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Energy migration and transfer of Tm^{3+}-Gd^{3+}-Dy^{3+} system in $NaGdF_4$ under VUV and UV excitations

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Abstract

Based on the basis of the quantum cutting principle, the possibility to obtain two blue photons under excitation of one VUV photon in $NaGdF_4$:Tm^{3+}, Dy^{3+} has been studied using spectroscopic technique. The $Gd^{3+} \rightarrow Dy^{3+}$ transfer preceded by energy migration among the Gd^{3+} ions is mainly governed by the exchange interaction. The quantum efficiencies for the $Gd^{3+} \rightarrow Dy^{3+}$ energy transfer have an optimal value for acceptor concentration at about $N_A = 0.6$ at% and concentration quenching can be observed obviously.

Keywords: $NaGdF_4$:Tm^{3+}; Dy^{3+}; Energy migration and transfer; Cross-relaxation; Quantum efficiency

1. Introduction

The vacuum ultraviolet (VUV)-excited phosphors required for mercury-free fluorescent lamps and plasma display panels (PDP) have recently been attracting more and more attention. Specially, on the basis of the principle of the so-called quantum cutting (down-conversion) [1,2], one VUV photon excitation results in two visible photons in $LiGdF_4$:Eu^{3+} and $LiGdF_4$:Er^{3+}, Tb^{3+}. Quantum efficiencies in two compounds are up to 195% and 130%, respectively.

In this paper, the possibility to obtain a new quantum cutting phosphor with a higher efficiency, a higher stability and higher VUV absorption based on $NaGdF_4$:Tm^{3+}, Dy^{3+} has been investigated. The spectroscopic techniques, including luminescent emission, excitation, decay, etc. were performed to characterize the donor Gd^{3+} ion → acceptor Dy^{3+} ion energy transfer preceded by energy migration among Gd^{3+} lattices in $NaGdF_4$ doped with different at% Dy^{3+} ions. By the theory on excited state relaxation processes, which was developed by Burshtein et al. [3,4], the donor → acceptor energy transfer parameter k_{DA} can be calculated from the decay of Gd^{3+} $^6P_{7/2}$ emission. The quantum efficiency η_{DA} of $Gd^{3+} \rightarrow Dy^{3+}$ energy transfer was derived as well.

2. Experiments

Powders of $NaGdF_4$:Tm^{3+} (1.5 at%) and $NaGdF_4$:Tm^{3+} (1.5 at%), Dy^{3+} (0.3 at%) were prepared by the hydrothermal technique [5], and that of $NaGdF_4$:Dy^{3+} (0.3, 0.6, 1, 3 and 5 at%) by the method described in Ref. [4]. The emission and excitation spectra were measured by home- made VUV spectrometer and F4500 monochrometer. The decay curves were obtained under excitation of OPO laser. All experiments were performed at room temperature.

3. Results and discussion

Under excitation of $4f^{12} \rightarrow 4f^{11}5d$ (157 nm) transition of Tm^{3+}, the 4f → 4f intraconfiguration transitions $^4D_2 \rightarrow {}^3F_4$ (457 nm), $^1G_4 \rightarrow {}^3H_6$ (483 nm) and $^4D_2 \rightarrow {}^3H_5$ (546 nm) of Tm^{3+} were observed in $NaGdF_4$:Tm^{3+} sample. Under $4f^{12} \rightarrow 4f^{11}5d$ excitation of Tm^{3+} (157 nm) the 4f → 4f transitions $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (470–500 nm) of Dy^{3+} are dominant in $NaGdF_4$:Tm^{3+}, Dy^{3+} emission spectra. There exists a cross-relaxation process which is probably the main channel that makes the energy transfer from Tm^{3+} to Gd^{3+} following with light blue emission $^1G_4 \rightarrow {}^3H_6$

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(483 nm) of Tm^{3+}. The energy migration and transfer of Gd^{3+} may result in the appearance of the adjacent Dy^{3+} ions to the $^4F_{9/2}$→excited state; afterwards another light blue emission $^4F_{9/2}\rightarrow{}^6H_{15/2}$ (470–500 nm) of Dy^{3+} will appear as well, see Fig. 1. Such a conversion of VUV energy to visible light due to the energy transfer from the 5d state of the Tm^{3+} ion to the Gd^{3+} ion by cross-relaxation and $Gd^{3+}\rightarrow Dy^{3+}$ energy transfers gives rise to the emission of two visible photons instead of emitting one ultraviolet quantum (quantum cutting). It is indicated that $NaGdF_4$:Tm^{3+}, Dy^{3+} is a good candidate from which two light blue photons can be obtained under one VUV photon excitation.

The $Gd^{3+}\rightarrow Dy^{3+}$ energy transfers which is preceded by energy migration among Gd^{3+} lattice in $NaGdF_4$: Dy^{3+}(0.3, 0.6, 1, 3 and 5 at%) sample were studied. The emission spectra under the excitation of 274 nm, corresponding to the transition $^8S_{7/2}\rightarrow{}^6I_J$ of Gd^{3+} ion are given in Fig. 2. The decay curves of the $^6P_J\rightarrow{}^8S_{7/2}$ (311 nm) of Gd^{3+} ions are shown in Fig. 3. The rise time observed in the decay curves is due to the instrument response.

