Vacuum ultraviolet spectroscopic properties of Pr^{3+} in MYF_4 (M = Li, Na, and K) and $LiLuF_4$

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Abstract

$LiYF_4$, $NaYF_4$, KYF_4 and $LiLuF_4$ doped with Pr^{3+} were synthesized by hydrothermal technique. Vacuum ultraviolet excitation and emission properties were investigated at 20 K. A new type of photon cascade emission was observed in $LiYF_4:Pr^{3+}$ and $LiLuF_4:Pr^{3+}$, i.e. a first-step $4f5d \rightarrow 4f^2$ emission followed by a second $4f^2 \rightarrow 4f^2$ emission. In addition, the internal quantum efficiency of Pr^{3+} in $NaYF_4$ and KYF_4 within visible range was proved to be larger than unity using the branching ratios data corrected by the emission spectra of $YF_3:Pr^{3+}$.
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1. Introduction

The photon cascade emission (PCE) phenomenon was first observed in YF_3 [1,2], and recently intense studies on the PCE materials have been triggered by the need for new vacuum ultraviolet (VUV) phosphors and scintillator materials. In order to observe PCE by Pr^{3+}, it was required that the lowest energy 4f5d state was higher than the $^1S_0$ state, otherwise PCE could not take place generally [3].

In this paper, we present another PCE process in which the first step is parity-allowed interconfigurational $4f5d \rightarrow 4f^2$ transition, and the second step is parity-forbidden intraconfigurational $4f^2 \rightarrow 4f^2$ transition, even if the $^1S_0$ state is higher than the lowest 4f5d state, the PCE still could be observed. Moreover, we get the internal quantum efficiency of Pr^{3+}-doped $NaYF_4$ and KYF_4 in the visible range with branching ratios values corrected by $YF_3:Pr^{3+}$ spectra.

2. Experimental

MYF_4 (M = Li, Na, and K) and $LiLuF_4$ powders were synthesized by hydrothermal method. The starting materials were NH_4HF_2 (A.R.), M_2CO_3 (A.R.), Y_2O_3 (99.99%) or Lu_2O_3 (99.99%), $Pr(NO_3)_3$, and HF (A.R.). HF was added to modulate the pH value of starting reactant mixture to 3–4 and the details of hydrothermal method can be obtained from Ref. [4].

The products were checked by X-ray powder diffraction recorded on a Rigaku D/max-2400 powder diffractometer with $CuK\alpha$ radiation. The excitation and emission spectra were measured on the VUV Station of Beijing Synchrotron Laboratory (H7421-50 Photomultiplier) and National Synchrotron Radiation Laboratory (H5920-01 Photomultiplier) in University of Science and Technology of China. The excitation spectra were calibrated using sodium salicylate.

3. Results and discussion

The emission spectra of the investigated Pr^{3+}-doped MYF_4 (M = Li, Na, K) and $LiLuF_4$ are presented in

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Fig. 1. Emission spectra of Pr^{3+}-doped $LiLuF_4$ and MYF_4 (M = Li, Na, K) measured at 20 K.
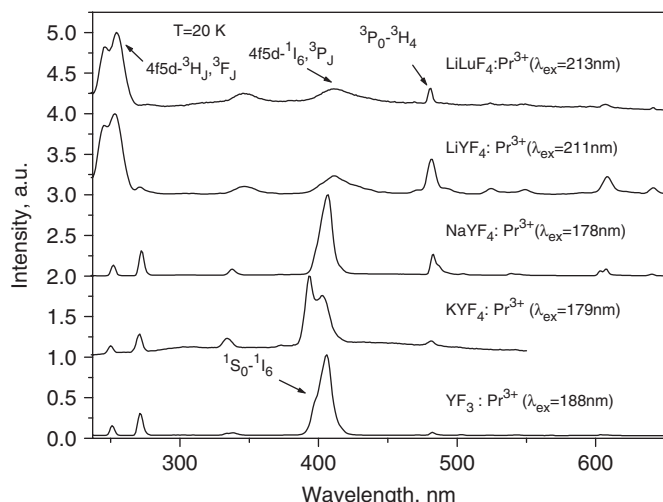
Fig. 2. Excitation spectra of Pr^{3+}-doped $LiLuF_4$ and MYF_4 (M = Li, Na, K) measured at 20 K.

