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Study of the correlation of scintillation decay and emission wavelength

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HIGHLIGHTS

- The correlation between emission wavelength and scintillation decay time is investigated.
- Photoluminescence decay times are also evaluated and compared with scintillation decay times.
- It is proved the relaxation process in emission center is dominant even in scintillation decay.

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ABSTRACT

In photoluminescence which directly excites the emission center of phosphor material is known to have a correlation between the emission wavelength and the decay time based on quantum mechanics. In scintillation phenomenon, host lattice of the material is first excited by ionizing radiation and then the excitation energy is transferred to emission centers. For the first time, we investigated the correlation between the scintillation decay and the emission wavelength by using pulse X-ray equipped streak camera system which could observe time and wavelength resolved scintillation phenomenon. Investigated materials were Ce^{3+}, Pr^{3+} and Nd^{3+} doped oxides and fluorides which all showed 5d-4f transition based emission. As a result, we obtained the relation that τ (scintillation decay time) was proportional to the $\lambda^{2.15}$ (emission wavelength).

1. Introduction

Scintillation materials which convert high energy ionizing radiation to a numerous UV-visible photons have been investigated since 1895 when the phosphorescence of uranium salt was discovered. They are used in many fields, such as high energy particle physics (Danevich et al., 2005), astrophysics (Yamaoka et al., 2005), medical imaging (Yanagida et al., 2010b, Persson and Cederwall 2011), security (Kim et al., 2011), and mineral resource searching. In scintillator, one of the important properties is a scintillation decay time, which directly relates with the timing resolution of radiation detectors. The decay time fundamentally depends on the speed of transfer of free electrons and holes from ionization track to the emission center and the life time of the luminescence state of the activator. In photoluminescence, the luminescence decay time can be analytically deduced as

$$\Gamma = \frac{1}{\tau} \propto \frac{n}{\lambda^3}\left(\frac{n^2+2}{3}\right)^2 \sum_f |< f|\mu|i >|^2,$$

where Γ, τ, n, and λ represent the decayrate of an excited state, decay time, refractive index, and emission wavelength, respectively. The matrix element connecting an initial state $|i>$ with a final state $|f>$ via the dipole operator μ will only be of appreciable size for transitions between states of different parity (Henderson and Imbush, 1989). Although the other process of the energy migration from the host lattice to emission centers occurs, scintillation decay time will be in proportional to approximately λ^3. Previously, the relation between the scintillation decay time and refractive

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index was well studied experimentally (Dorenbos, 2010). However, to our knowledge, the relation between the scintillation decay time and the emission wavelength was not studied enough, possibly because most of measurement methodologies of scintillation decay time were not resolved in wavelength.

Recently, we developed pulsed X-ray equipped streak camera system to investigate time and wavelength resolved scintillation phenomenon (Yanagida et al., 2010a; Furuya et al., 2011). This instrument enables us to observe the scintillation decay time and X-ray excited emission wavelength simultaneously. The purpose of the present study is to investigate this relation using 5d-4f transition related emission of Nd^{3+}, Pr^{3+}, and Ce^{3+}, and compare the results with photoluminescence by using vacuum ultra violet (VUV) photoluminescence based streak camera system (Furukawa et al., 2009).

2. Samples and experimental procedures

Evaluated samples were Ce^{3+}, Pr^{3+} an Nd^{3+} doped oxides and fluorides which all showed 5d-4f transition based emission because most recent trends of scintillators were fast emission due to this parity and spin allowed transition. The used scintillators by us are summarized in Table 1 and origins and basic properties of these materials can be seen in references in this Table. Except Ce doped GSO and YAP fabricated by Hitachi Chemical, all scintillators were prepared by us using the micro-pulling down, Czochralski, and vacuum sintering methods. Pr:YAG and Ce:LSO were also made by us but referred typical literatures because we did not report their growth procedures and emission wavelength under radiation excitation. All the samples were polished to typical dimensions to $2-5 \times 5-8 \times 2-5$ mm^3.

The time and wavelength resolved scintillation decay times were evaluated by our original setup, pulse X-ray equipped streak camera system (Yanagida et al., 2010a; Furuya et al., 2011). The root of the excitation was a laser diode (PLP10-063, Hamamatsu). It emits at 638 ± 20 nm and shows the pulse width of 50 ps and with maximum 100 MHz repetition frequency. Emitted photons hit a multi-alkali photocathode of X-ray tube (N5084, Hamamatsu) and were converted into electrons. The photocathode quantum efficiency at 650 nm was around 3%. The electrons were accelerated by 40 kV of high voltage bias and led to a tungsten target by a strong electric field. Bremsstrahlung X-rays were then generated and led to the sample through 20 mm $\varphi \times 0.5$ mm thick Be window. The mean energy of X-ray quanta was $\sim$ 30 keV and the endpoint energy of the bremsstrahlung spectrum was $\sim$ 40 keV. At present, the instrumental response to this X-ray pulse shows full width at half maximum (FWHM) of about 80 ps.

