Investigation on Up‑conversion Luminescence Properties and Mechanism in Tm³⁺‑doped BaY₂F₈ Single Crystal

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Abstract

The 4.0 mol% Tm³⁺-doped BaY₂F₈ single crystal has been grown by the temperature gradient method. The absorption spectra were measured and investigated in the ultraviolet-visible and near-infrared ranges at room temperature. In order to determine the energy level assignment and position, the energy gap also has been calculated between any two levels. The up-conversion spectra at room temperature were recorded under excitation of 650 nm, respectively. Meanwhile, the up-conversion mechanism was also analyzed in detailed. The results show the ground state absorption (GSA), excited state absorption (ESA), multiphonon relaxation (Wij), cooperative upconversion (CUC) and cross relaxation (CR) play important roles in the up-conversion process.

Keywords

Luminescence; Up-conversion Spectrum; Phonon; Tm³⁺ Ions; BaY₂F₈ Single Crystal.

1. Introduction

Thulium-doped optical materials play important roles in potential applications, such as high-temperature superconductor, high-intensity discharge light source, gas detection, laser displays, etc [1]. The luminescence of the Tm^{3+} ions depends on the host materials. In order to obtain highly efficient fluorescence signals, choosing the appropriate host materials is very important. The crystals of fluoride compounds with ordered structure form an important class of materials [2-7]. Barium yttrium fluoride (BaY_2F_8-BaYF) is a good candidate. The BaY_2F_8 single crystal as a host material has very wide transparency spectra ranging from vacuum UV to far-infrared regions, which contributes to decreasing the host absorption so that the better spectral properties can be obtained. Moreover, the BaY_2F_8 single crystal also has important mechanical and thermal features. For example, the very low phonon energy ($\hbar\omega \sim$360-380 cm-1) reduces occurrence of non-radiative processes with respect to the radiative ones. Compared with the refractive index of oxides (the largely used YAG $n = 1.84$), the low refractive index ($n = 1.52$) of the BaY_2F_8 single crystal suggests a low thermal lensing effect, whicha contributes to the luminescence of the activators[8-11].

BaY_2F_8 crystals belong to the monoclinic crystallographic system, with space group $C_{2h}^3 - C2/m$ and lattice parameters $a = 0.6972$ nm, $b = 1.0505$ nm, $c = 0.4260$ nm, $\alpha = \gamma = 90^\circ$, $\beta = 99^\circ 45'$ [6-8]. The primitive unit cell of the BaY_2F_8 single crystal contains two molecules of BaY_2F_8 and the Tm^{3+} ions occupy the Y^{3+} lattice sites (C_2 local point symmetry) [9-11]. The growth of Tm^{3+}-doped BaY_2F_8 crystals have been reported extensively in the literature. In the present work, we focus on the up-conversion luminescence of Tm^{3+}-doped BaY_2F_8 crystals grown by the temperature gradient method. More attentions are paid to revealing the up-conversion mechanism and analyzing the up-conversion process in detail.

2. Experimental procedures

The BaY_2F_8 crystal doped with Tm^{3+} ions were grown by temperature gradient method [6-9]. High-purity synthesized powders (>99.99%) of commercially available BaF_2, YF_3 and TmF_3 were applied

to crystal growth and these raw materials were mixed in stoichiometric amounts according to the following equation:

$$BaF_2 + 2(1-x)YF_3 + 2xTmF_3 \rightarrow BaY_{2(1-x)}Tm_{2x}F_8 \tag{1}$$
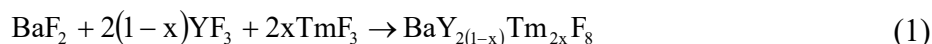
Where x is the concentration of Tm^{3+} ions. In this paper, the concentration of Tm^{3+} ions is 4.0 mol% (x=0.04).

Absorption spectra were measured by Shimadu UV-3101PC spectrometer in the ultraviolet-visible and near infrared ranges (200 nm-1700 nm) at room temperature. The tested sample is a slice cutting from the Tm^{3+}-doped BaY_2F_8 single crystal.

Up-conversion luminescence spectrum excited at 650 nm was recorded with the FlouroMax-P spectrophotometer at room temperature.

