

Temporal dynamics of upconversion luminescence in Er^{3+} , Yb^{3+} co-doped crystalline $\text{KY}(\text{WO}_4)_2$ thin films

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Abstract

Crystalline Er^{3+} and Yb^{3+} singly and doubly doped $\text{KY}(\text{WO}_4)_2$ thin films were grown by low-temperature liquid-phase epitaxy. Absorption, luminescence, excitation and temporal evolution measurements were carried out for both Er^{3+} and Yb^{3+} transitions from 10 K to room temperature. Green Er^{3+} upconversion luminescence was observed after Yb^{3+} and Er^{3+} excitation. The mechanisms responsible for the upconversion phenomena detected in each case were identified.

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1. Introduction

Potassium rare-earth tungstate matrices have got remarkable optical properties that make them promising hosts for optical solid-state lasers. In $\text{KY}(\text{WO}_4)_2$ (KYW), Er^{3+} and Yb^{3+} impurities are located in the C_2 site replacing Y^{3+} ions with doping levels up to 100% [1]. Thin layers have an additional interest because of their potential applications as thin-disk and waveguide lasers [2,3]. Recently, VIS emissions of Er^{3+} in bulk KYW: 0.4% Er^{3+} , 3.8% Yb^{3+} after Yb^{3+} $^2\text{F}_{5/2}$ (981 nm) and $^4\text{I}_{9/2}$ Er^{3+} (798 nm) excitation have been observed [4].

In this report, we characterize the upconversion phenomena of a crystalline layer of Er^{3+} , Yb^{3+} doubly doped KYW. A detailed analysis of the spectroscopic data allows us to distinguish the UC process in each case.

2. Experimental

KYW thin films doped with 2.5% Er^{3+} , 0.2% Er^{3+} and 0.2% Yb^{3+} , as well as co-doped with 2.5% Er^{3+} and 2.5% Yb^{3+} , were grown on *b*-oriented KYW substrates by the low-temperature liquid-phase epitaxy technique [5].

For luminescence, excitation and fluorescence lifetime experiments, the 8 ns laser pulses of an OPO laser were used. The sample luminescence was dispersed by a 0.5 m monochromator with 750 nm blazed and 1200 groves/mm gratings and recorded by using a photon counting system. The temporal evolution was detected by a digital oscilloscope. All the spectra were corrected for the system response. Low-temperature measurements (10–300 K) were obtained using a closed-cycle He cryostat.

3. Results and discussion

Fig. 1 shows the unpolarized 10 K absorption spectrum of KYW: 2.5% Er^{3+} , 2.5% Yb^{3+} . Fig. 2 compares the 100 K luminescence spectra of KYW: 2.5% Er^{3+} , 2.5% Yb^{3+} after Er^{3+} excitation at 19,231 cm^{-1} (a) with Er^{3+} UC emission after exciting Yb^{3+} at 10,190 cm^{-1} (b). The additional peaks of Fig. 2(b) around 10,000 cm^{-1} are assigned to the Yb^{3+} $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ and Er^{3+} $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$ transitions. VIS Er^{3+} UC luminescence is observed after selectively pumping into the Yb^{3+} $^2\text{F}_{5/2}$ and Er^{3+} $^4\text{I}_{11/2}$ excited states. Excitation around 12,500 and 15,361 cm^{-1} resonant into the $^4\text{I}_{9/2}$ and $^4\text{F}_{9/2}$ Er^{3+} multiplets leads to similar Er^{3+} UC luminescence spectra to similar to Fig. 2(b).