On the basis of the theory developed by Burshtein et al. [3], the decay of the donor emission can be successfully described by an exponential function. It is written as

$$I(t) = I(0)\exp[-t/\tau_0 - k_{DA}t - \Delta], \quad (1)$$

where $1/\tau_0$ is the decay rate of the isolated donor ion, k_{DA} a parameter which characterizes the donor→acceptor (i.e. the $Gd^{3+}\rightarrow Dy^{3+}$) energy transfer preceded by energy migration among the donor ions and $\exp(-\Delta)$ represents the portion of the excitation energy that is not lost by direct transfer. The parameters k_{DA} for the various at% Dy^{3+} were obtained by fitting the decay curves of Gd^{3+} donors by Eq. (1), listed in Table 1.

For donor→acceptor transfer via dipole–dipole interaction with high donor concentrations, the following

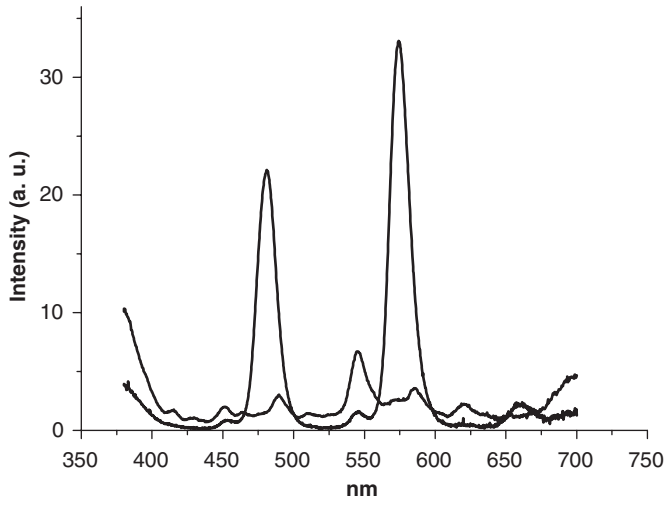

Fig. 1. Emission spectra of $NaGdF_4$:Tm^{3+} (a) and $NaGdF_4$:Tm^{3+}, Dy^{3+} under excitation of 157 nm.

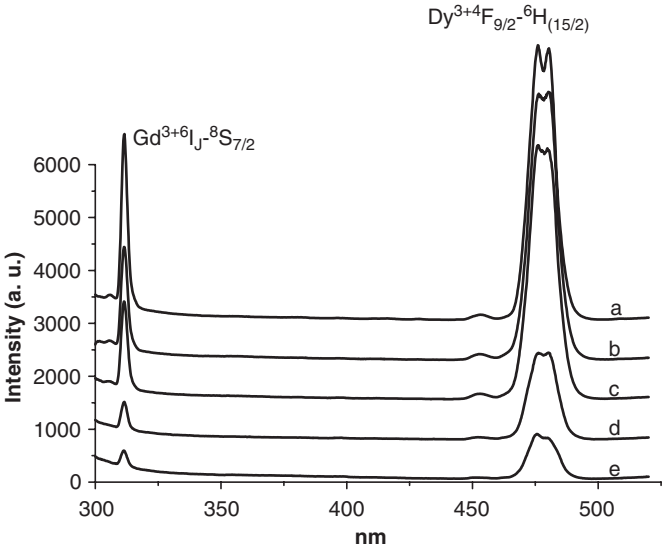

Fig. 2. Emission spectra of $NaGdF_4$: Dy^{3+}(0.3(a), 0.6(b), 1(c), 3(d) and 5 at%(e)) upon excitation of 274 nm.

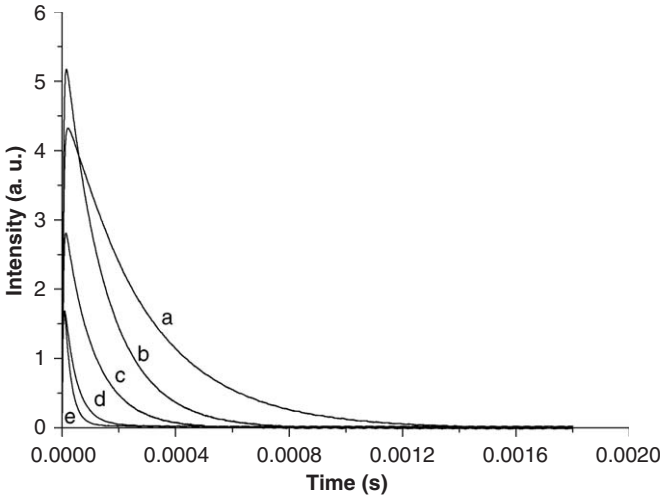

Fig. 3. Decay curves of the Gd^{3+} $^6P_{7/2}$ emission (311 nm) in $NaGdF_4$:Dy^{3+}(0.3(a), 0.6(b), 1(c), 3(d) and 5 at%(e)). Excitation is the $^8S_{7/2}\rightarrow{}^6I_J$ (274 nm) of Gd^{3+}.

