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Efficient up-conversion in $KYb_{0.8}Eu_{0.2}(WO_4)_2$ crystal

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Abstract

Efficient visible anti-Stokes emission was observed in the $KEu_{0.2}Yb_{0.8}(WO_4)_2$ crystal after a direct excitation of the Yb^{3+} ion. This emission is associated with the Eu^{3+} ion and originates not only from the $^5D_0$ state but also from the $^5D_2$ and $^5D_1$ states. The process of up-conversion was investigated at 300 K as a function of excitation power. It was demonstrated that the process was non-linear and changed with the incident power as P^n_{exc}, $n=1.5$. The mechanism of up-conversion processes occurring in the $KEu_{0.2}Yb_{0.8}(WO_4)_2$ crystal is briefly discussed.

Keywords: Anti-Stokes emission; Up-conversion

1. Introduction

Recently, great interest has been observed in studying the frequency up-conversion in rare-earth-doped materials (crystals, glasses, powders, fibers) resulting in anti-Stokes emission (for review see Ref. [1]). This interest is important because of the possibility of utilising this phenomenon in the construction of up-conversion lasers operating in the UV region [2]. The up-conversion effect resulting from the co-operative interactions was observed in single-doped systems for Nd, Pr, Tm, Ho, Er ions as well as doubly doped materials such as (Yb,Er), (Yb,Ho), (Yb,Tm), (Yb,Pr). The most important criteria allowing an efficient up-conversion process are the presence of energy resonance between the donor and acceptor ions and the close distance between interacting ions. In this paper, we report the up-conversion effect occurring between Eu^{3+} and Yb^{3+} ions in the $KYb(WO_4)_2$ crystal after a direct excitation of the Yb^{3+} ion. In this crystal, the Yb^{3+}-excited state $^2F_{7/2}$ is far off resonance with the closest Eu^{3+} states. The mechanism of up-conversion in this system is briefly discussed. It will be shown that the up-conversion effect is associated with a three-ion interaction process.

2. Experimental

The $KYb_{0.8}Eu_{0.2}(WO_4)_2$ and $KYb_{0.8}Tb_{0.2}(WO_4)_2$ crystal samples were kindly supplied by Dr. A.N. Titov from Vavilov State Optical Institute, Sankt Petersburg, Russia. They were grown by the flux top-seeded solution method. Absorption spectra were measured at room temperature on a Cary 5 spectrophotometer. Emission spectra were measured on a Jobin Yvon THR 1000 spectrophotometer using an argon and excimer lasers as excitation sources. The spectra were measured at room and liquid nitrogen temperatures. For up-conversion experiments, we applied the setup consisting of laser diode (Opto Power, model OPC –A020-mmm-CN) and the Ocean Optics spectrophotometer.

3. Results and discussion

The absorption spectrum of $KYb_{0.8}Eu_{0.2}(WO_4)_2$ crystal was measured at the room temperature range. It is shown in Fig. 1. The assignment of absorption transition bands is given in the figure. One can note that the absorption band of the Yb^{3+} ion prescribed to the $^2F_{7/2}\rightarrow{}^2F_{5/2}$ dominates, by several order of magnitudes, the transition bands of the Eu^{3+} ion due to the higher concentration of Yb^{3+} ions and higher oscillator strength compared to the Eu^{3+} ion.

The emission spectrum of the $KYb_{0.8}Eu_{0.2}(WO_4)_2$ crystal excited by the 308-nm line of excimer laser is shown in Fig. 2. The spectrum consist of the bands associated with the $^5D_0\rightarrow{}^7F_J$ transitions of Eu^{3+} ion and the $^2F_{5/2}\rightarrow{}^7F_{7/2}$ transition of the Yb^{3+} ion. The emission of the Eu^{3+} ion originates from the $^5D_0$ level to the ground ^7F_J multiplets ($J=0$–6). Only the transitions up to $J=4$

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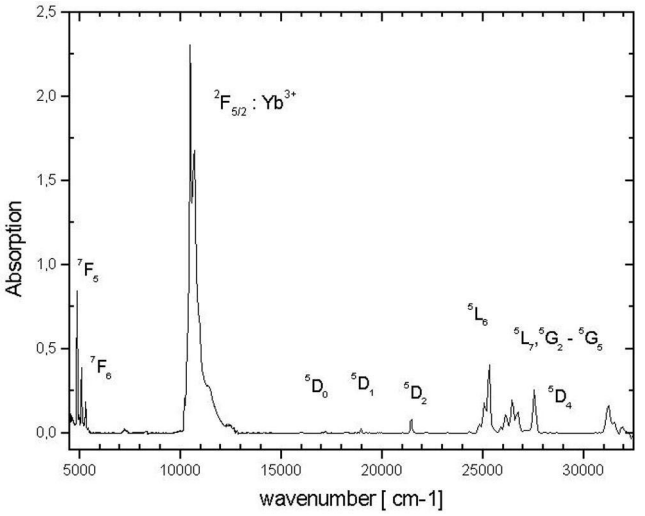

Fig. 1. Absorption spectrum of $KEu_{0.2}Yb_{0.8}(WO_4)_2$ crystal measured at 15 K.

