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Luminescence study of the *f-f* transition of Pr^{3+} $^1D_2$ and $^3P_0$ states in KYF_4 crystals and powders

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KYF_4:Pr^{3+} was prepared in the two forms of single crystal and polycrystalline powder. The visible photoluminescence properties of KYF_4:Pr^{3+} single crystal and powder have been comparatively investigated, and the special attentions were paid to the luminescence in the red region from the *f-f* transition of Pr^{3+} $^3P_0$ and $^1D_2$ states. We used two different pump sources of an Argon-ion laser tuned to a wavelength of 457.9 nm, 445 nm and a blue GaN laser diode emitting at 445 nm, exciting the $^3P_1$ and $^3P_2$ states of Pr^{3+} ion, respectively. The observed strong and sharp emission line at 594.6 nm for the KYF_4:Pr^{3+} powder and crystal should be ascribed to $^3P_0$-$^3H_6$ transition of Pr^{3+}, and an increase in the $^3P_0$ emission upon 457.9 nm excitation was also observed and was attributed to the $[^3P_0,{}^3H_4] \rightarrow [^3H_6,{}^1D_2]$ cross-relaxation mechanism. Further study on room temperature lifetime and temperature-dependent fluorescence emission of $^1D_2$-$^3H_4$ and $^3P_0$-$^3H_6$ transitions indicated that there was obvious lifetime difference for the $^1D_2$ and $^3P_0$ states of Pr^{3+} in the present KYF_4 host.

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1. Introduction

Pr^{3+} ion has rich emission spectral lines in the UV, visible, and near-infrared regions owing to its intricate energy level scheme with energy gaps of different magnitudes [1-2]. In the past several decades, tremendous progress has been achieved in the investigations on the optical properties and variable applications in fiber laser amplifier, compact visible lasers, and red-emitting phosphors for the Pr^{3+} doped fluoride and oxide powers, crystals and glasses [3-4]. Owing to the very low phonon energy, inorganic bulk fluorides have been selected as the suitable host lattice in many kinds of luminescence materials, moreover fluorides are relatively hard, not hygroscopic and not prone to aging problems, therefore they posses a better power scalability in practical use [5-6]. Among them, rare-earth-doped KYF_4 and KY_3F_{10} single crystals are well-known solid-state laser materials. Laser action has been reported for Yb^{3+}, Tm^{3+}, Ho^{3+} ions in KYF_4 and for Pr^{3+}, Yb^{3+}, Tm^{3+} ions in KY_3F_{10} [7-9]. It is accepted that, due to the recent appearance and the future improvement of Argon-ion lasers and diode lasers operating in the violet to blue region from 400 to 480 nm, the ground $^3H_4$ energy level of Pr^{3+} can be pumped to the $^3P_{0,1,2}$ emitting levels, which in turn forms the visible emission light from 480 nm to 700 nm [10-11]. Accordingly, the interest on KYF_4:Pr^{3+} material is rising owing to the potential application as the laser pumped solid-state white-light emitters [12].

In this paper, the visible photoluminescence of KYF_4:Pr^{3+} single crystal and powder has been comparatively investigated, and the special attentions were paid to the luminescence in the red region from the *f-f* transition of Pr^{3+} $^1D_2$ and $^3P_0$ states by using different pump sources of an Argon-ion laser exciting at 457.9 nm, 445 nm and a GaN laser diode emitting at 445 nm, respectively. Further, room temperature lifetime and temperature-dependent fluorescence emission of $^1D_2$-$^3H_4$ and $^3P_0$-$^3H_6$ transitions for KYF_4:Pr^{3+} have also been studied in detail.

