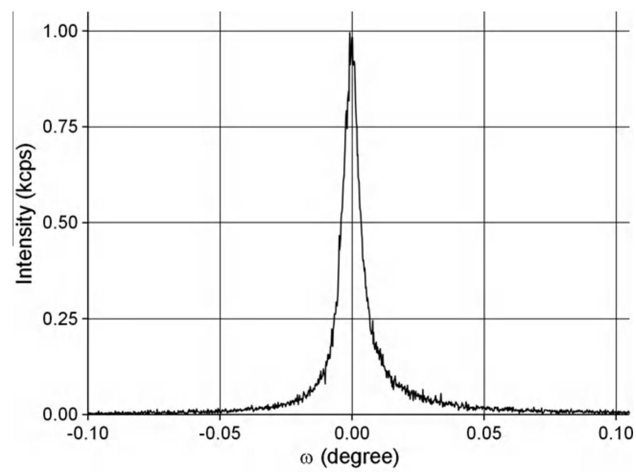

Fig. 3. X-ray rocking curve of the grown crystal with [0 0 1] orientation.

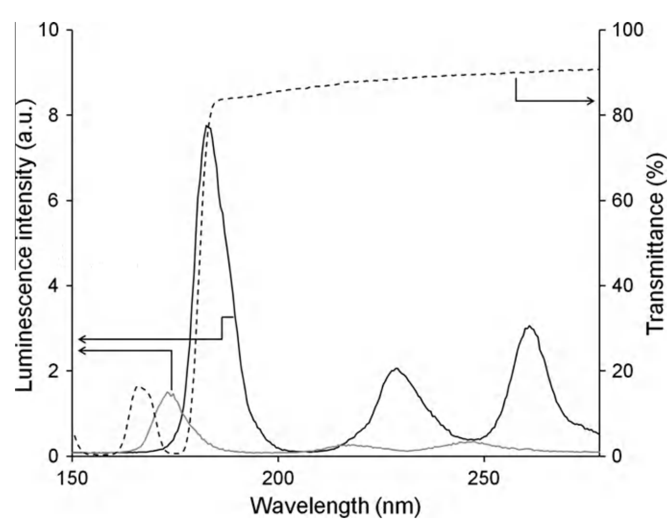

Fig. 4. Radioluminescence spectra of Nd:$LiLuF_4$ (solid line) and Nd:LaF_3 (dashed line), and transmittance spectrum of Nd:$LiLuF_4$ (gray line).

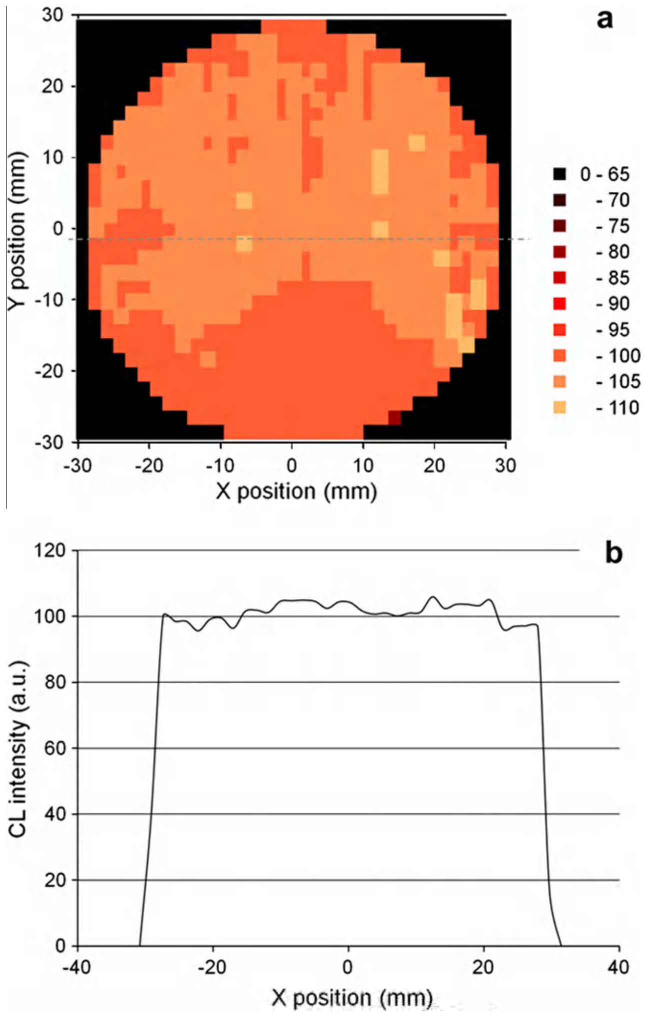

Fig. 5. Cathode-ray luminescence map (a) and line profile along the dashed line in the map (b).