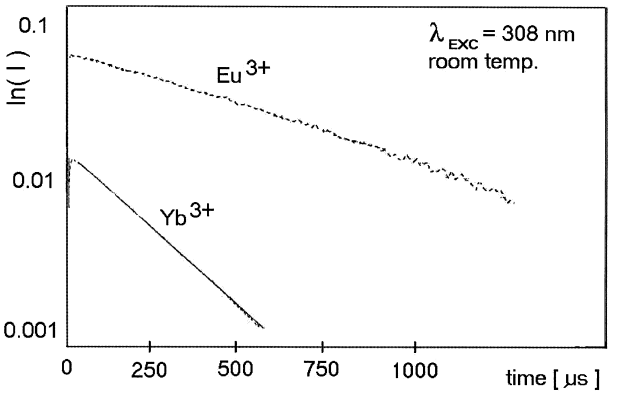

Fig. 3. Emission decay profiles of Eu^{3+} and Yb^{3+} emission in the $KEu_{0.2}Yb_{0.8}(WO_4)_2$ measured at room temperature.

were observed. The $^5D_0 \rightarrow {}^7F_5$ and $^5D_0 \rightarrow {}^7F_6$ transitions usually are much weaker and were not measured, however they should appear in the range of 750 and 820 nm, respectively.

The emission decay profiles of Eu^{3+} and Yb^{3+} ions were measured at room temperature. They are shown in Fig. 3. Both the measured emission decay curves have exponential character. The emission decay times were determined to be 490 and 215 μs for Yb^{3+} and Eu^{3+} ions, respectively.

The presence of the Yb^{3+} emission following an excitation of the Eu^{3+} ion points to an efficient energy transfer from Eu^{3+} to Yb^{3+}. The energy transfer is of the nonresonant type because of a large energy mismatch between the $^5D_0 \rightarrow {}^7F_J$ emission transitions of Eu^{3+} and the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ absorption transition (see energy levels diagram in Fig. 4).

The energy transfer from Eu^{3+} to Yb^{3+} ions was earlier observed by Yamada et al. [3] in Y_2O_3 crystals. They found that the process was quite efficient.

As is known, the nonresonant energy transfer is associated with emission or absorption of phonons to balance the energy mismatch ΔE. According to the Miyakawa and Dexter theory [4,5] the probability of the process k_{PAT} is described by:

$$k_{PAT}(\Delta E) = \left[\frac{n+1}{n}\right]^N k_{PAT}(0)\, e^{-\beta \Delta E}$$

where β is the electron-phonon coupling parameter and $N = \Delta E/\hbar\omega_{max}$. The smallest energy gap ΔE takes place for the emission $^5D_0 \rightarrow {}^7F_6$. In this case $\Delta E \approx 2300\ cm^{-1}$ and $\hbar\omega_{max} = 1000\ cm^{-1}$ which means that $N = 2$.

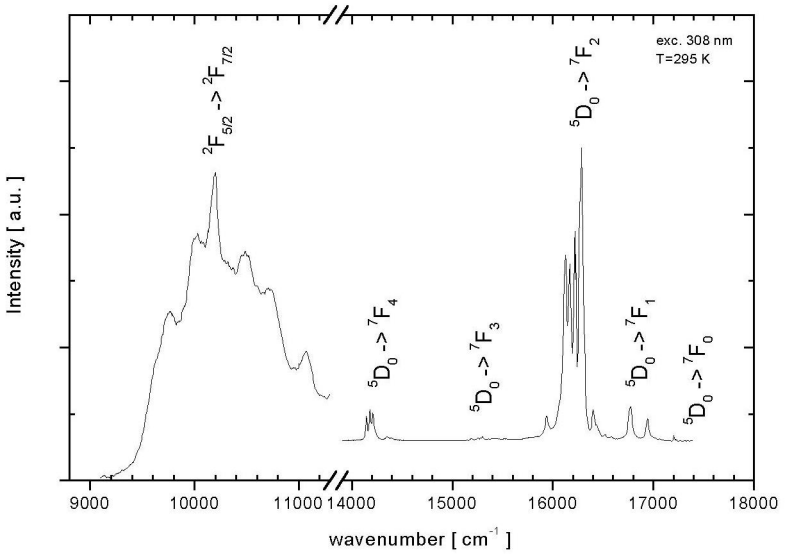

Fig. 2. Emission spectra of $KEu_{0.2}Yb_{0.8}(WO_4)_2$ crystal measured at room temperature.

