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Effect of 14-MeV neutrons on strontium–aluminate-based long-lasting phosphor

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A B S T R A C T

Long-lasting phosphor (LLP) emits photons for a long period of time after the cessation of irradiation without external excitation. LLP exhibits not only a long-lasting emission but also strong fluorescence. The fluorescence and long-lasting emission properties of two types of strontium-aluminate-based LLPs – $SrAl_2O_4$:Eu^{2+}, Dy^{3+} and $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} – are examined under 14-MeV neutron irradiation. The fluorescent spectra of the LLPs have characteristic peaks due to their dopants and the fluorescent intensity of $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} shows good radiation resistance for the neutrons, with a slight change after increasing the irradiation fluence up to 10^{19} n/m^2. Long-lasting emissions are exhibited after neutron irradiation, and the emission spectra have one peak due to Eu^{2+}. A peak due to Dy^{3+} ends immediately when the irradiation is stopped. Further, it is found that there is an optimum neutron fluence at which the longest decay time is obtained.

1. Introduction

Long-lasting phosphor (LLP) emits photons for a long period of time after the cessation of irradiation, without external excitation [1]. Strontium-aluminate-based long-lasting phosphors – $SrAl_2O_4$:Eu^{2+}, Dy^{3+} and $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} – are usually used as LLPs [2,3]. LLP exhibits not only a long-lasting emission but also strong fluorescence. Therefore, LLP is a good candidate for a radiation detection element on account of its strong luminescence [4,5]. Here, the luminescent material is a good candidate for the measurement tool of radiation intensity in ITER-like fusion reactor that is a strong electromagnetic field, because conventional electrical detector cannot use by the disturbance of electromagnetic force [6]. However, no irradiation test has been conducted for fusion neutrons of two types of strontium-aluminate-based LLPs. This study examines the fluorescence and long-lasting emission properties of two types of strontium-aluminate-based LLPs—$SrAl_2O_4$:Eu^{2+}, Dy^{3+} and $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} – under 14-MeV neutron irradiation.

2. Experimental

14-MeV neutron irradiation was performed at the deuterium–tritium neutron irradiation facility of the Fusion Neutronics Source (FNS) in the Japan Atomic Energy Agency (JAEA). Atomic displacement was the dominant interaction between the irradiated materials and the 14-MeV neutrons, and it caused electronic excitation as a secondary effect. The energy spectrum of the neutrons exhibited a sharp peak at 14 MeV, and the flux was in the range of 10^{10}–10^{13} n/m^2 s; the associated electronic excitation dose rate was less than a few milligray per second. The irradiation was carried out at RT for several days with an irradiation time of 7 h per day. Each day, at the end of irradiation, measurements of the long-lasting emission of the specimens were performed.

Two types of strontium–aluminate-based LLPs – $SrAl_2O_4$:Eu^{2+}, Dy^{3+} and $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} (NP-2830 and NP-2820, NICHIA Corporation) – were attached at one end of radiation-resistant optical fibers with a core diameter of 0.2 mm. Luminescence generated from a specimen under 14-MeV neutron irradiation and after the cessation of the irradiation was measured by an optical detector, which covered a distance of 40 m from the irradiation area to the detector. The optical fibers connecting the LLPs and the optical detector were generally placed in a low radiation area and shielded from direct exposure to the fast neutron irradiation. Thus, radiation-induced phenomena in the optical fibers were minimal. Detailed setups of the irradiation can be found elsewhere [5].

3. Results and discussion

The fluorescent spectra of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} and $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} exhibited under 14-MeV neutron irradiation are shown in Fig. 1. There are characteristic peaks arising from their dopants. The major peak of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} at 520 nm is attributed to the Eu^{2+}-substituted Sr^{2+} sites of the $SrAl_2O_4$ hosts. The peaks of $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} at 400 and 480 nm are also attributed to Eu^{2+}. Here, the $Sr_4Al_{14}O_{25}$ hosts have two different crystallographic sites for Sr^{2+} ions; further, the Eu^{2+} ion substitutes the Sr^{2+} site, leading

