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Luminescence of $NaGdF_4:Tb^{3+}$, Eu^{3+} under vacuum ultraviolet excitation

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Abstract

Luminescence and excitation spectra of $NaGdF_4:Tb^{3+}$, Eu^{3+} have been investigated. The luminescence spectrum consists of the luminescence lines originating from the f–f transition of Tb^{3+} and Eu^{3+} ions. In the excitation spectrum for the luminescence line of Eu^{3+} ions at 614 nm, excitation bands arising from the f–d transition of Tb^{3+} ions are observed in the vacuum ultraviolet (VUV) spectral region ranging from 160 to 210 nm. It is found that, by replacing Gd^{3+} with Y^{3+}, the intensities of the luminescence lines from Eu^{3+} ions weaken compared to those from Tb^{3+} ions. The luminescence of Eu^{3+} ions is found to weaken with decreasing temperature. On the basis of the present results, we discuss the energy transfer process in $NaGdF_4:Tb^{3+}$, Eu^{3+} under the VUV excitation.

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Keywords: Energy transfer; Vacuum ultraviolet; Fluorides; Rare-earth ions

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1. Introduction

Rare-earth ions doped fluoride phosphors have been actively studied with the aim of developing new phosphors suitable for use in xenon dimer (Xe_2) discharge fluorescent lamps. Since Xe_2 discharge generates vacuum ultraviolet (VUV) light peaking at ∼172 nm, the phosphors for white light fluorescent lamps need to convert the VUV light efficiently into blue, green and red light.

According to [1], $LiGdF_4:Eu^{3+}$ absorbs the VUV light (∼172 nm) due to the $4f^7 \rightarrow 4f^7$ (f–f) transition in Gd^{3+} ions, and yields red light (614 nm) arising from the f–f transition in Eu^{3+} with high conversion efficiency, as compared to $LiYF_4:Eu^{3+}$. When the Gd^{3+} ion in $LiGdF_4:Eu^{3+}$ is excited by one VUV photon, two red photons can be emitted by the Eu^{3+} ions through a two-step energy transfer from Gd^{3+} to Eu^{3+} ions. Such a conversion process is called "quantum cutting" [1]. However, the absorption due to the dipole-forbidden f–f transition is weak, so that the conversion of the VUV light through the absorption by Gd^{3+} ions is inefficient.

A possible way out of the problem is introducing of sensitizers that strongly absorb the VUV light, and efficiently give the absorbed energy to activators yielding the visible luminescence. It has been found that Tb^{3+} ions in $LiYF_4$ strongly absorb the VUV light ranging from 170 to 220 nm due to the dipole-allowed $4f^8 \rightarrow 4f^7\,5d$ (f–d) transition [2]. This implies that Tb^{3+} ions act as sensitizers suitable for the excitation of VUV light generated from Xe_2 discharge. We expect that $NaGdF_4:Tb^{3+}$, Eu^{3+} efficiently absorbs the VUV light in Tb^{3+} ions and gives the absorbed energy to Eu^{3+} ions.

In this study, we have investigated luminescence and excitation spectra of $NaGdF_4:Tb^{3+}$, Eu^{3+}. The luminescence spectrum consists of the luminescence lines originating from the f–f transition of Eu^{3+} and Tb^{3+} ions. In the excitation spectrum for the luminescence line of Eu^{3+} ions at 614 nm, there appear excitation bands arising from the f–d transition of Tb^{3+} ions in the VUV spectral region ranging from 160 to 210 nm. By replacing Gd^{3+} with Y^{3+}, the luminescence lines

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from Eu^{3+} ions weaken compared to those from Tb^{3+} ions. In addition, the luminescence lines of Eu^{3+} ions weaken with decreasing temperature. On the basis of the present results, we discuss the energy transfer process in $NaGdF_4$:Tb^{3+}, Eu^{3+} excited by the VUV light.

2. Experiment

Fluoride powders of NaF, YF_3, EuF_3, GdF_3 and TbF_3 were used as starting materials for firing. After dried by heating at 500 °C in vacuum for 2 h, the mixture in a carbon crucible was heated up to 750 °C in an Ar gas atmosphere (0.5 atm) for 5 h.