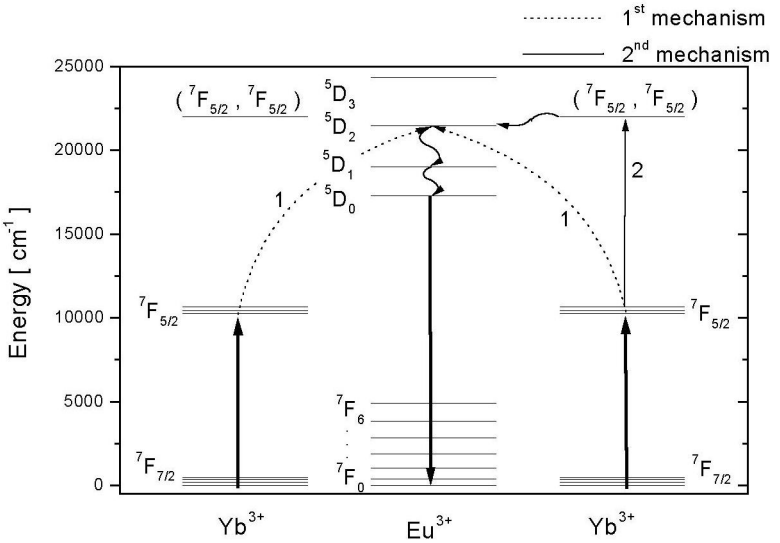

Fig. 4. Energy diagrams of Eu^{3+} and Yb^{3+} ions and schemes of cross relaxation and up-conversion transitions.

We have measured the dependence of Yb^{3+} emission on the Eu^{3+} incident excitation power. It is shown in Fig. 5. We have found that this dependence was almost linear, however, we have found that the Yb^{3+} emission increased slightly slower compared to the Eu^{3+} emission. A source of such difference could be the fact that during illumination not all Eu^{3+} ions transfer (some of the ions contribute to the Eu^{3+} emission) its excitation to the Yb^{3+} ions.

In the course of our experiments, we have directly excited the Yb^{3+} ion with the laser diode 0.98 μm. We have observed an efficient up-conversion process resulting in the Eu^{3+} emission. It is shown in Fig. 6.

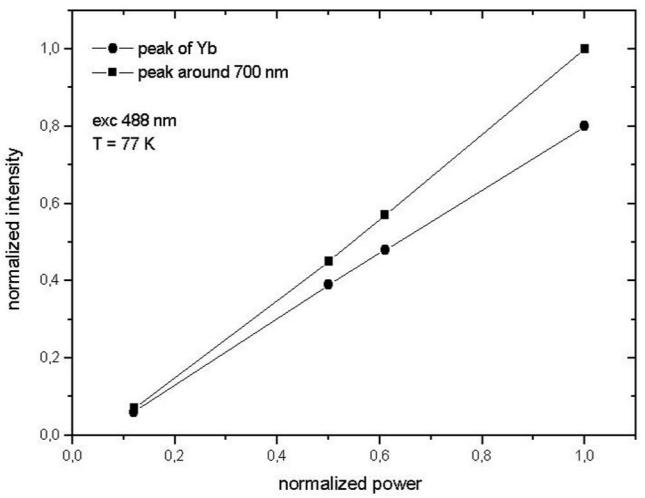

Fig. 5. The power dependence of Eu^{3+} and Yb^{3+} emissions in the $KEu_{0.2}Yb_{0.8}(WO_4)_2$ crystal following excitation of the Eu^{3+} ion.

The dependence of up-conversion on the incident laser excitation power was investigated using a laser diode under a pump power 1–14 W (see Fig. 7). The dependence of the Eu^{3+} emission intensity for the $^5D_0 \rightarrow {}^7F_2$ band as a function of the excitation power was found to vary as P^n_{exc} with $n = 1.5$.

To discuss the possible mechanism of up-conversion process let us see that there is no possibility of a direct transfer of the excited Yb^{3+} ion energy to Eu^{3+} ion (see Fig. 4). A simple analysis of the energy level diagram of both ions allows us to propose the following two mechanisms: The first is combined with the simultaneous interaction of two Yb^{3+} ions in the excited state transferring energy to the $^5D_2$ state of Eu^{3+} ion (see Fig. 4). Such a process is termed the co-operative sensitisation [1].