Fig. 1. The emission spectra characteristics of Pr^{3+}-doped KYF_4 and $NaYF_4$ are similar to those of YF_3:Pr^{3+} and typical for the systems where the $^1S_0$ state of the Pr^{3+} $4f^2$ configuration lies below the lowest energy 4f5d state. Therefore, in the emission spectrum the bands at about 251, 272, 336, and 400 nm are observed, which are characteristic of the transitions from the $^1S_0$ to the $^3F_4$, $^1G_4$, $^1D_2$, and $^1I_6$ multiplets, respectively. In the visible range the emission line at 482 nm, corresponding to the $^3P_0 \rightarrow {}^3H_4$ transition, can be observed, indicating that in both $NaYF_4$ and KYF_4 the kind of PCE process consisting of two steps $^1S_0 \rightarrow {}^3P_J + {}^1I_6$, and $^3P_0 \rightarrow {}^3H_4$ takes place. Furthermore, through comparison with the emission of Pr^{3+} in YF_3, it can be concluded that the $^3P_0 \rightarrow {}^3H_4$ emission is more efficient in both hosts, especially for $NaYF_4$:Pr^{3+}.

The emission spectra of Pr^{3+}-doped $LiLuF_4$, $LiYF_4$ are dominating $4f5d \rightarrow 4f^2$ emission. Accordingly, in the VUV range the band emission can be attributed to the $4f5d \rightarrow {}^3H_J + {}^3F_J$ (about 250 nm), $4f5d \rightarrow {}^1G_4$ (about 270 nm), $4f5d \rightarrow {}^1D_2$ (about 346 nm), $4f5d \rightarrow {}^3P_J + {}^1I_6$ (about 410 nm). In the visible range the stronger line at 483 nm due to the $^3P_0 \rightarrow {}^3H_4$ emission can also be observed under the $4f^2 \rightarrow 4f5d$ excitation of Pr^{3+}. The appearance of this emission can be connected with the second stage of PCE. In this process there is the first $4f5d \rightarrow {}^3P_J + {}^1I_6$ resulting in the wide-band emission around 410 nm. So we can conclude that the PCE in Pr^{3+}-doped hosts arises not only from the $^1S_0$ state but also from the lowest 4f5d state. Therefore, this quantum splitting effect has many important applications such as tunable UV laser and quantum cutter.

The emission spectra of Pr^{3+} in MYF_4 (M = Li, Na, K) are different. The fact is that in a first approximation the crystal-field splitting of 5d orbital decreases with the distance from a RE ion to its first neighbor anions, i.e., shorter is the distance, stronger is the splitting.
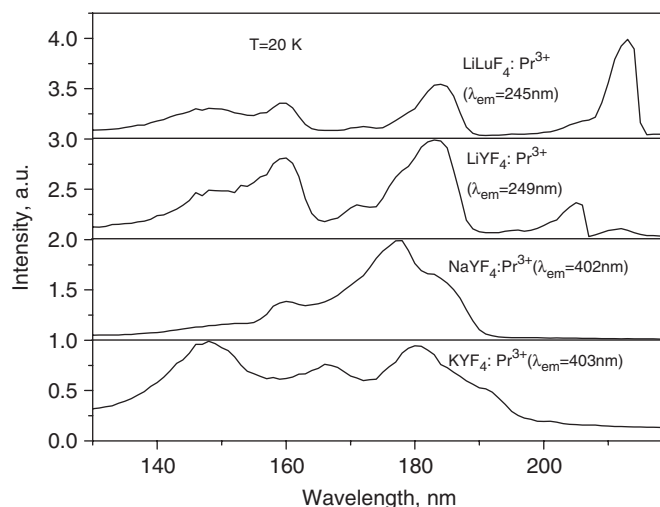
In Fig. 2 we present the excitation spectra of Pr^{3+}-doped $LiLuF_4$ and MYF_4 (M = Li, Na, K) at 20 K and it can be concluded that Pr^{3+}-doped $NaYF_4$ and KYF_4 have similar high-energy configurations. At the same time there are analogous 4f5d states features in Pr^{3+}-doped $LiLuF_4$ and $LiYF_4$. We have not observed the $^3H_4 \rightarrow {}^1S_0$ excitation line in all the hosts.