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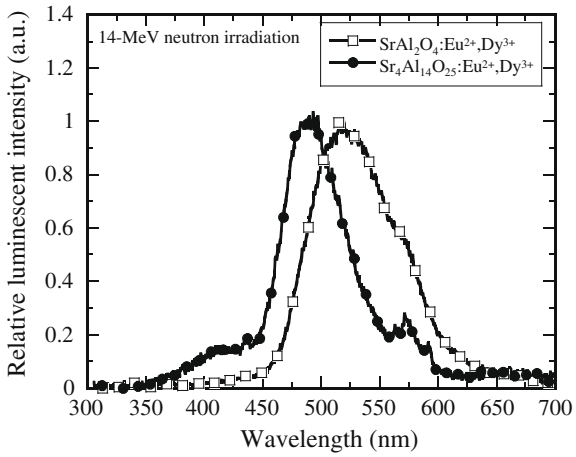

Fig. 1. Fluorescent spectra of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} and $Sr_4Al_{14}O_{25}$:Eu^{2+} under 14-MeV neutron irradiation.

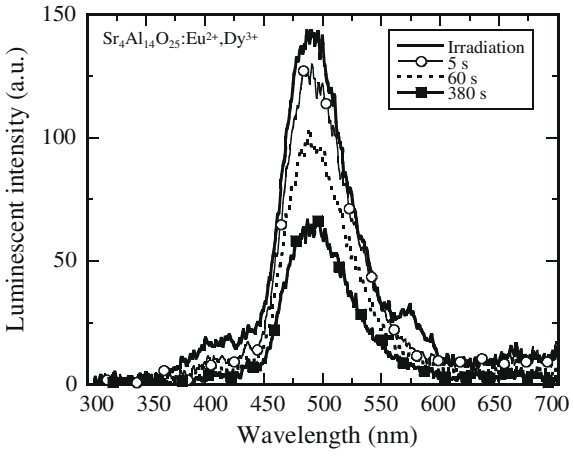

Fig. 3. Fluorescent spectrum and long-lasting emission spectra of $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+}. Time is set to zero when 14-MeV neutron irradiation is stopped.

to two types of Eu^{2+} sites [2]. Two peaks from Eu^{2+} in the fluorescent spectrum of $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} originate from the coordinate difference between the two Eu^{2+} sites. Moreover, the fluorescence attributed to Dy^{3+} is exhibited in both spectra at approximately 570 nm. In particular, the fluorescence of Dy^{3+} is clearly seen in the spectrum of $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+}. There are no reports of a fluorescent peak attributed to Dy^{3+}, although some researchers have performed ultraviolet (UV) irradiation experiments on strontium-aluminate-based materials. In typical materials that have dopants as a luminescent center, fluorescence is usually generated in the dopant by electronic excitation or external excitation. Therefore, it is considered that the electronic excitation in Eu^{2+} is mainly caused by UV irradiation, because the electronic excitation dose rate of UV irradiation is low. In this 14-MeV neutron irradiation, the local electronic excitation dose rate is high and electronic excitation is caused not only in Eu^{2+} but also in Dy^{3+}; this results in the generation of the fluorescence of Dy^{3+}, although the intensity is small as compared with the fluorescence of Eu^{2+}.

The 14-MeV neutron fluence dependencies of the intensities of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} at 520 nm and $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} at 480 nm are shown in Fig. 2. Here, some scatter of the measured intensity can be observed; this is caused by a large fluctuation in the 14-MeV neutron flux, which is due to the fluctuation of the deuteron beam current striking the tritiated target, and a low optical intensity of the signal. The fluorescent intensity of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} decreases as the irradiation fluence increases, although the fluorescent intensity of $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} shows good radiation resistance for the neutrons, with a slight change after increasing the irradiation fluence. $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} maintains the respective fluorescent intensities up to a fast neutron fluence of 10^{19} n/m^2.