For measurements of luminescence spectra, the samples were excited by an ArF excimer laser (oscillation wavelength: 193 nm, pulse width: 15 ns) operating at a repetition rate of 20 Hz. The energy density on the samples was about ~50 μJ/cm^2 per pulse. The detection was performed by using a grating spectrometer (focal length: 25 cm) equipped with a CCD. The luminescence spectra were corrected by the sensitivity of the detection system. The sample was cooled down to 12 K by a closed-cycle cryogenic refrigerator. Measurements of excitation spectra were carried out with the use of synchrotron orbital radiation at the beam line 1B of UVSOR facility (Institute for Molecular Science, Okazaki, Japan). A 1 m Seya-Namioka type monochromator was used to obtain the monochromatic exciting light. The luminescence from the samples was detected by a photomultiplier tube equipped with a grating monochromator (focal length: 30 cm). The excitation spectra were corrected by the intensity distribution of the exciting light.

3. Results and discussion

On the right-hand side of Fig. 1 (300–750 nm) are shown luminescence spectra of $NaGdF_4$:Eu^{3+} (1 mol%) and $NaGdF_4$:Tb^{3+} (1 mol%), Eu^{3+} (1 mol%) excited by an ArF excimer laser (193 nm) measured at 300 K. The spectra have been normalized at the maximum. In the luminescence spectrum of $NaGdF_4$:Eu^{3+}, a number of luminescence lines are recognized. Almost all the luminescence lines are attributed to the f–f transition of Eu^{3+} ions. The most prominent line at 614 nm is assigned to the transition from $^5D_0$ to $^7F_2$ state [3]. On the other hand, the luminescence spectrum of $NaGdF_4$:Tb^{3+}, Eu^{3+} consists of the luminescence lines arising from the f–f transition of both Eu^{3+} and Tb^{3+} ions. The luminescence line at 545 nm is attributable to the transition from $^5D_4$ to $^7F_5$ state in Tb^{3+} ions [4].

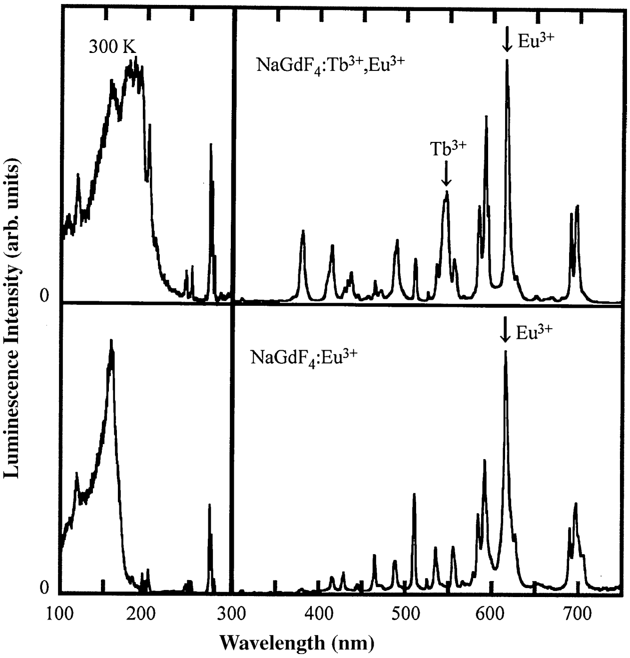

Fig. 1. Luminescence spectra (300–750 nm) excited by an ArF excimer laser (193 nm) and excitation spectra (100–300 nm) monitoring the luminescence lines at 614 nm for $NaGdF_4$:Eu^{3+} (1 mol%) and $NaGdF_4$:Tb^{3+} (1 mol%), Eu^{3+} (1 mol%) measured at 300 K.

Spectra on the left-hand side of Fig. 1 (100–300 nm) show excitation spectra monitoring the luminescence lines at 614 nm for the two samples. In both of the excitation spectra, there appear several excitation lines originating from the f–f transition of Gd^{3+} ions in the UV spectral region ranging from 200 to 300 nm. Specifically, the excitation lines at around 200, 250 and 270 nm are attributed to the transition from $^8S_{7/2}$ ground state to ^6G_J, ^6D_J and ^6I_J state of Gd^{3+}, respectively [3]. This indicates that Gd^{3+} ions provide the absorbed energy for Eu^{3+} ions. An excitation band observed at ~150 nm has been unsettled in origin, but probably associated with Gd^{3+} ions. By comparing the excitation spectra in the VUV spectral region, we notice that additional excitation bands appear in the spectral range of 160–210 nm in $NaGdF_4$:Tb^{3+}, Eu^{3+}. One can ascribe these excitation bands to the f–d transition of Tb^{3+} ions [2]. Accordingly, it is obvious that the energy transfer from Tb^{3+} to Eu^{3+} ions takes place in $NaGdF_4$:Tb^{3+}, Eu^{3+} at room temperature. It should be pointed out that most of the VUV light generated by Xe_2 discharge is absorbed by the Tb^{3+} ions, because the absorption due to the dipole-allowed f–d transition of Tb^{3+} is strong [5].