is valid:

$$k_{DA} = N_A C_{DA} \sum_{i=1}^{\infty} R_i^{-6}, \quad (2)$$

where C_{DA} is the donor→acceptor interaction parameter, N_A is at% concentration of the acceptor. For donor→acceptor transfer via exchange interaction, we have

$$k_{DA} = N_A C_{DA} \sum_{i=1}^{\infty} \exp(-2R_i/L_{DA}), \quad (3)$$

where $L_{DA}\approx 0.29$ Å is the effective Bohr radius of Gd^{3+} [6]. Fitting the data in Fig. 4. with Eqs. (2) and (3), $C_{DA} = 3.4\times 10^{-58}\,s^{-1}$ and $C_{DA} = 1.6\times 10^{8}\,s^{-1}$ can be derived, respectively. From the former, the critical distance for energy migration among the Gd^{3+} ions $R_{cr}^{DA} = (\tau_0 C_{DA})^{1/6} =$

Table 1
Concentration of Dy^{3+} in NaGdF4, fit parameter k_{DA} and quantum efficiencies

$NaGdF_4$: Dy^{3+} (at%)	k_{DA} ($10^3\,s^{-1}$)	η_{DA}
0.3	3.1	0.34
0.6	6.8	0.44
1	9.5	0.32
3	18.7	0.06
5	39.4	0.04

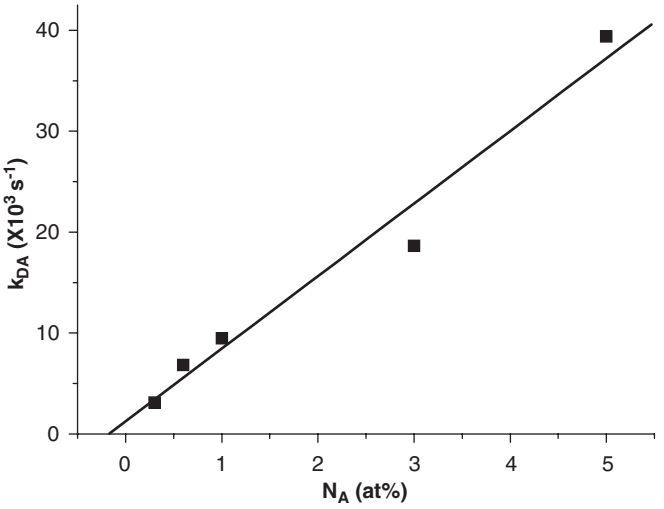

Fig. 4. The fit parameter k_{DA} of the Gd^{3+} $^6P_{7/2}$ emission curves in $NaGdF_4$:Dy^{3+} dependence of relative concentration N_A for the acceptor Dy^{3+}.

1.17 Å <4 Å ([6]) was derived. It means that energy transfer $Gd^{3+}\rightarrow Dy^{3+}$ does not have to be preceded by energy migration among the Gd^{3+} ions. Obviously, Eq. (2) for donor→acceptor transfer via dipole–dipole interaction cannot be used to describe this process perfectly. The latter seems more reasonable. The result that $Gd^{3+}\rightarrow Dy^{3+}$ transfer in $NaGdF_4$ is governed by exchange interaction is in line with conclusions in other studies on the energy migration [6] in $NaGdF_4$.

The decay time dependence of Eq. (1) implies a quantum efficiency given by

$$\eta_{DA} = \left[\int_0^\infty I(t)\mathrm{d}t\right] \Big/ \int_0^\infty I(0)\exp(-t/\tau_0)\mathrm{d}t = 1/\tau_0 \int_0^\infty \exp(-t/\tau_0 - k_{DA}t - \Delta)\mathrm{d}t. \quad (4)$$

The integral in Eq. (4) can be solved by standard technique,

$$\eta_{DA} = (1/\tau_0 k)\{1 - \sqrt{\pi}\, x\, \exp(x^2)[1 - \mathrm{erf}(x)]\} \quad (5)$$

where $k = 1/\tau_0 + k_{DA} + \Delta$, $x = k'_{DA}/2\sqrt{k}$, k'_{DA} is a parameter that characterizes the donor→acceptor process without energy migration, and erf(x) is the error function. The quantum efficiencies of $Gd^{3+}\rightarrow Dy^{3+}$ transfer obtained by Eq. (5) have been listed in Table 1. The two points are shown that the quantum efficiencies have an optimal value at $N_A = 0.6$ at% and concentration quenching obviously.

4. Conclusions

The possibility to obtain a new phosphor with a higher efficiency, a higher stability and higher VUV absorption based on $NaGdF_4$:Tm^{3+}, Dy^{3+} has been studied. It is indicated that $NaGdF_4$:Tm^{3+}, Dy^{3+} is a good candidate from which two light-blue photons can be obtained etc. under one VUV photon excitation. The $Gd^{3+}\rightarrow Dy^{3+}$ transfer is mainly governed by the exchange interaction. The quantum efficiencies for the $Gd^{3+}\rightarrow Dy^{3+}$ transfer have an optimal value at $N_A = 0.6$ at% and concentration quenching obviously.

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