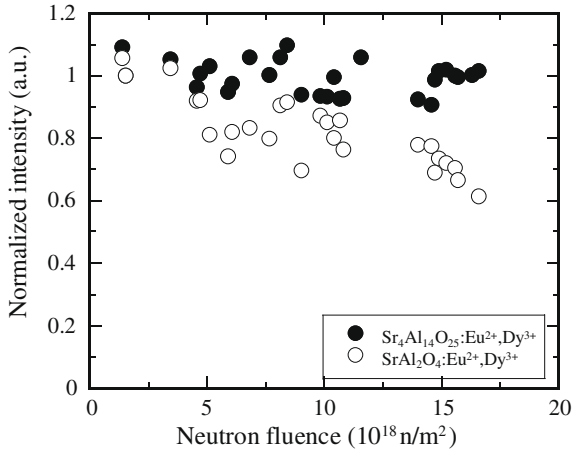

Fig. 2. 14-MeV neutron fluence dependencies of relative fluorescent peak intensities of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} at 520 nm and $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} at 480 nm.

Fig. 3 shows the fluorescent spectrum and long-lasting emission spectra of $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+}. Here, the time was set to zero when the fast neutron irradiation was stopped. Long-lasting emissions were exhibited after the 14-MeV neutron irradiation, similar to UV irradiation. The emission spectra have only the peaks attributed to Eu^{2+}, while the peak attributed to Dy^{3+} ends immediately when the fast neutron irradiation is stopped. Thus, a rapid change in the neutron flux could be monitored by the fluorescent peak intensity at 570 nm. The mechanism of long-lasting emission is explained as follows. The electrons and holes generated by external excitations are captured by Eu and Dy, respectively. After the external excitation is stopped, the trapped holes are released and recombine with the electrons in Eu, and long-lasting emission is observed in the energy transition of Eu. Therefore, only the peaks attributed to Eu^{2+} are observed, as shown in Fig. 3. In summary, Eu and Dy act as electron and hole trap centers, respectively. However, as seen in Figs. 1 and 3, Dy acts as not only a hole trap center but also a fluorescent center. Therefore, it is considered that Dy captures not only holes but also electrons. It is found that the number of electrons captured by Dy is much smaller than the number of electrons captured by Eu, because the fluorescent intensity of Dy is low and $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} shows a long-lasting property.

By changing the neutron fluence, a difference in the irradiation effect of 14-MeV neutrons for strontium-aluminate-based LLPs was observed. The elapsed time dependence of the long-lasting emission intensity of $SrAl_2O_4$:Eu^{2+},Dy^{3+} at 520 nm and that of $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} at 480 nm after the fast neutron irradiation was stopped is shown in Figs. 4 and 5, respectively, as a function of the neutron fluence. In both figures, some scatter of the measured intensity is caused by the low optical intensity of the signal. It is found that there is an optimum neutron fluence at which the longest decay time is obtained. In this experiment, $SrAl_2O_4$:Eu^{2+}, Dy^{3+} and $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} have the longest decay time due to the irradiation at the neutron fluences of 5.12×10^{18} and 7.58×10^{18} n/m^2, respectively. The decay time is analyzed by curve fitting [3]. The obtained decay data can be successfully fitted based on the following multiple exponential equation:

$$I = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right) + A_3 \exp\left(\frac{-t}{\tau_3}\right) \quad (1)$$

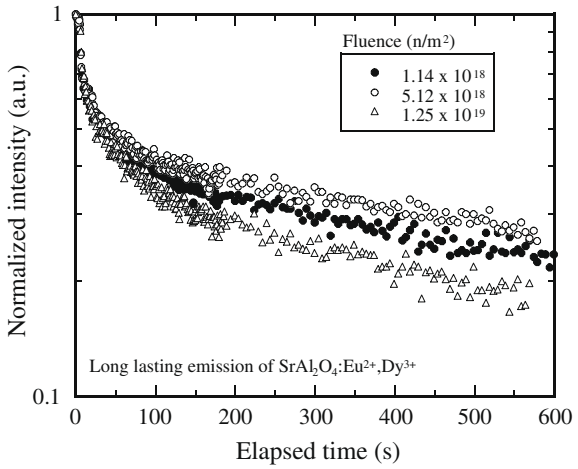

Fig. 4. Elapsed time dependence of long-lasting emission intensity of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} at 520 nm after fast neutron irradiation is stopped as a function of neutron fluence.