3. Results and discussion

Fig. 1 shows the absorption spectra of Tm^{3+}-doped BaY_2F_8 single crystal in the ultraviolet-visible and near infrared ranges at room temperature. The several observed absorption bands correspond to transitions $^3H_6 \rightarrow ^3P_1$ (260 nm), $^3H_6 \rightarrow ^1D_2$ (355), $^3H_6 \rightarrow ^1G_4$ (461 nm), $^3H_6 \rightarrow ^3F_2$ (650 nm), $^3H_6 \rightarrow ^3F_3$ (680 nm), $^3H_6 \rightarrow ^3H_4$ (780 nm), $^3H_6 \rightarrow ^3H_5$ (1205 nm) and $^3H_6 \rightarrow ^3F_4$ (1645 nm), respectively. The absorption coefficient, absorption cross section, integrated absorption cross section, intensity parameters, radiative probabilities, radiative lifetime and integrated emission cross-sections have been published in Ref. [12]. In order to determine the energy level assignment and position, the energy gap (transition wavelength) also has been calculated between any two levels, as shown in table 1. However, it must be noted that we only consider the spin-orbit coupling of trivalent rare earth ions and do not take account of Stark splitting under the influence of the crystal field. These data can provide a basic reference for the energy level assignment and position. For some other special energy level transitions, it needs to be combined with various published literatures [13-18].
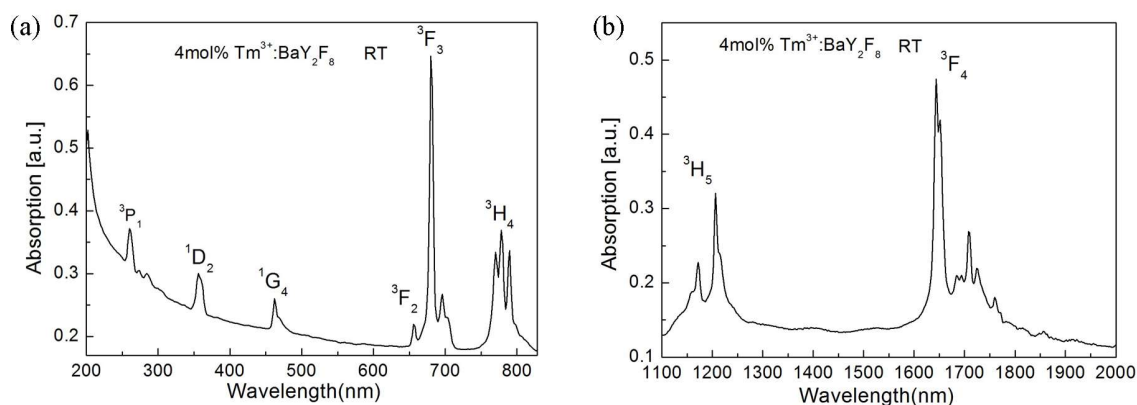

Fig. 1. Ultraviolet-visible (a) and near infrared (b) absorption spectra of 4.0 mol% Tm^{3+}-doped BaY_2F_8 single crystal at room temperature.

Table 1 Transition wavelength between any two energy levels.

| Energy level/nm^{-1}	Energy State	$^3P_1$	$^1D_2$	$^1G_4$	$^3F_2$	$^3F_3$	$^3H_4$	$^3H_5$	$^3F_4$	$^3H_6$
0.003846	$^3P_1$	0	971.58	596.32	433.33	420.95	390.00	331.53	308.81	260.00
0.002817	$^1D_2$			1543.90	782.20	742.77	651.53	503.26	452.69	355.00
0.002169	$^1G_4$				1585.46	1431.43	1127.22	746.65	640.50	461.00
0.001538	$^3F_2$					14733.4	3900.02	1411.26	1074.62	650.00
0.001471	$^3F_3$						5304.03	1560.76	1159.17	680.00
0.001282	$^3H_4$							2211.52	1483.35	780.00
0.00083	$^3H_5$								4505.01	1205.00
0.000608	$^3F_4$									1645.01
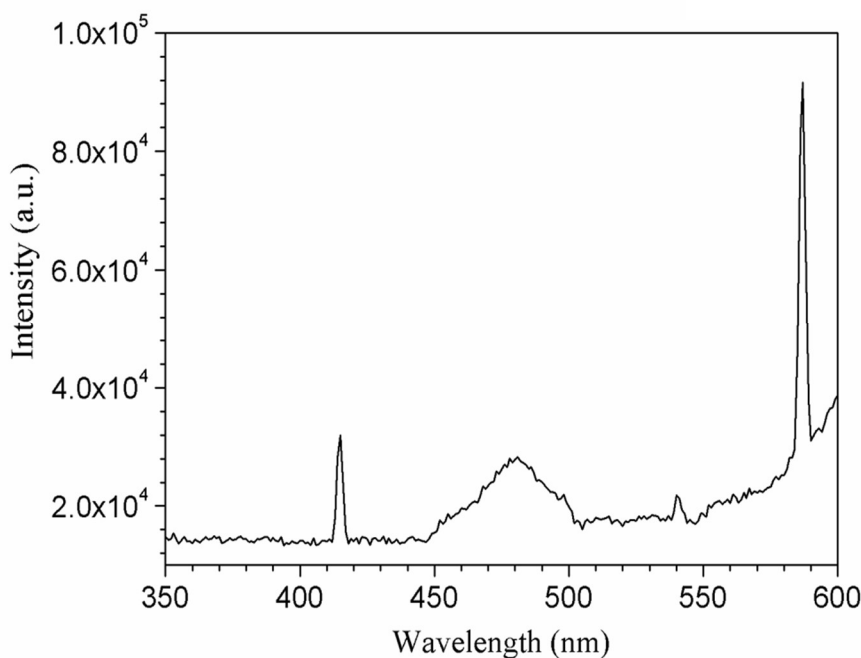
Fig. 2 Up-conversion spectrum of Tm^{3+}-doped BaY_2F_8 sing crystal with 650 nm as an excitation wavelength.