2. Experimental

KYF_4:3%Pr^{3+} powder was prepared by a conventional solid state route. All the starting materials (KF, YF_3 and PrF_3) were purified to a purity of 99.999%, and NH_4HF_2 was purified to a purity of 99.9%. For that a stoichiometric mixture of KF, YF_3, PrF_3 and NH_4HF_2 (1:0.97:0.03:0.5) were thoroughly mixed in an agate mortar, in which NH_4HF_2 was chosen to supply the fluoride atmosphere in order to compensate for the volatilization of this material at high temperatures. The mixture was then cold pressed into pellets with 10 mm in diameter and 1.5-2 mm in thickness under 8 MPa pressure. Further the KYF_4:3%Pr^{3+} powder pellet was sintered for 5 h at 700 °C in a furnace to obtain the final KYF_4:3%Pr^{3+} powder. KYF_4:1.25%Pr^{3+} crystal was grown in a home made computer-controlled

Czochralski furnace with resistive heating. Crystal growth was carried out in purified Argon atmosphere (purity 99.999%). The pull rate used for these crystals varied from 0.5 to 1 mm/h and the rotation rate was 5 rpm. The furnace was provided with an optical computer-controlled apparatus for diameter control.

The phase formation was proven by XRD analysis using the SHIMADZU model XRD-6000 *X*-ray powder diffractometer (Cu Kα radiation, 40 kV, 30 mA and a scanning speed 2.0°(2θ)/min.). The excitation and emission spectra of KYF$_4$:3%Pr^{3+} powder and KYF$_4$:1.25%Pr^{3+} crystals were recorded by using a Perkin-Elmer LS-50B fluorescence spectrophotometer with a photomultiplier tube operating at 400 V, and a 150-W Xe lamp was used as the excitation lamp. As a comparison, the laser-induced fluorescence emission spectra of KYF$_4$:3%Pr^{3+} powder and KYF$_4$:1.25%Pr^{3+} crystal were acquired at room temperature after exciting with different pump sources of an Argon-ion laser tuned to a wavelength of 457.9 nm, 445 nm and a blue GaN laser diode emitting at 445 nm, respectively, and the polarized emission was collected by a lens, mechanically chopped and filtered by a monochromator of 320 mm focal length equipped with a 1200 g/mm grating for the 360–750 nm region. The signal was detected by a photomultiplier and processed by a lock-in amplifier, and then collected by a program connected to a computer.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of as-prepared KYF$_4$:3%Pr^{3+} powder and JCPDS Card file No. 79-1688 of tetragonal KYF$_4$. By careful comparison among the measured XRD pattern and standard file of KYF$_4$, it is found that the corresponding positions and intensities of the main peaks are nearly the same, except for some minor diffraction peaks of the residual starting materials, which would not affect the following optical measurements. As many reported references in our group about the crystal growth of fluoride single crystals, such as BaY$_2$F$_8$, LiYF$_4$, LiLuF$_4$, and KYF$_4$, the famous Czochralski method can be used to obtain high quality single crystals [13-14]. In the present work, the KYF$_4$:1.25%Pr^{3+} crystal has been grown by the Czochralski furnace, as given in Fig. 1(b), which shows the internal structure of Czochralski growth furnace. By this Czochralski method, crystal rods of Pr^{3+}-doped KYF$_4$ with the nominal composition of KYF$_4$:1.25%Pr^{3+} was obtained. As given in Fig. 1(c), it shows the plate-like 1.25%Pr^{3+}:KYF$_4$ crystals cut from as-grown crystal rods and the dimensions of the plate-like crystal is 1 × 3 × 6 mm^3. Further, we can find that the crystal is transparent, and there are no visible inclusions or cracks in the crystals. The wide surfaces of the crystal is polished and then used for the following optical experiments.

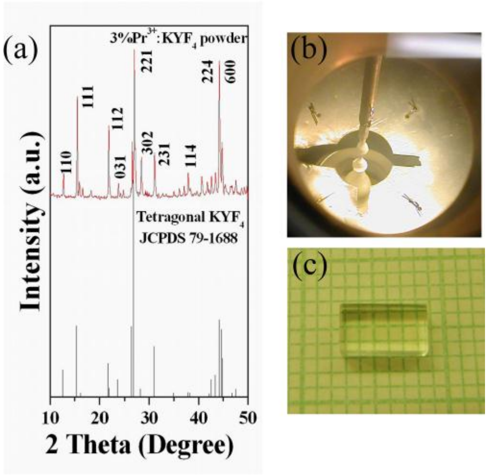

Fig. 1. (a) XRD pattern of as-prepared KYF$_4$:3%Pr^{3+} powder and JCPDS Card (No. 79-1688) of KYF$_4$, (b) the internal structure of Czochralski growth furnace and KYF$_4$:1.25%Pr^{3+} crystal during growing, and (c) the processed KYF$_4$:1.25%Pr^{3+} crystal used to optical measurement.

