Energy transfer in $NaGdF_4$: Pr^{3+}, Eu^{3+} under vacuum ultraviolet excitation

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Several groups have actively researched fluoride phosphors that efficiently convert vacuum ultraviolet (VUV) light generated by Xe dimer (Xe_2) discharge (wavelength ~172 nm) into visible (VIS) or ultraviolet (UV) light. Wegh *et al.* reported that Eu^{3+} and Gd^{3+} ions in $LiYF_4$ absorb the VUV light at around 170 nm due to the *f-f* transitions, and yield red luminescence (614 nm) and UV luminescence (311 nm), respectively [1]. Unfortunately, the conversion of the VUV light in the Eu^{3+} and Gd^{3+} ions is unlikely to be efficient, since the absorption of the VUV light by those ions should be weak because of the dipole-forbidden *f-f* transitions.

One of ideas to solve the problem is that, into the fluorides doped with activated ions such as Eu^{3+} and Gd^{3+} ions, one introduces certain ions called sensitizers that strongly absorb the VUV light and efficiently give the absorbed energy to the activated ions. Pr^{3+} ions are expected to act as suitable sensitizers, because strong absorption of the VUV light generated from the Xe_2 discharge (~172 nm) is possible due to the dipole-allowed *f-d* transition. In fact, it has been found in YF_3: Pr^{3+}, Gd^{3+} phosphors that the Pr^{3+} ions absorb the VUV light (~180 nm) and give the absorbed energy to the Gd^{3+} ions, yielding the UV luminescence (311 nm) [2]. On the other hand, it has been reported that, in $NaGdF_4$: Ce^{3+}, Eu^{3+} phosphors, the Ce^{3+} ions absorb UV light (~250 nm) due to the *f-d* transitions and the absorbed energy is transferred to the Eu^{3+} ions through the sublattice formed by the Gd^{3+} ions [3]. In the present study, we have examined whether the energy transfer from the Pr^{3+} ions to the Eu^{3+} ions through the Gd^{3+} sublattice occurs or not in $NaGdF_4$: Pr^{3+}, Eu^{3+} phosphors.

On the right-hand side of Fig. 1 are shown luminescence spectra of (a) $NaGdF_4$, (b) $NaGdF_4$: Pr^{3+}, (c) $NaGdF_4$: Eu^{3+} and (d) $NaGdF_4$: Pr^{3+}, Eu^{3+} at room temperature. The excitation was made by an ArF excimer laser (193 nm). The spectra on the left-hand side show excitation spectra for the luminescence lines denoted by the arrows. Measurements of the excitation spectra were carried out with the use of synchrotron orbital radiation (UVSOR facility, Institute for Molecular Science, Okazaki, Japan).

In the luminescence spectra of $NaGdF_4$ and $NaGdF_4$: Pr^{3+} (Fig. 1(a) and (b)), a prominent luminescence line is observed at 311 nm. This luminescence line is attributable to the *f-f* transition from $^6P_{7/2}$ state to $^8S_{7/2}$ ground state in the Gd^{3+} ion. One can see from the results of the excitation spectra that there appear excitation bands at around 180 nm in $NaGdF_4$: Pr^{3+}, unlike the case of $NaGdF_4$. The excitation bands originate from the *f-d* transitions in the Pr^{3+} ion. This result indicates that the Gd^{3+} sublattice can accept the absorbed energy from the Pr^{3+} ion.

In the luminescence spectra of $NaGdF_4$: Eu^{3+} and $NaGdF_4$: Pr^{3+}, Eu^{3+} (Fig. 1(c) and (d)), a number of luminescence lines can be seen in the VIS region. Almost all the luminescence lines arise from the *f-f* transitions of the Eu^{3+} ion. The noticeable luminescence line at 615 nm is attributed to the transition from $^5D_0$ to $^7F_2$ state in the Eu^{3+} ion. In the excitation spectrum of $NaGdF_4$: Pr^{3+}, Eu^{3+}, extra excitation bands can be observed at around 180 nm, as contrasted with that of $NaGdF_4$: Eu^{3+}. The excitation bands are surely due to the *f-d* transition of the Pr^{3+} ion. Accordingly, the results show the *f-d* absorption in the Pr^{3+} ion results in the VIS luminescence of the Eu^{3+} ion via the Gd^{3+} sublattice.

The energy transfer process from the Pr^{3+} ions to the Eu^{3+} ions through the Gd^{3+} sublattice in $NaGdF_4$: Pr^{3+}, Eu^{3+} will be discussed in detail. The results of $NaGdF_4$: Tb^{3+}, Eu^{3+} will be also presented.

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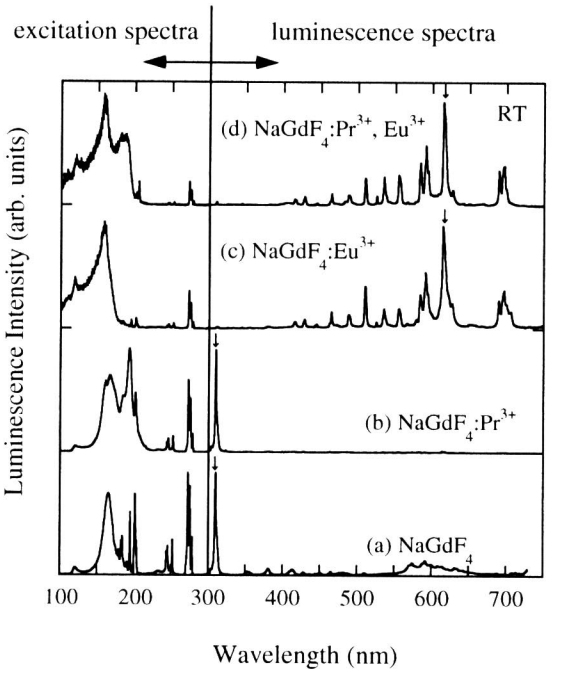

Fig. 1. Luminescence spectra (300-750 nm) excited with an ArF excimer laser (193 nm) and excitation spectra (100-300 nm) for the luminescence lines denoted by the arrows in (a) $NaGdF_4$, (b) $NaGdF_4$: Pr^{3+}, (c) $NaGdF_4$: Eu^{3+} and (d) $NaGdF_4$: Pr^{3+}, Eu^{3+} at room temperature.