The second may be combined with the pair state [$^2F_{5/2}$, $^2F_{5/2}$] whose energy is about 22 000 cm^{-1} (see Fig. 4). This state is very close to the absorption band associated with the transition from the thermally populated $^7F_1$ state to the state of Eu^{3+} ion. Schematically we can describe the visible up-conversion as the following sequential processes:

1. [$^2F_{7/2}$, $^2F_{7/2}$]⇒[$^2F_{5/2}$, $^2F_{5/2}$] — the co-operative absorption and
2. ([$^2F_{5/2}$, $^2F_{5/2}$], $^7F_1$)⇒([$^2F_{7/2}$, $^2F_{7/2}$], $^5D_2$) — the cross relaxation process as a result of which the Eu^{3+} becomes excited.

The dependence of up-conversion emission should be quadratically dependent on the incident power. In our experiment it was smaller $n = 1.5$. This deviation is very often observed for the up-conversion processes combined

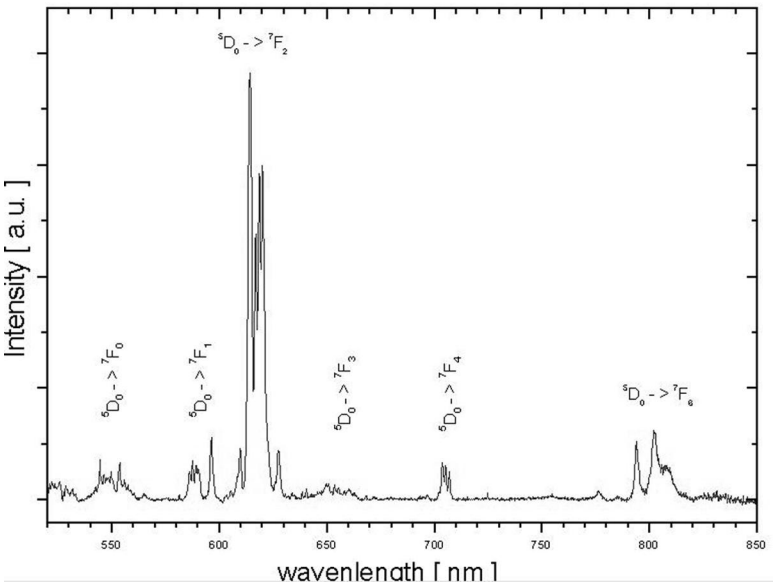

Fig. 6. Anti-Stokes emission in the $KEu_{0.2}Yb_{0.8}(WO_4)_2$ crystal following the Yb^{3+} excitation with 0.98-μm diode laser.

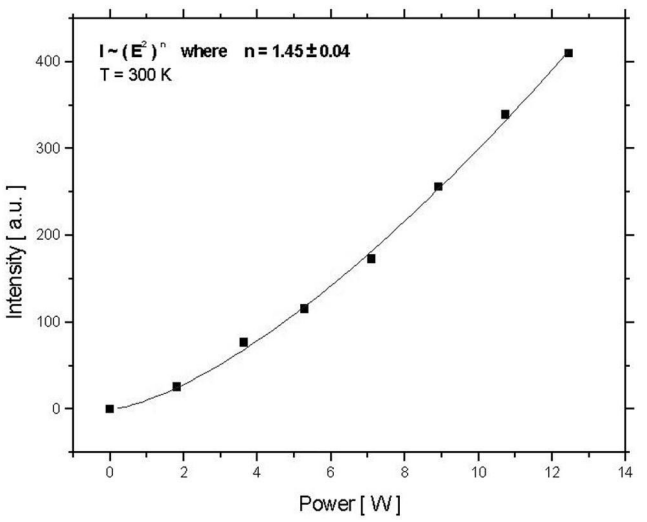

Fig. 7. The power dependence of anti-Stokes emission of $KEu_{0.2}Yb_{0.8}(WO_4)_2$ crystal following the Yb^{3+} excitation with the 1.0-μm diode laser.

with the long-lived emission of intermediate states [6].

In summary, we have reported the visible up-conversion emission in the $KEu_{0.2}Yb_{0.8}(WO_4)_2$ crystal after a direct excitation of Yb^{3+} ions. It is a three ion interaction process in which two Yb^{3+} ions and an Eu^{3+} ion take part. This process was found to be fairly intense.

References

[1] F. Auzel, in: B. Di Bartolo (Ed.), Nonlinear Spectroscopy of Solids, Plenum Press, New York, 1994.
[2] R. Scheps, Prog. Quant. Electr. 20 (1996) 271.
[3] N. Yamada, S. Shionoya, T. Kushida, J. Phys. Soc. Jap. 32 (1972) 157.
[4] T. Miyakawa, D.L. Dexter, Phys. Rev. B1 (1970) 2961.
[5] W. Strek, Phys. Rev. B29 (1984) 6957.
[6] T. Hebert, R. Wannemacher, W. Lenth, R.M. Macfarlane, Appl. Phys. Lett. 57 (1990) 1727.