In photoluminescence decay times, Ce^{3+} and Pr^{3+} doped scintillators were measured by FLS920 spectrometer (Edinburgh Instrument) equipped with nano seconds flush lamp. The timing resolution of the instrument was approximately 1 ns and was sufficient to evaluate Ce^{3+} (typically 20–60 ns) and Pr^{3+} (typically 10–20 ns) decay times. On the other hand, Nd^{3+} 5d-4f emission generally appears in VUV region and requires vacuum spectrometer and excitation source. Thus, we used VUV photoluminescence based streak camera system (Furukawa et al., 2009) equipped with F_2 laser as an excitation source. In this system, the excitation wavelength was set to be 157 ± 5 nm.

Table 1
Emission wavelengths of used scintillators.

	Emission wavelength (nm)	Reference
NdF_3	175	Furuya et al., 2010
Nd:LaF_3	180	Fukuda et al., 2010
Nd:$LuLiF_4$	185	Yanagida et al., 2010c
Nd:LuF_3	180	Yanagida et al., 2011a
Pr:LuAG	315	Kamada et al., 2008
Pr:LSO	300	Totsuka et al., 2011
Pr:LuYAP	280	Yanagida et al., 2010d
Pr:YAG	320	Wisniewska et al., 2002
Pr:YAP	280	Yanagida et al., 2010e
Ce:LuAG	550	Yanagida et al., 2011b
Ce:GAGG	520	Kamada et al., 2011
Ce:GSO	445	Takagi and Fukazawa, 1983
Ce:LSBO	390	Yanagida et al., 2011c
Ce:$LuLiF_4$	315	Yanagida et al., 2011c
Ce:YAG	520	Takahashi et al., 2006
Ce:YAP	365	Lempicki et al., 1995
Ce:$YLiF_4$	315	Yokota et al., 2010
Ce:LiCAF	290	Yoshikawa et al., 2009
Ce:LSO	420	Cutler et al., 2009

3. Results and discussion

Fig. 1 exemplifies the streak image of Nd:LuF_3. Time and wavelength resolved scintillation phenomenon was clearly observed and only 5d-4f transition based emission was derived. Then, Figs. 2 and 3 demonstrate streak images of Pr:LuAG and Ce:LSO. In these Figures, it was confirmed that Ce^{3+}, Pr^{3+}, and Nd^{3+} 5d-4f transition based scintillation phenomena were detected in our system. In photoluminescence based streak system, similar images were obtained and analytical procedures were same.

After all the samples were measured, each image was projected on the time axis to analyze decay time. Fig. 4 exemplifies the scintillation decay curve of Ce:LSO. All the decay curves were well reproduced by the single exponential assumption. Photoluminescence decay curves obtained by FLS920 were also evaluated by the same manner.

Finally, Fig. 5 compares scintillation and photoluminescence decay time constants against the emission wavelengths. Observer data sets were fitted by the function $a \times \lambda^b$, where a and b denoted fitting parameters. As shown in the Figure, the decay time τ is in proportional to $\lambda^{2.15}$ in scintillation. Compared with the direct excitation of the emission center in the photoluminescence ($\tau \propto \lambda^{2.22}$), the wavelength dependence on the decay time is slightly small. The prediction of $\tau \propto \lambda^3$ basically represents the situation of photoluminescence (Henderson and Imbush, 1989) and it is natural that the photoluminescence results are near to $\tau \propto \lambda^3$. However, the difference between the scintillation and photoluminescence decay were quite small. Previous results exhibited the relation between the refractive indices and the decay time (Dorenbos, 2010; Duan and Reid, 2006) so that it was difficult to compare the present results with others. Present results at least confirm even in a scintillation decay via the energy migration from the host lattice to the emission center, the emission process from the excited state to the ground state is still dominant.

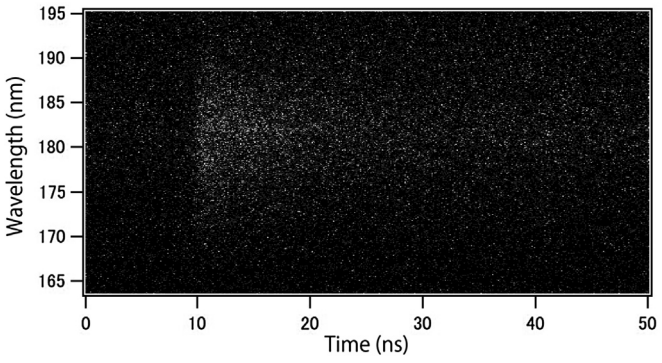

Fig. 1. Streak image of Nd:LuF_3.

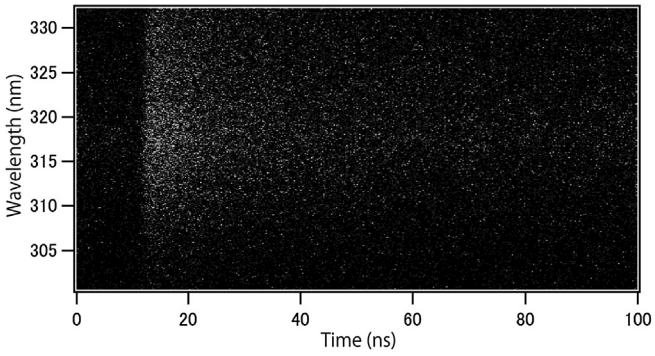

Fig. 2. Streak image of Pr:LuAG.