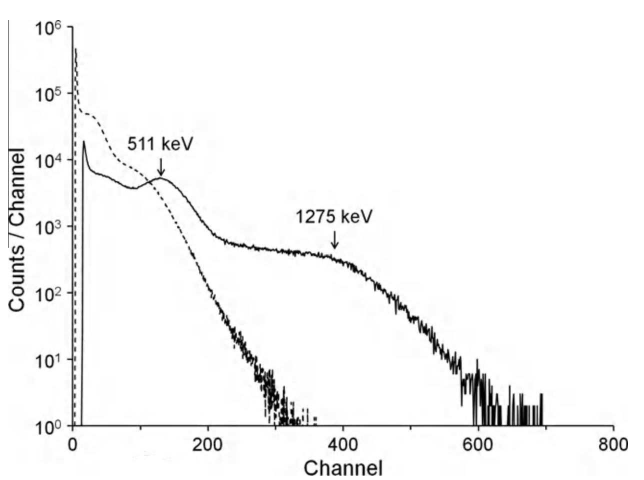

Fig. 6. The pulse height spectra of Nd:$LiLuF_4$ (solid line) and Nd:LaF_3 (dashed line) under ^{22}Na irradiation.

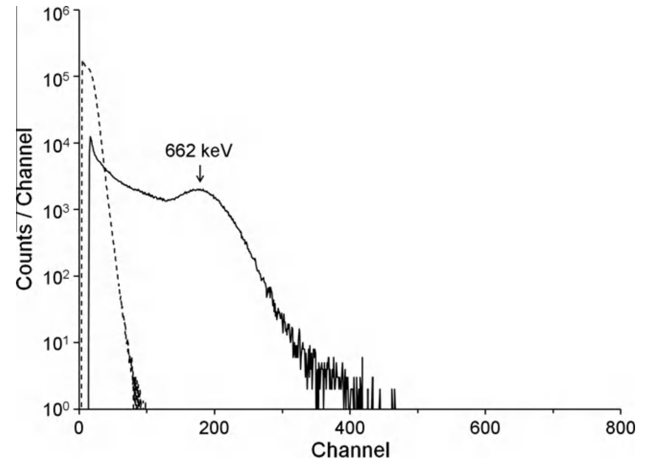

Fig. 7. The pulse height spectra of Nd:$LiLuF_4$ (solid line) and Nd:LaF_3 (dashed line) under ^{137}Cs irradiation.

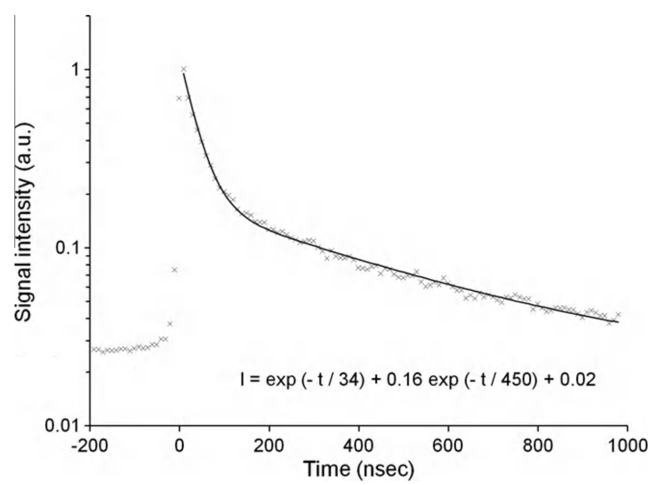

Fig. 8. The scintillation decay curve of Nd:$LiLuF_4$.

concentration of NdF_3 in the starting material was 1 and 10 mol% for Nd:$LiLuF_4$ and Nd:LaF_3 respectively. The preheating treatment under vacuum was performed to eliminate water and oxygen traces from the growth chamber and starting materials. Subsequently, high-purity CF_4/Ar gas was introduced into the furnace. Thereafter, the starting material was melted and crystal was pulled up along c-axis using undoped seed crystal.