Fig. 2 shows the up-conversion (UC) luminescence spectrum of Tm^{3+}-doped BaY_2F_8 single crystal between 350 nm and 600 nm regions which is excited at 650 nm and room temperature. The UC luminescence bands centered at 418 nm, 480 nm and 589 nm have been observed and these emission bands are attributed to the $^3P_1\rightarrow^3F_3$, $^1G_4\rightarrow^3H_6$ and $^3P_0\rightarrow^1G_4$, respectively. Although, the up-conversion luminescence process of Tm^{3+}-doped BaY_2F_8 crystal excited at 650 nm was described in our previous work [8], in this paper more attentions are paid to revealing the roles of ground state absorption (GSA), excited state absorption (ESA), multiphonon relaxation (Wij), cooperative upconversion (CUC) and cross relaxation (CR) in more details. As can be seen from the energy level assignment and position of Tm^{3+} ion in the BaY_2F_8 crystal, the energy-level scheme is very symmetrical. This implies that the cross relaxation (CR) and excited state absorption (ESA) are very significant. Fig. 3 shows the up-conversion luminescence process.
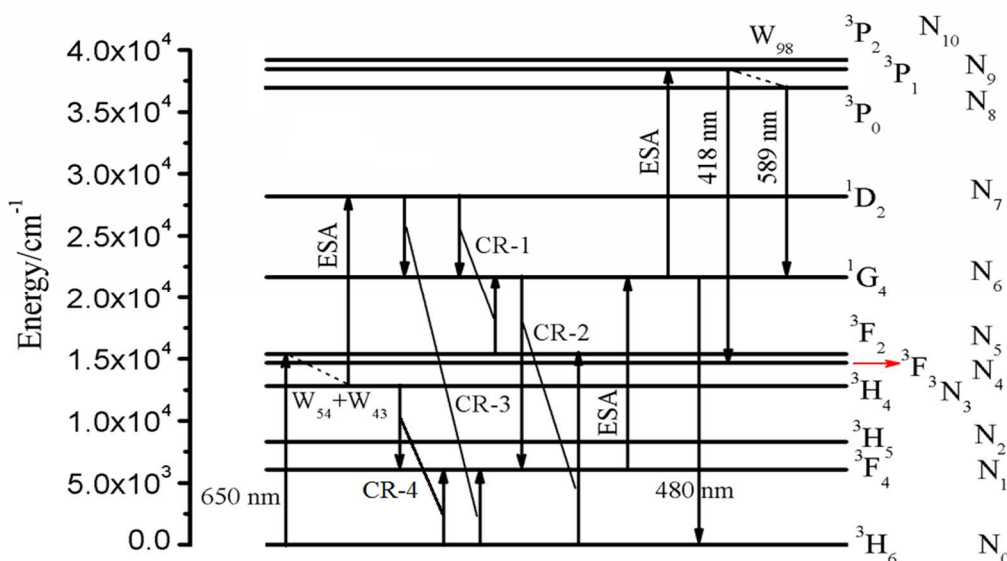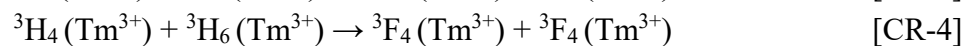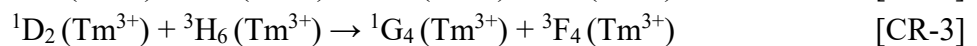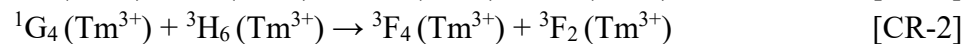

Fig. 3 Up-conversion mechanism of Tm^{3+}-doped BaY_2F_8 crystal.