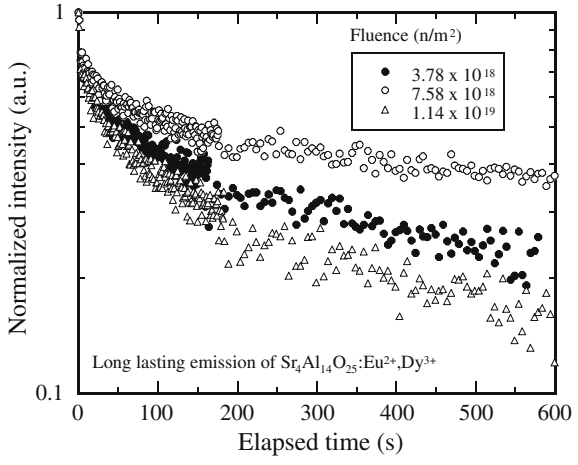

Fig. 5. Elapsed time dependence of long-lasting emission intensity of $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+} at 480 nm after fast neutron irradiation is stopped as a function of neutron fluence.

where I represents the long-lasting emission intensity; A_1, A_2, and A_3 are constants; t is the time; and τ_1, τ_2, and τ_3 are the decay times for the exponential components. The parameters τ_1, τ_2, and τ_3 are calculated from Figs. 4 and 5, and the results are shown in Tables 1 and 2. The decay times of the strontium-aluminate-based LLPs change due to the 14-MeV neutron irradiation. The decay time components of τ_3 have the largest values in both the LLPs, although the change in the other decay time components has no regularity for the increase in the neutron fluence. τ_2 and τ_3 of $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+} have the largest values with a fluence of 5.12×10^{18} n/m^2, and the decay time of τ_3 is longer than tripled than lower neutron fluence. The 14-MeV neutron irradiation primarily causes atomic displacement effects. The decay time of the LLPs is mainly based on the energy levels of the hole trap centers, and a longer decay time has a deeper hole trap level. Therefore, it is considered that

Table 1
Decay times of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} at 520 nm with different 14-MeV neutron fluences.

Fluence (n/m^2)	Decay time (τ, s)		
	τ_1	τ_2	τ_3
1.14×10^{18}	7.39	62.12	1225.6
5.12×10^{18}	7.46	54.54	1391.5
1.25×10^{19}	8.91	70.35	1047.7

Table 2
Decay times of $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+} at 480 nm with different 14-MeV neutron fluences.

Fluence (n/m^2)	Decay time (τ, s)		
	τ_1	τ_2	τ_3
3.77×10^{18}	2.22	53.06	857.5
7.58×10^{18}	2.19	79.69	2801.6
1.14×10^{19}	1.67	60.32	723.6

the material structure of the LLPs, particularly Dy and/or the surrounding atoms of Dy, is modified by the displacement effects of neutron irradiation. Therefore, energy levels change and/or new hole trap levels are generated; this results in a change in the decay time.

4. Conclusion

Irradiation tests for two types of strontium-aluminate-based LLPs – $SrAl_2O_4:Eu^{2+}$, Dy^{3+} and $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+} – have been carried out under 14-MeV neutron irradiation to examine their fluorescence and long-lasting emission properties. The fluorescent spectra have characteristic peaks caused by their dopants, Eu^{2+} and Dy^{3+}. The peak at 570 nm is attributed to the luminescence of Dy^{3+}; it exhibits no luminescence after the irradiation has been stopped. The other peaks are attributed to the luminescence of Eu^{2+} and exhibit the long-lasting emission property. Radiation damage is different in both the phosphors, and the fluorescent intensity of $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+} shows good radiation resistance for the neutrons, with a slight change after increasing the irradiation fluence up to 10^{19} n/m^2. Long-lasting emissions are exhibited after the 14-MeV neutron irradiation, and the emission spectra have one peak due to Eu^{2+}. Further, it is found that there is an optimum neutron fluence at which the longest decay time is obtained, and in this experiment, $SrAl_2O_4:Eu^{2+}$, Dy^{3+} and $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+} have the longest decay time due to the irradiation at the neutron fluences of 5.12×10^{18} and 7.58×10^{18} n/m^2, respectively.

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