Fig. 2 presents the excitation [photoluminescence excitation] (PLE); λem = 609 nm] and emission (PL; λex = 444 nm) spectra of KYF$_4$:3%Pr^{3+} powder and KYF$_4$:1.25%Pr^{3+} crystal. It is found that there are similar spectra profiles for both KYF^4:Pr^{3+} powder and crystal except for the relative high emission and excitation intensity of KYF$_4$:1.25%Pr^{3+} crystal. As also given in the PLE spectra of Fig. 2, a broad band from 420 to 500 nm are identified, which are assigned to the overlap of electronic transitions of 3H4-3P2 at 444 nm, 3H4-3P1 at 467 nm, and 3H4-3P0 at 480 nm, respectively. Further, there are only two obvious emission bands in the red emission region from 570 nm to 670 nm, and they should be originated to 1D2-3H4 (at 609 nm) and 3P0-3F2 (at 641 nm) transitions of Pr^{3+} in KYF$_4$ host.

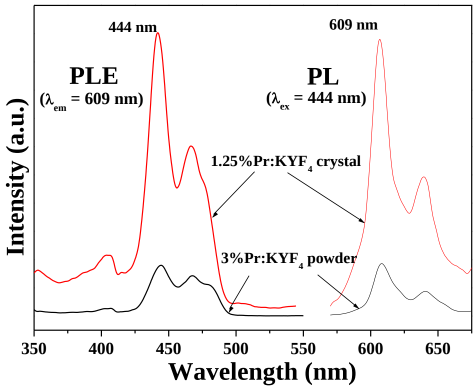

Fig. 2. Comparison of room temperature photoluminescence excitation (PLE) and photoluminescence (PL) spectra of KYF$_4$:3%Pr^{3+} powder and KYF$_4$:1.25%Pr^{3+} crystal.

In order to check precisely on the f-f transition emission of Pr^{3+} 3P0 and 1D2 states, we measured the room temperature fluorescence spectra in red spectral region of KYF_4:3%Pr^{3+} powder and KYF_4:1.25%Pr^{3+} crystal by using an Argon-ion laser tuned to a wavelength of 457.9 nm and 445 nm, respectively. As show in Fig. 3, there are similar spectra profiles between KYF_4:3%Pr^{3+} powder and KYF4:1.25%Pr^{3+} crystal except for the more sharp emission lines in KYF_4:1.25%Pr^{3+} crystal. It is also found that a sharp emission line at 594.5 nm can be found for the both samples, which is different from the PL spectra measurements results by using the Perkin-Elmer LS-50B fluorescence spectrophotometer. The possible reason on that should be ascribed to the low resolution for the former spectrophotometer. Especially, the sharp emission line at 594.5 nm gives more intense intensities by a 457.9 nm excitation. Accordingly, the origin on the sharp emission line at 594.5 nm, also including the possible reason on the enhanced intensities at 594.5 nm by the 457.9 nm excitation can be explained by the cross-relaxation mechanism for the Pr^{3+} in the present KYF_4 system.