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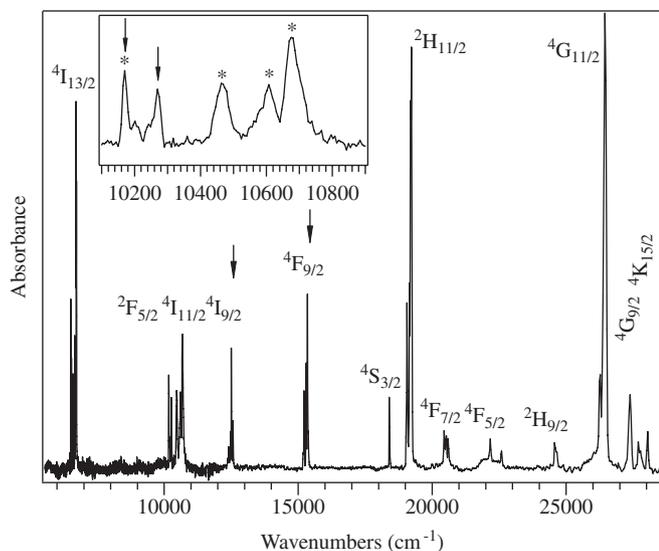


Fig. 1. 10 K unpolarized survey absorption spectrum of KYW: 2.5%Er³⁺, 2.5%Yb³⁺. The excited states of Er³⁺ and Yb³⁺ are labeled. The inset shows a zoom-in of the Yb³⁺ ²F_{7/2} → ²F_{5/2} transitions (marked with asterisks) and the ⁴I_{15/2} → ⁴I_{11/2} transitions in Er³⁺. Arrows indicate the UC excitation energies.

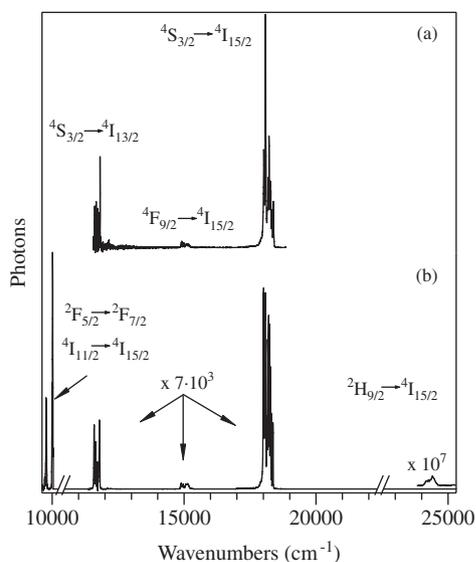


Fig. 2. 100 K unpolarized survey luminescence spectra in KYW: 2.5%Er³⁺, 2.5%Yb³⁺ after direct Er³⁺ ²H_{11/2} excitation at 19,231 cm⁻¹ (a) and after Yb³⁺ excitation at 10,190 cm⁻¹ (b). All luminescence peaks are assigned. Note the different scaling factors for (b) spectrum.

Fig. 3 compares the 10 K temporal evolution of the Er³⁺ ⁴S_{3/2} → ⁴I_{15/2} luminescence of KYW: 2.5%Er³⁺, 2.5%Yb³⁺ after exciting at 20,508 cm⁻¹ (a), 10,190 cm⁻¹ (b), and 10,290 cm⁻¹ (c).

The UC luminescence spectrum of KYW: 2.5%Er³⁺, 2.5%Yb³⁺ pumping at 10,190 cm⁻¹ can be explained with the well-known mechanism described in Fig. 4a. The green Er³⁺ ⁴S_{3/2} → ⁴I_{15/2} emission observed after 10,290 cm⁻¹ excitation is explained by a GSA/ESA UC process within

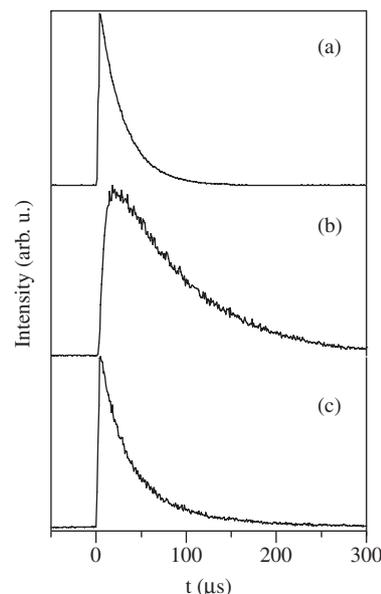


Fig. 3. Normalized 10 K temporal evolution of Er³⁺ ⁴S_{3/2} → ⁴I_{15/2} luminescence intensity in KYW: 2.5%Er³⁺, 2.5%Yb³⁺ detecting at 18,083 cm⁻¹ after short pulses excitation at 20,508 cm⁻¹ (a), 10,190 cm⁻¹ (b) and 10,290 cm⁻¹ (c).