In order to clarify the role of Gd^{3+} ions in the energy transfer from Tb^{3+} to Eu^{3+} ions, we have examined luminescence spectra by replacing Gd^{3+} ions with Y^{3+} ions at room temperature. The results of $NaY_{1-x}Gd_xF_4$:Tb^{3+}, Eu^{3+} ($0 \leq x \leq 1$) are shown in Fig. 2. Each spectrum has been normalized at the maximum. For the Gd^{3+} concentration $x = 1$–0.75, the luminescence spectrum remains almost unchanged. As x decreases from 0.5 to 0, the relative intensity of luminescence lines of Tb^{3+} ions (left-hand side arrow) to those of Eu^{3+} ions (right-hand side one) gradually increases. From this result, the energy transfer rate from Tb^{3+} to Eu^{3+} ions reduces by replacing Gd^{3+} ions with Y^{3+} ions.

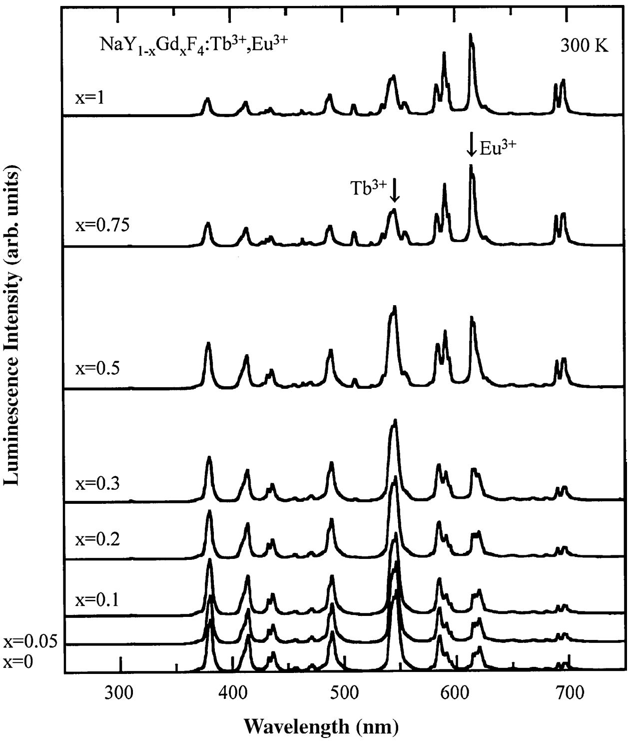

Fig. 2. Luminescence spectra of $NaY_{1-x}Gd_xF_4$:Tb^{3+}, Eu^{3+} ($0 \leq x \leq 1$) excited by an ArF excimer laser at 300 K.

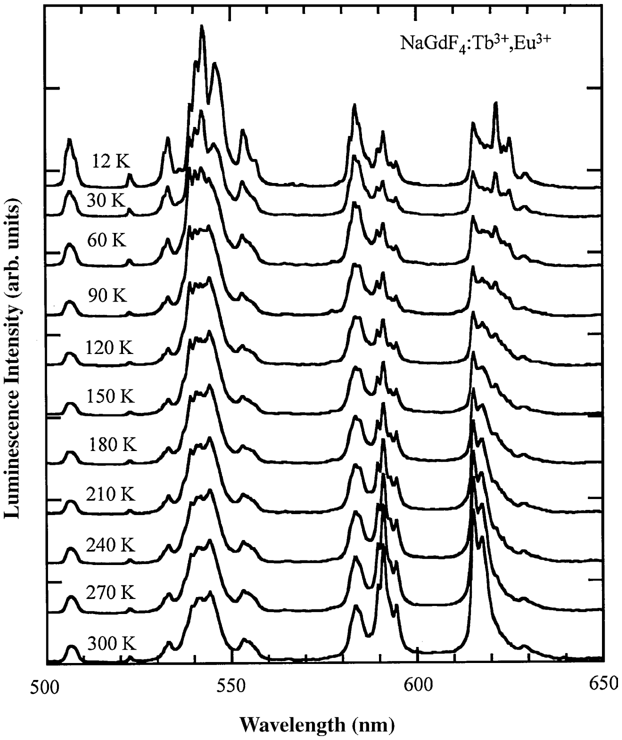

Fig. 3. Luminescence spectra (500–650 nm) of $NaGdF_4$:Tb^{3+}, Eu^{3+} excited by an ArF excimer laser, measured at various temperatures (12–300 K).