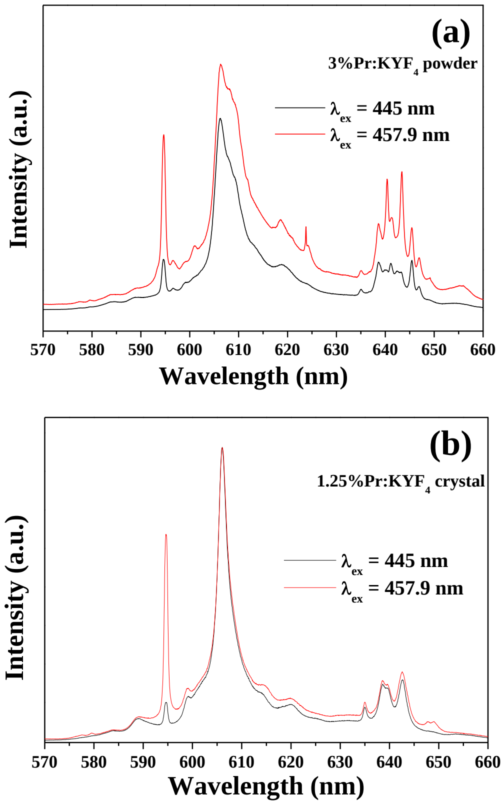

Fig. 3. Room temperature fluorescence spectra in red spectral region of KYF_4:3%Pr^{3+} powder (a) and KYF_4:1.25%Pr^{3+} crystal (b) for different pumping source of 445 nm and 457.9 nm.

Fig. 4 shows the energy level diagram showing the studied excitation and emission lines of Pr^{3+} in KYF_4 host lattice and the proposed cross-relaxation mechanism.

As given in Fig. 4, a Pr^{3+} ion is excited by a 445 nm photon from ground state (3H4) to (3P2), and the photons at 3P2 will relax to 3P0. As a comparison, a Pr^{3+} ion is excited by a 457.9 nm photon from ground state (3H4) to (3P0). The energy gap between the 3P0 level and the nearest low lying one (1D2) is about 3500 cm^{-1}. Moreover, the gap between the 1D2 level and the 1G4 level is larger, about 7000 cm^{-1} [15]. Therefore, both the multi-phonon relaxation rates from the 3P0 and 1D2 levels are very low. The 3P0 emission quenching is most probably due to a cross-relaxation (CR) mechanism between Pr^{3+} ion pairs involving the 1D2 or the 1G4 levels [16]. A possible CR mechanism could be [3P0, 3H4] - [3H6, 1D2], as shown in Fig. 4. This energy level and mechanism imply that the observed strong and sharp emission line at 594.6 nm for the KYF_4:Pr^{3+} powder and crystal should be ascribed to 3P0-3H6 transition of Pr^{3+}. Especially, the excitation energy by 457.9 nm will induce more photons at 3P0 energy level, which will in turn enhance the emission line at 594.6 nm.

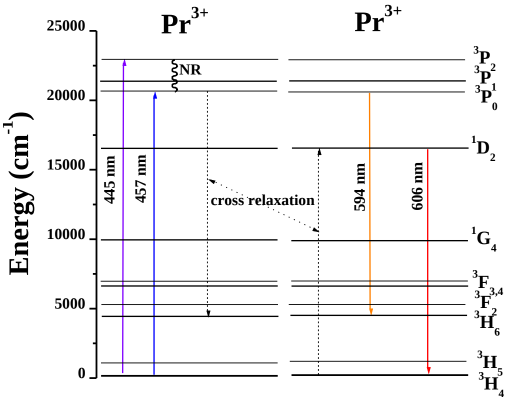

Fig. 4. Energy level diagram showing the studied excitation and emission lines of Pr^{3+} in KYF_4 host lattice and the proposed [3P0,3H4] → [3H6,1D2] cross-relaxation mechanism.

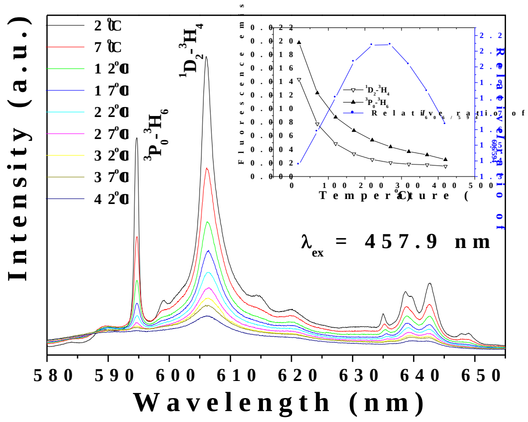

Fig. 5. Temperature dependent fluorescence spectra of KYF_4:1.25%Pr^{3+} crystal in red spectral region under excitation at 457.9 nm. Inset shows the respective intensities of 1D2-3H4, 3P0-3H6 transitions and relative ratio versus increasing heat - treatment temperature.