Er³⁺ dopant ions (Fig. 4b). This is only true for low Er³⁺ dopant concentrations.

Temporal evolution of the Er³⁺ ⁴S_{3/2} → ⁴I_{15/2} luminescence obtained after Yb³⁺ excitation at 10,190 cm⁻¹ confirms the underlying UC mechanism proposed above. As shown in Fig. 3b, the UC luminescence transient exhibits a clear rise followed by decay. This is a clear fingerprint of an energy transfer process. We have fit the experimental data to $I(t) = Ae^{-Bt} - Ce^{-Dt}$, where B and D , related to an energy transfer rate constant (W_{ETU}) and the ²F_{5/2} and ⁴S_{3/2} intrinsic lifetimes, represent the decay and rise of the transient. The best fit in Fig. 3b corresponds to $B = 84 \mu\text{s}$ and $D = 9 \mu\text{s}$. In KYW: 2.5%Er³⁺, 2.5%Yb³⁺, the intrinsic Er³⁺ ⁴S_{3/2} → ⁴I_{15/2} lifetime at 10 K is 27 μs (excitation at 20,508 cm⁻¹) (Fig. 3a). The ⁴S_{3/2} intrinsic lifetime measured in the 2.5%Er³⁺ singly doped thin film is 29 μs , similar to 30 μs found in KYW: 0.2%Er³⁺. Therefore, the increase of the impurities concentration has no relevant effect in the lifetime. However, in the doubly doped sample, the upconversion decay time is lengthened compared to these values. Different temporal evolutions of the UC emissions were observed exciting at 10,290 and 10,190 cm⁻¹ in KYW: 2.5%Er³⁺, 2.5%Yb³⁺. In the former case, the UC intensity decays immediately after a short laser pulse (35 μs) slightly longer than the ⁴S_{3/2} intrinsic lifetime (27 μs). The single-ion GSA/ESA process is thus the dominant UC process. However, the increase of the lifetime is a clear fingerprint of the presence of other less efficient UC mechanism involving energy transfer between neighboring Er³⁺ ions. If two excited Er³⁺ ions are close enough, the ETU can take place, leading to longer lifetime of the ⁴I_{11/2} intermediate level. In 0.2%Er³⁺ and 2.5%Er³⁺ singly doped layers, 10 K Er³⁺ ⁴I_{11/2} intrinsic

