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JOURNAL OF RARE EARTHS, Vol. 34, No. 8, Aug. 2016, P. 757
JOURNAL OF RARE EARTHS
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Optical and scintillation properties of Nd-doped $SrAl_2O_4$ crystals

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Received 15 December 2015; revised 11 March 2015

Abstract: Nd-doped $SrAl_2O_4$ (Nd:$SrAl_2O_4$) crystals were prepared by a floating zone (FZ) method with different dopant concentrations. The photoluminescence (PL) measurements under visible light excitations confirmed strong near infrared (NIR) emissions around 890 nm, which is due to the 4f-4f transitions of Nd^{3+}, and the decay time constants were 300–400 μs. Furthermore, VUV excitations revealed two broad emissions around 250–450 and 500–700 nm, which were attributed to self-trapped excitons (STEs) perturbed by Nd^{3+}. Moreover, the X-ray induced scintillation spectra showed some small peaks at around 380 nm in addition to NIR emissions at 1064 nm similarly seen in PL. The former scintillation decay time constants were 30–40 μs. In the undoped sample, these emissions mentioned above were not present but a weak broad emission around 450 nm appeared. In thermally stimulated luminescence (TSL) after X-ray irradiation, strong TSL glow peaks were observed in the Nd-doped samples at around 100 and 250 ºC.

Keywords: scintillation; photoluminescence; storage luminescence; single crystal; rare earths

Inorganic scintillators convert ionizing radiation to thousands of low energy photons (1–6 eV) immediately, so they have been playing an important role in various fields of radiation detections including medical imaging[1], security[2], astrophysics[3], and geophysical and resources exploration, e.g. oil-dwelling[4]. In these applications, market volumes of medical and security fields are especially large, so scintillators for particular X-ray and γ-ray detectors have been intensively studied. A conventional scintillation detector consists of a scintillator, which emits scintillation photons, and a photodetector, which converts the incident photons to electrons. Generally, visible light emitting scintillators are preferable because the most conventional photodetector, PMT, has a high sensitivity around the blue wavelength. In addition to such a conventional visible emitting scintillator, vacuum ultra violet (VUV), UV and near infrared (NIR) scintillators are also attractive for various applications[5,6]. To achieve such a wavelength functionality, rare-earth ions are generally doped as an emission center in bulk insulator or semiconductor materials.

In this study, we investigated the scintillation properties of Nd-doped $SrAl_2O_4$ (Nd:$SrAl_2O_4$) crystals. In addition, we evaluated the dosimetric properties in order to comprehensively understand the material system. Rare-earth-doped $SrAl_2O_4$ have been widely studied in the fields of phosphorescent phosphors[7], and scintillation from Eu and Dy doped $SrAl_2O_4$ in the nano powder or sintered ceramic forms has also been reported[8–12]. Although most scintillation detectors utilize single crystals mainly due to their high detection efficiency and high optical quality, most reported studies of $SrAl_2O_4$ materials are in the powder form. For scintillator uses, a bulk form is particularly important since the interaction probability of ionizing radiations with materials simply depends on the detector volume, so except for some specific detectors, most practical detectors use bulk crystalline scintillators. While Nd-doped materials have been regarded as one of the most popular NIR phosphors in laser systems[13], it is also of our great interest as a new generation NIR emitting scintillator. Nd is known to show NIR emission due to the 4f-4f transitions, which has great transparency to biological tissue[14], so it has a considerable potential for bio-imaging applications[6]. It is worth mentioning here that scintillation detectors are usually classified into photon-counting and integration types as commonly utilized in positron emission tomography (PET) and X-ray computed tomography (X-ray CT), respectively. Unlike photon-counting based detection, the integration type does not strictly require a fast scintillator and lifetime of such typical scintillators is on an order of micro-seconds. Up to now, our group also investigated some Nd-doped materials[15,16], and most of them showed detectable scintillation and some materials

Foundation item: Project supported by the Aid for Scientific Research ((A)-26249147) from the Ministry of Education, Culture, Sports, Science and Technology of the Japanese government (MEXT), JST A-step, Green Photonics Research from MEXT, the Adaptable and Seamless Technology Transfer Program (A-STEP) by the Japan Science and Technology (JST) Agency, the Murata Science Foundation, and a cooperative research project of the Research Institute of Electronics, Shizuoka University

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DOI: 10.1016/S1002-0721(16)60090-X

were found to be usable even in the photon-counting mode. As far as we are aware, no studies have been reported for the scintillation properties of Nd-doped $SrAl_2O_4$.

1 Experimental

Nd-doped $SrAl_2O_4$ crystals were synthesized by a floating zone (FZ) method using an FZ furnace (FZD0192, Canon Machinery Inc.). We used $SrCO_3$ (99.99%, 1.0 equiv.), Al_2O_3 (99.999%, 1.0 equiv.) and Nd_2O_3 (99.99%, x/2 mol.%, x=0, 0.5, 1.0 and 2.0) powders as raw materials. Hereafter, the molar ratio of Nd ions with respect to the $SrAl_2O_4$ compound are used to identify the samples. Here, the Nd ion is expected to substitute the Sr site. These starting compounds were mixed first, and the mixture was shaped to the cylinder by the hydrostatic pressure. Then the cylinder was sintered at 1500 °C for 6 h. The sintered rod was put into the FZ furnace and the crystal growth was conducted with the pulling rate of 5 mm/h and the rotation rate of 20 r/min. The heat radiation source of the FZ furnace is halogen lamp. The synthesized sample was characterized by the measurements below.