The as-grown crystal with [0 0 1] orientation was cut and polished into φ 60 mm × 2 mm and 2 × 10 × 1 mm^3 for the evaluation of crystallinity and scintillation property respectively.

The crystallinity of Nd:$LiLuF_4$ was characterized by X-ray rocking curve (XRC) analysis using Bruker AXS D8 Discover with a 4-bounce Ge (0 2 2) monochromator.

The transmittance spectra in the VUV region and X-ray excited luminescence spectra were measured using Bunkoh-keiki kV-201 spectrometer equipped with nitrogen-purged sample chamber, deuterium lamp as a light source and X-ray tube with a tungsten anode as X-ray source. X-ray tube was directly mounted to the sample chamber and operated at 60 kV and 40 mA.

Cathode-ray luminescence (CL) spectra were taken by VUV spectrometer (Horiba Jobin Yvon) connected to FE-SEM (Hitachi, SU-6600) [4]. FE electron gun was operated at acceleration voltage of 20 kV and whole part of the φ 60 mm disk was scanned using automatic stage controller and wide area CL map was created for homogeneity evaluation.

To examine the γ-ray response, the sample crystal with dimensions of 15 × 15 × 15 mm^3 was optically polished and coupled with VUV-enhanced PMT (Hamamatsu R8778) by optical grease Krytox 16350 (Dupon). The pulse height spectra were measured under γ-ray irradiation and compared with $Nd:LaF_3$ described in [5], and the scintillation decay curve was measured under α-ray irradiation as well. In this experiment, ^{22}Na and ^{137}Cs were used as γ-ray sources and ^{241}Am was used as α-ray source.

3. Results and discussion

Large single crystal of 60 mm in diameter and 45 mm in length was successfully grown. It was free from any visible inclusion or cracks (Fig. 2).

XRC analysis was performed to examine the crystallinity of the crystal. The FWHM of XRC was measured to be 28 arcsec by the ω scan for the reflection from (0 0 4) plane (Fig. 3). This result shows that the grown crystal has high crystallinity that is comparable to that of commercial optical grade materials.

Fig. 4 shows the radioluminescence spectra of $Nd:LiLuF_4$ and $Nd:LaF_3$. The intense luminescence from $Nd:LiLuF_4$ peaking at 182 nm has been observed and the intensity was approximately five times higher than that of $Nd:LaF_3$. Furthermore, this crystal shows good transparency above 180 nm and no remarkable absorption due to the unfavorable impurities or color centers was observed.

Fig. 5 shows the prepared disk of $Nd:LiLuF_4$ and CL map created from CL intensity at 182 nm. Homogeneous luminescence intensity was achieved within whole the disk. This result is promising toward the application of large area detectors in the combination with MPGDs.

The pulse height spectra of $Nd:LiLuF_4$ and $Nd:LaF_3$ under ^{22}Na and ^{137}Cs irradiation is shown in Figs. 6 and 7 respectively. The pulse height of the $Nd:LiLuF_4$ is significantly higher than that of $Nd:LaF_3$. In the pulse height spectra of Fig. 6, peaks were observed around 120–140 ch and 320–440 ch. Assuming the conversion factor of 3.9 keV/ch, these peaks are assigned to the photo–electric absorption for 511 keV and 1275 keV γ-ray from ^{22}Na respectively. Similarly, in Fig. 7, the peak around 160–190 ch corresponds to 662 keV γ-ray from ^{137}Cs. These values are three times higher than that of $Nd:LaF_3$. Therefore, assuming the light yield of $Nd:LaF_3$ from recent study [5], the light yield under γ-ray irradiation was calculated to be 420 ± 30 photons/MeV.

The scintillation decay curve was investigated by the digital oscilloscope. As a result, the decay curve was described by two components with the decay constant of 34 and 450 ns respectively (Fig. 8). The fast component is ascribed to 5d–4f transition of Nd^{3+} ion. The slow component can be considered as the delayed luminescence however further study is expected to clarify the origin of delay.

4. Conclusions

The large size $Nd:LiLuF_4$ single crystals was grown by the Czochralski technique.

The excellent crystallinity of the grown crystal was found by XRC and CL measurement. The grown crystal has also shown the good transparency free from the absorption due to the unfavorable impurities.

As is found in the X-ray excited luminescence spectra, $Nd:LiLuF_4$ has significantly higher light yield than that of $Nd:LaF_3$. Owing the higher light yield and large atomic number, $Nd:LiLuF_4$ has performed sufficient γ-ray response in the combination with VUV-enhanced PMT.

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