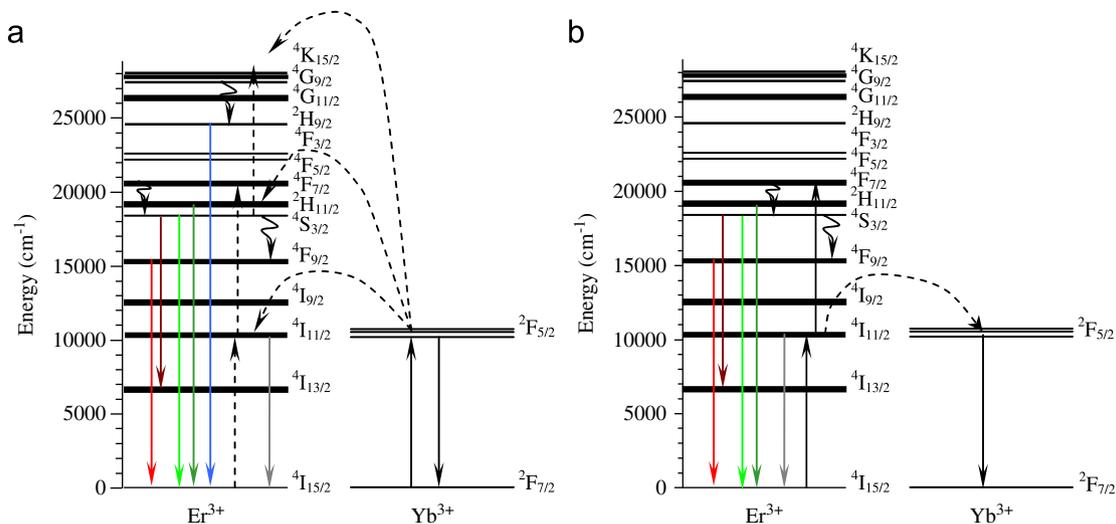


Fig. 4. Representation of the upconversion processes in KYW: 2.5%Er³⁺, 2.5%Yb³⁺ after Yb³⁺ excitation at 10,190 cm⁻¹ (a) and after Er³⁺ excitation at 10,290 cm⁻¹ (b). Full arrows indicate radiative processes of GSA, ESA and luminescence, dashed arrows represent non-radiative energy transfer processes and wavy arrows correspond to multiphonon relaxation processes.

lifetimes are 115 and 113 μ s, respectively. A 29 μ s lifetime of the $4F_{7/2}$ state in KYW: 0.2%Er³⁺ was measured after 10,290 cm⁻¹ excitation, whereas a lifetime of 44 μ s is found for the $4I_{11/2}$ in the KYW: 2.5%Er³⁺ thin film. This increase is due to the long lifetime of the $4I_{11/2}$ reservoir state required for the ETU process, therefore both results clearly evidence that the GSA/ETU mechanism becomes more relevant upon increasing Er³⁺ concentration. The different Er³⁺ $4I_{11/2}$ lifetime between KYW: 2.5%Er³⁺, 2.5%Yb³⁺ and KYW: 2.5%Er³⁺ thin films after 10,290 cm⁻¹ excitation is due to the additional deactivation channel of the former one, i.e., to the energy transfer from Er³⁺ to Yb³⁺.

When pumping at 10,190 cm⁻¹, only those Er³⁺ ions adjacent to a Yb³⁺ ion (a minority) are responsible for the GSA/ETU mechanism described in Fig. 4a. In the doubly doped sample 2.5%Er³⁺, 2.5%Yb³⁺, the Yb³⁺ intrinsic lifetime is 155 μ s. This lifetime is significantly shorter than the decay time found in KYW: 0.2%Yb³⁺ (395 μ s). Such a dramatic lifetime reduction cannot be only explained by the increase of the impurity concentration. This shortening of the measured lifetime in KYW: Er³⁺, Yb³⁺ is mainly the result of the Yb³⁺ \rightarrow Er³⁺ energy transfer which causes significant non-radiative depopulation of the Yb³⁺ excited state. Therefore, the Yb³⁺ lifetime provides evidences of the energy transfer efficiency. We have also analyzed the dynamic response of Yb³⁺ luminescence after Er³⁺ excitation at 10,290 cm⁻¹. It rises from zero immediately after the pulse (data not shown) reflecting the energy transfer step from Er³⁺ to Yb³⁺. The same behavior was observed for the temporal dependence of the Er³⁺ $4I_{11/2} \rightarrow 4I_{15/2}$ luminescence pumping with short pulses resonant to Yb³⁺ the $2F_{5/2}$ excited state.

In conclusion, time dependence of the UC luminescence provides proofs for the assignment of the UC mechanisms involved in each case. The most efficient UC process is achieved after Yb³⁺ excitation around 1 μ m. This is due to the efficient energy transfer (GSA/ETU) from Yb³⁺ to Er³⁺. Green emission found after excitation into the Er³⁺ $4I_{11/2}$ is explained by a competition between GSA/ESA and GSA/ETU (involving Er³⁺ pairs) processes. The Er³⁺ \rightarrow Yb³⁺ energy transfer also observed after Er³⁺ excitation is a source of efficiency reduction of the green UC process.

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