There is an important factor for the application of phosphors, i.e. quantum efficiency of visible range η_{total}, and from simple analysis which only considers the reduced matrix elements square $\|U^\lambda\|^2$ and oscillator strengths we can conclude that the Judd–Ofelt parameters Ω_2/Ω_6 and Ω_4/Ω_6 determine the internal quantum efficiency of visible light η_{vis} [5]. Smaller these ratios, higher the branching ratio of $^1S_0 \rightarrow {}^1I_6$ and η_{vis}. The values of Ω_2/Ω_6 and Ω_4/Ω_6 can be obtained by fitting the experimentally corrected branching ratios. For difficulties in correcting emission spectra, we can get corrected value by comparing the emission spectra of YF_3:Pr^{3+} obtained from experimental measurement and Ref. [6]. The corrected branching ratios from the emission spectra for $NaYF_4$:Pr^{3+} and KYF_4:Pr^{3+} have been given in Table 1. In the fitting procedure we find that the corrected branching ratios can be well reproduced by values of Ω_2/Ω_6 and Ω_4/Ω_6. Hence we can roughly get $\Omega_2/\Omega_6 = 0.015$ and $\Omega_4/\Omega_6 = 0.08$ for $NaYF_4$, at the same time $\Omega_2/\Omega_6 = 0.013$ and $\Omega_4/\Omega_6 = 0.07$ for KYF_4. Then, we can conclude that the η_{vis}s for $NaYF_4$:Pr^{3+} and KYF_4:Pr^{3+} are larger than unity by comparing that of YF_3:Pr^{3+} [6] ($\eta_{vis} = 157\%$ obtained from $\Omega_2/\Omega_6 = 0.013$ and $\Omega_4/\Omega_6 = 0.07$). Therefore, Pr^{3+}-doped $NaYF_4$ and KYF_4 are also suitable for PCE materials.

4. Conclusions

$LiLuF_4$:Pr^{3+} and MYF_4:Pr^{3+} (M = Li, Na, K) were synthesized by hydrothermal method. The VUV excitation

Table 1
Transition branching ratios and correction factors for the determination of η_{vis}

Emission $^1S_0 \rightarrow$	YF$_3$:Pr^{3+}			NaYF$_4$:Pr^{3+}		KYF$_4$:Pr^{3+}	
	β_{YF_3} [6]	β_{exp,YF_3}	$C = \beta_{YF_3} \big/ \beta_{exp,YF_3}$	$\beta_{exp,NaYF_4}$	$\beta_{corre,NaYF_4}$	β_{exp,KYF_4}	β_{corre,KYF_4}
$^1I_6$	0.789	0.709	1.11	0.676	0.776	0.763	0.847
$^1D_2$	0.015	0.045	0.333	0.052	0.018	0.051	0.017
$^1G_4$	0.128	0.167	0.766	0.186	0.147	0.101	0.077
$^3F_4$	0.053	0.079	0.671	0.086	0.06	0.084	0.056

β_{YF_3}: branching ratios data (corrected) for YF$_3$:Pr^{3+} [6], β_{exp,YF_3}: measured (uncorrected) branching ratios for YF$_3$:Pr^{3+} using our setup, C: correction factors corresponding to our experimental setup, $\beta_{exp,NaYF_4}$: measured (uncorrected) branching ratios for NaYF$_4$:Pr^{3+}, $\beta_{corre,NaYF_4}$: corrected branching ratios by use of C for NaYF$_4$:Pr^{3+}. β_{exp,KYF_4}: measured (uncorrected) branching ratios for KYF$_4$:Pr^{3+}, β_{corre,KYF_4}: corrected branching ratios using C for KYF$_4$:Pr^{3+}.

and emission spectra indicated that there was another PCE process in the LiLuF$_4$:Pr^{3+} and LiYF$_4$:Pr^{3+}, i.e. the first step was 4f5d$\rightarrow$4f^2 emission, and the second step was the 4f$^2 \rightarrow$4f^2 emission. Furthermore, the internal quantum efficiency of Pr^{3+}-doped NaYF$_4$ and KYF$_4$ emission in the visible range was proved to be larger than unity. Then it was concluded that NaYF$_4$:Pr^{3+} and KYF$_4$:Pr^{3+} were also the potential efficient PCE materials.

Acknowledgements

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