Four kinds of cross relaxation can be found as follows:

$$^1D_2\,(Tm^{3+}) + {}^3F_2\,(Tm^{3+}) \rightarrow {}^1G_4\,(Tm^{3+}) + {}^1G_4\,(Tm^{3+}) \qquad [CR-1]$$
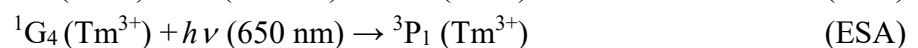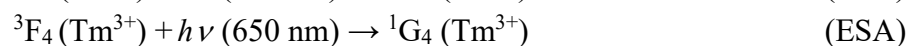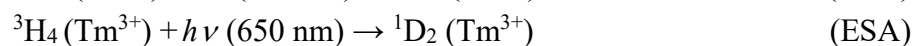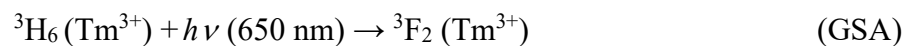
$$^1G_4\,(Tm^{3+}) + {}^3H_6\,(Tm^{3+}) \rightarrow {}^3F_4\,(Tm^{3+}) + {}^3F_2\,(Tm^{3+}) \qquad [CR-2]$$

$$^1D_2\,(Tm^{3+}) + {}^3H_6\,(Tm^{3+}) \rightarrow {}^1G_4\,(Tm^{3+}) + {}^3F_4\,(Tm^{3+}) \qquad [CR-3]$$

$$^3H_4\,(Tm^{3+}) + {}^3H_6\,(Tm^{3+}) \rightarrow {}^3F_4\,(Tm^{3+}) + {}^3F_4\,(Tm^{3+}) \qquad [CR-4]$$
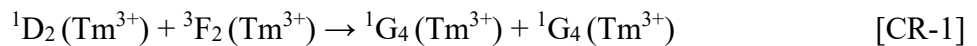
The energy-level mismatches of the four cross relaxation are 172 cm^{-1}, 240 cm^{-1}, 406 cm^{-1} and 664 cm^{-1}, respectively. Therefore, the probability of the CR-4 is very low. The phonon plays a very important role in the up-conversion process. Under the help of the phonon, the

When the Tm^{3+}-doped BaY$_2$F$_8$ crystals are excited, the Tm^{3+} ion at the $^3H_6$ ground state absorbs a 650 nm photon and populates the $^3F_2$ metastable state. Under the help of the phonons, the ions at $^3F_2$ excited states can populate lower energy state through nonradiative relaxation, such as the $^3F_3$ and $^3H_4$ states. Similarly, the ions at $^3P_1$ excited states can also populate $^3P_0$ lower energy state through nonradiative relaxation. In addition to multiphonon relaxation (Wij) and cross relaxation (CR), the ground state absorption (GSA) and excited state absorption (ESA) exist in the whole up-conversion luminescence process, they can be shown as follows:

$$^3H_6\,(Tm^{3+}) + h\nu\,(650\ nm) \rightarrow {}^3F_2\,(Tm^{3+}) \qquad (GSA)$$

$$^3H_4\,(Tm^{3+}) + h\nu\,(650\ nm) \rightarrow {}^1D_2\,(Tm^{3+}) \qquad (ESA)$$

$$^3F_4\,(Tm^{3+}) + h\nu\,(650\ nm) \rightarrow {}^1G_4\,(Tm^{3+}) \qquad (ESA)$$

$$^1G_4\,(Tm^{3+}) + h\nu\,(650\ nm) \rightarrow {}^3P_1\,(Tm^{3+}) \qquad (ESA)$$

In summary, under the help of the ground state absorption (GSA), excited state absorption (ESA), multiphonon nonradiative relaxation (MPR) and cross relaxation (CR), The radiative transitions ($^3P_1\rightarrow{}^3F_3$, $^1G_4\rightarrow{}^3H_6$ and $^3P_0\rightarrow{}^1G_4$) give rise to the 418 nm, 480 nm and 589 nm up-conversion emission, respectively. The $^1G_4\rightarrow{}^3H_6$ transition is responsible for two-photon absorption, while $^3P_1\rightarrow{}^3F_3$ and $^3P_0\rightarrow{}^1G_4$

transitions are three-photon absorption process.

4. Conclusion

The absorption spectra of the Tm^{3+}-doped BaY$_2$F$_8$ single crystal were measured and investigated in the ultraviolet-visible and near-infrared ranges at room temperature. In order to determine the energy level assignment and position, the energy gap also has been calculated between any two levels. The up-conversion spectra at room temperature were recorded under excitation of 650 nm. Meanwhile, the up-conversion mechanism was also analyzed in detailed. The results show the ground state absorption (GSA), excited state absorption (ESA), multiphonon relaxation (Wij), cooperative upconversion (CUC) and cross relaxation (CR) play important roles in the up-conversion process.

Acknowledgements

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