On the basis of the above analysis, further study on temperature-dependent fluorescence emission and lifetime of 1D2-3H4 and 3P0-3H6 transitions of Pr^{3+} in KYF_4 host lattice have been investigated in detail. Fig. 5 shows the temperature dependent fluorescence spectra of KYF_4:1.25%Pr^{3+} crystals in red spectral region under excitation at 457.9 nm. The inset in Fig. 5 shows the respective intensities of 1D2-3H4, 3P0-3H6 transitions and relative ratio versus increasing temperature. It is found that the emission intensities of 1D2-3H4 and 3P0-3H6 transitions both decreases with increasing temperature from the room temperature 20 oC to the higher temperature 420 oC, as also given in Fig. 5. As shown in the inset, the relative ratio of 1D2-3H4 and 3P0-3H6 transitions firstly increases with increasing temperature, and reaches the maximum at 220 ^{o}C and 270 oC, and it further decreases with increasing temperature. It reflects that the transition possibilities for the 1D2-3H4 and 3P0-3H6 transitions are different [17]. Accordingly, since luminescence lifetime is a key parameter for luminescence probe [18], therefore, fluorescence decay curve of KYF_4:1.25%Pr^{3+} crystal for the 3P0 mutiplet at 594 nm and 1D2 mutiplet at 606 nm are measured and shown in Fig. 6, respectively. As shown in Fig. 6, for the two cases, the decay curves for 3P0 and 1D2 mutiplet of Pr3+ at room temperature can be well fitted into a single exponential function as

$$I(t) = A\ \exp(-t/\tau) \tag{1}$$

Where I is the luminescence intensity at time t, A is constants, t is the time, and τ is the decay time for the exponential components. For emission 1D2-3H4 (606 nm) and 3P0-3H6 (594 nm) of Pr3+, the lifetimes are t = 16.7 μs and t = 13.5 μs, respectively. Considering the difference of the lifetime for the 3P0 mutiplet at 594 nm and 1D2 mutiplet at 606 nm, obvious lifetime difference for the 1D2 and 3P0 states of Pr^{3+} can be found in the present KYF_4 host.

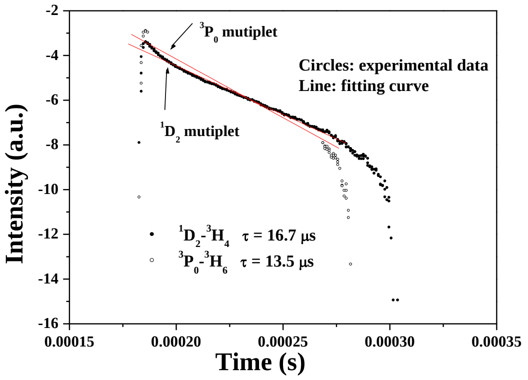

Fig. 6. Room temperature fluorescence decay curve of KYF_4:1.25%Pr^{3+} crystal for the 1D2 mutiplet at 594 nm and 3P0 mutiplet at 606 nm under 457.9 nm excitation.

4. Conclusions

KYF4:Pr3+ was prepared in the two forms of single crystal and polycrystalline powder, and the visible photoluminescence has been investigated in the red region from the f-f transition of Pr3+ 3P0 and 1D2 states. By using two different pump sources of an Argon-ion laser tuned to a wavelength of 457.9 nm, 445 nm and a blue GaN laser diode emitting at 445 nm, the observed strong and sharp emission line at 594.6 nm for the KYF4:Pr3+ powder and crystal should be ascribed to 3P0-3H6 transition of Pr3+, and an increase in the 3P0 emission upon 457.9 nm excitation was also observed and was attributed to the [3P0,3H4] → [3H6,1D2] cross-relaxation mechanism. Room temperature lifetime and temperature-dependent fluorescence emission of 1D2-3H4 and 3P0-3H6 transitions indicates that there are obvious lifetime difference and variation tendency of the intensities for the 1D2 and 3P0 states of Pr3+ in the present KYF4 host.

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