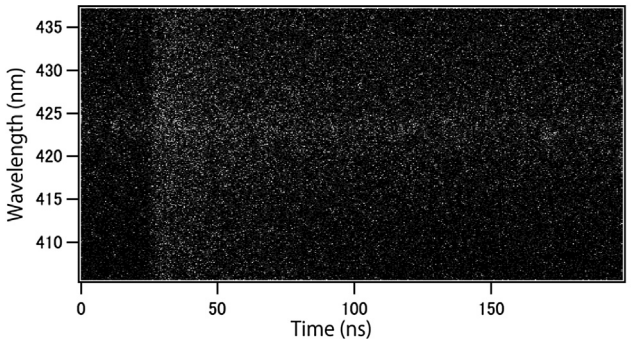

Fig. 3. Streak image of Ce:LSO.

The other interesting point is that even in a photoluminescence, the result differs with the theoretical value. In the analytical formula, only the electron transition of the emission center in vacuum is assumed and in realistic materials the situation is more complicated. If we apply the formula to realistic materials, 100% doping (e.g., NdF_3) of the emission center where only the cation can emit would be close to the assumption. Although 5d-4f emission from 100% doped materials are quite rare due to the concentration quenching, CeF_3 (17.6 ns at 303 nm, Wojtowicz et al., 1994) and NdF_3 (3.8 ns at 175 nm, Furuya et al., 2010) well matches on the $\tau \propto \lambda^3$ relation, as an example. Through the present study, it is confirmed that in most cases photoluminescence and wavelength-resolved scintillation decay time are similar, and the decay time is in proportional to $\sim\lambda^{2.1-2.2}$ in realistic materials.

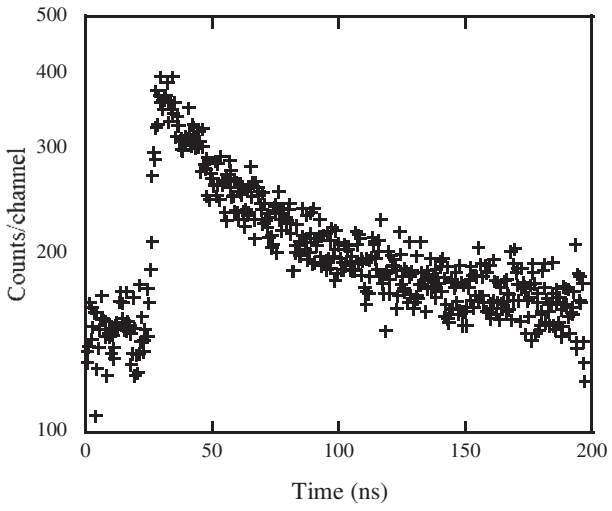

Fig. 4. Scintillation decay time profile of Ce:LSO.

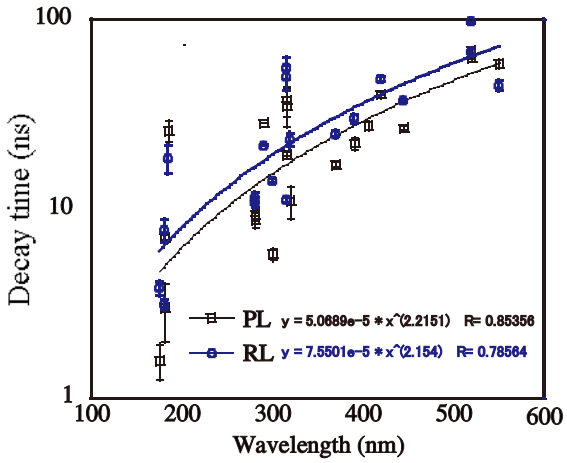

Fig. 5. Decay time (ns) plotted against the emission wavelength (nm) in photo- (black) and radio- (blue) luminescence. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Concerning the above discussion, this relation gives us a fundamental limitation of the speed of scintillators using 5d-4f transitions. Concerning the 5d-4f transition based emission, Tm^{3+} or Er^{3+} exhibit the shortest emission wavelength of approximately 160 nm (Yanagida et al., 2011a) in radioluminescence spectra and they will give the fastest scintillation decay time of ~3 ns under high energy photon (X- or γ-ray) excitation from present results. Such a fast decay time was actually observed in DESY synchrotron facility (Wegh and Meijerink, 1999) under vacuum ultra violet or extra ultra violet excitation. The present experimental evidence will be a good help to understanding the luminescence phenomenon and material design for radiation measurements.

4. Conclusions

For the first time, the correlation between the scintillation decay time and emission wavelength was investigated by using pulse X-ray equipped streak camera which enabled us to observe wavelength resolved scintillation phenomenon. Compared with photoluminescence based results, the wavelength dependence of the decay time was slightly smaller. The present result shows experimentally the relaxation process in the emission center is a dominant process even in a scintillation decay.

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