To identify the obtained crystalline phase, powder X-ray diffraction (XRD) pattern was measured with a diffractometer (MiniFlex600, Rigaku) over the 2θ range of 5º–70º. The X-ray source is a conventional X-ray tube with a CuKα target operated at 40 kV and 15 mA. The photoluminescence (PL) and PL excitiation (PLE) spectra were measured by using a spectrofluorometer (FP8600, JASCO), and PL quantum yield (QY) were evaluated by using Quantaurus-QY (Hamamatsu Photonics). The PL decay time profile monitoring at 890 nm under 575–625 nm excitation was evaluated by using Quantaurus-τ (Hamamatsu Photonics). The excitation source was a white light source, and the band pass filter (11K0350, OptoSigma) was used to select excitation photons. The decay time was deduced by the single exponential fitting. In addition, the emission spectra under VUV photon excitations were measured at the synchrotron facility (UVSOR). The tested excitation wavelength was from 50 to 200 nm.

As a scintillation property, X-ray induced radioluminescence (RL) spectra were measured by utilizing our original setup[17]. The irradiation source was X-ray generator equipped with a tungsten anode target (XRB80P&N200X4550, Spellman). During the measurements, the X-ray generator was supplied with the voltage of 80 kV and tube current of 2.5 mA. While the sample was irradiated by X-rays, the scintillation emissions from the sample were fed into the spectrometer through a 2 m optical fiber to measure the scintillation spectrum. The spectrometer (Andor DU-420-BU2 CCD for visible and Andor DU492A-1.7 for NIR wavelengths with Shamrock SR163 monochromator) was cooled down to 188 K by a Peltier module to reduce the thermal noise. Furthermore, we have measured the scintillation decay time and afterglow profiles using a pulsed X-ray source equipped afterglow characterization system[18]. In both PL and scintillation decay time profiles, we fitted the data only in the tail part assuming a single exponential function because we cannot evaluate an instrumental response. Here, the afterglow level (A) is represented by A (%)=100×(I_2–I_0)/(I_1–I_0), where I_0, I_1 and I_2 denote the averaged signal intensity before the X-ray irradiation, the averaged signal intensity during X-ray irradiation and signal intensity at t=20 ms after the X-ray cut off, respectively. Although the evaluation manners of the afterglow differ in each company, we referred the formula from the manner of NIHON KESSHO KOGAKU CO., LTD. which is one of the famous companies for integrated-type scintillation detectors.

In order to characterize relatively shallow trapping centers, the thermally stimulated luminescence (TSL) glow curves were measured by TL-2000 (Nanogray, Japan) with the heating rate of 1 ºC/s over the temperature range from 50 to 490 ºC[19]. Except for the TSL, the sample for all the other measurements mentioned above was at room temperature.

2 Results and discussion

The synthesized undoped and Nd:$SrAl_2O_4$ crystals are shown in Fig. 1. The samples doped with 0–1.0 at.% Nd look white and translucent, and the 2.0%Nd-doped sample looks colorless and transparent. Since the 2.0%Nd-doped sample has the strongest NIR absorption due to the 4f-4f transitions of Nd^{3+} where the halogen lamp equipped with the FZ furnace has the peak emission wavelength, the crystal growth was stably performed without much creation of cracks and defects. We broke

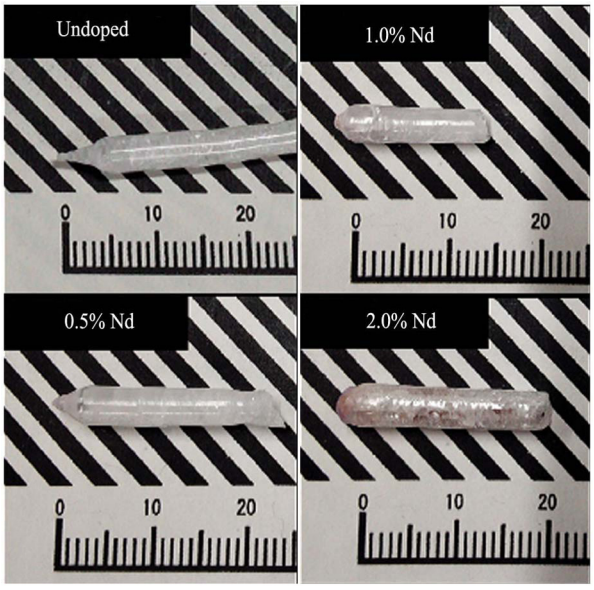

Fig. 1 Appearances of the synthesized Nd:$SrAl_2O_4$ crystals