Fig. 3 demonstrates luminescence spectra of $NaGdF_4$:Tb^{3+}, Eu^{3+} measured at various temperatures (12–300 K) in the visible spectral region (500–650 nm). As is shown in Fig. 3, the energy transfer rate from Tb^{3+} to Eu^{3+} ions is also dependent on temperature. As the temperature decreases, the luminescence from Eu^{3+} ions gradually weakens, but remains almost unchanged below ~150 K. On the other hand, the luminescence from Tb^{3+} ions strengthens with decreasing temperature at ~150 K. The intensities of luminescence lines of Tb^{3+} ions become stronger than those of Eu^{3+} ions at lower temperatures. The result shows that the energy transfer rate from Tb^{3+} to Eu^{3+} ions becomes small at low temperatures. This suggests that the energy transfer involves thermal activation process.

On the basis of the energy transfer process reported for Gd compounds so far, we can interpret the energy transfer process in $NaGdF_4$:Tb^{3+}, Eu^{3+}. It has been reported that Ce^{3+} ions in $NaGdF_4$:Ce^{3+}, Eu^{3+} absorb the UV light generated from Hg discharge (254 nm) due to the dipole-allowed f–d transition, and the absorbed energy is efficiently transferred to the Eu^{3+} ions, yielding the luminescence of the f–f transition by the medium of Gd^{3+} ions [6]. Recently, we have found that Pr^{3+} ions in $NaGdF_4$:Pr^{3+}, Eu^{3+} absorb the VUV light (~172 nm) due to the f–d transition, and the absorbed energy is transferred to Eu^{3+} ions through the three-step energy transfer process: (1) from Pr^{3+} to Gd^{3+} ions; (2) from Gd^{3+} to Gd^{3+} ions; and (3) from Gd^{3+} to Eu^{3+} ions [7].

After Tb^{3+} ions in $NaGdF_4$:Tb^{3+}, Eu^{3+} absorb the VUV light, some of the excited Tb^{3+} ions relax from $4f^75d^1$ states to $4f^8$ states accompanied by the phonon emission, and give rise to the luminescence due to the f–f transition. Other Tb^{3+} ions supply the absorbed energy to the neighboring Gd^{3+} ions. Based on the energy overlap, the Tb^{3+} ions in the $4f^75d^1$ state would give the energy to the ^6D_J and/or ^6I_J state in the Gd^{3+} ions. The excited Gd^{3+} ions relax to the lowest ^6P_J excited state. After the relaxation, the excitation energy migration between the Gd^{3+} ions takes place [8,9].

According to [10], the energy migration is due to the exchange interaction between the Gd^{3+} ions, so that the migration rate is strongly dependent on the distance between the Gd^{3+} ions, namely the concentration of Gd^{3+} ions. It was also reported in [10] that there are trap states resulting from Gd^{3+} ions on some crystallographic sites in hexagonal $NaGdF_4$. Those trap states hamper the energy migration at low temperatures. The activation energy is smaller than the thermal energy at room temperature, so that the trap states are emptied and do not hamper the energy transfer at room temperature [9]. Owing to the energy migration through Gd^{3+} ions, the excitation energy can reach both Eu^{3+} and Tb^{3+} ions, yielding the luminescence of the f–f transition. Whether or not the quantum cutting process via the energy transfer from Tb^{3+} to Eu^{3+} occurs was unclear in the present experiment. The investigation is now in progress, and the results will be reported in the near future.

In conclusion, the efficient energy transfer from Tb^{3+} to Eu^{3+} through Gd^{3+} takes place in $NaGdF_4$:Tb^{3+}, Eu^{3+} excited by the VUV light generated from Xe_2 discharge at room temperature. As a result of the energy transfer, $NaGdF_4:Tb^{3+}$, Eu^{3+} shows reddish white luminescence which consists of the luminescence lines arising from the f–f transition of Tb^{3+} and Eu^{3+}.

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