Up- and down-conversion emissions from Er^{3+} doped K_2YF_5 and K_2YbF_5 crystals

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ABSTRACT

Crystals of Er^{3+} doped K_2YF_5 and K_2YbF_5 as well as stoichiometric K_2ErF_5 have been grown under hydrothermal conditions. Peculiarities of Er^{3+} luminescence in these crystals have been studied under different excitation wavelengths and, in particular, it has been discovered that in 5 at% Er^{3+}:K_2YbF_5, the energy transfer (ET) efficiency from Yb^{3+} to Er^{3+} reaches 67%. Under near-IR excitation at 980 nm, this crystal is characterized by intense yellow up-conversion luminescence with CIE coordinates: $x = 0.449$, $y = 0.465$. Under UV and visible excitation at 355 and 532 nm, respectively, clear evidences of the down-conversion process through the cross-relaxation have been found. The corresponding efficiency of ET from Er^{3+} to Yb^{3+} is 69%. These features make Er^{3+}:K_2YbF_5 crystals attractive for developing luminescent up- and down-converters for enhancing the performance of solar cells.

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1. Introduction

Up-conversion is a process when absorption of two or more low-energy pump photons is followed by an emission of one photon with a higher energy. Materials containing trivalent rare-earth ions like erbium (Er^{3+}) provide efficient up-conversion [1]. Er^{3+} ions can absorb light at around 980 nm which corresponds to the emission of well-developed InGaAs laser diodes and emit in both the green (~ 540 nm) and the red (~ 650 nm) spectral regions. Due to the special structure of Er^{3+} energy levels, several efficient processes that provide the population of the higher-lying excited states can be easily implemented namely excited-state absorption (ESA), cross-relaxation (CR) and energy-transfer (ET) [2]. The use of an Er^{3+}–Yb^{3+} couple is beneficial for increasing the up-conversion efficiency due to a rather strong absorption of the Yb^{3+} ions at ~ 1 μm. The potential applications of Er-doped phosphors are in the field of solid-state lighting [3], biological labeling [4,5] or enhancement of the solar-cell efficiency [6] as well as the data concerning Er^{3+} up-conversion visible lasers have been reported [7].

Down-conversion (that is frequently called quantum cutting) is a process when one high-energy photon (UV/visible) is cut into two lower energy photons (near-IR) [8]. This process can be very efficient for Yb^{3+}–RE^{3+} ions pairs (where RE stands for Tb, Pr, Tm, Er, Nd or Ho ions) [9,10]. Typically, absorption of UV/visible light by RE^{3+} ions leads to the emission of Yb^{3+} ions at ~ 1 μm corresponding to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition. Down-conversion is useful when considering the problem of spectral mismatch between the solar cells and solar spectrum. In particular, for the Er^{3+}–Yb^{3+} couple, absorption of sunlight by Er^{3+} in the UV/visible can lead to the Yb^{3+} emission with the energy matching the band gap energy of silicon [11]. The efficiency of such second-order down-conversion process depends strongly on the interionic distances between optically active ions and, thus, the materials with high rare earth ion concentrations are desirable. It is also important to note that down-conversion is a linear process [12] and thus it can be efficient even for non-concentrated sunlight.

An important point for the efficient up- and down-conversion is the vibronic properties of the host. The rate of non-radiative relaxation from the excited-states of RE^{3+} ions is lower for materials with a lower maximum phonon frequency ν_{max}. Thus, for such materials the lifetimes of RE^{3+} ions in the involved excited-states are longer which increases the probability of further excitation steps like ESA or CR leading in general to the increase of intensity of up- and down-conversion luminescence. For fluoride crystals, $\nu_{max} \sim 400$ to 600 cm^{-1} which is much lower as compared with their oxide counterparts ($\nu_{max} \sim 1000$ cm^{-1}). Indeed,

Er^{3+} and Er^{3+}/Yb^{3+} doped fluoride and oxyfluoride materials (in the form of single crystals, glass–ceramics or nanopowders) provide intense up- and down-conversion luminescence [1–8].

In the present work, an attention is paid to the study of up- and down-conversion in fluoride K_2YF_5 crystals doped with Er^{3+} and Yb^{3+} ions as well as crystals of the stoichiometric compositions like K_2ErF_5 and K_2YbF_5 have been studied. Potassium yttrium penta-fluoride, K_2YF_5, belongs to the orthorhombic system, space group $Pna2_1$ (33) [13]. In the K_2YF_5 structure each Y^{3+} ion is surrounded by seven F^- ions with C_{2v} symmetry and the YF_7 polyhedra form chains parallel to the c-axis. The intrachain Y^{3+}–Y^{3+} distance is around 3.7 Å, and the shortest distance between the ions of different chains reaches $\sim$5 Å [14]. Such a structure is favorable for high doping concentrations of rare-earth ions. Indeed, isostructural series $K_2Y_{1-x}Er_xF_5$, $K_2Y_{1-x}Yb_xF_5$ and $K_2Y_{1-x-y}Yb_xEr_yF_5$ (with $0 < x < 1$ and $0 < y < 1$) exist. In addition, K_2YF_5 is characterized with a relatively low maximum phonon frequency $\nu_{max} \sim 418$ cm^{-1} [15] that is lower than in typical fluoride hosts, CaF_2 (477 cm^{-1}) or $LiYF_4$ ($\sim$490 cm^{-1}) and only slightly higher than in LaF_3 ($\sim$400 cm^{-1}). These features determine a potential for achievement of high up- and down-conversion efficiencies with rare-earth ion doped K_2YF_5. To the date, the spectroscopic properties of Nd^{3+} [16–19], Tb^{3+} [20], Pr^{3+} [21–24] and Tm^{3+} [25,26] ions in the K_2YF_5 have been studied. As for Er^{3+} ions, some data of crystal filed splitting and lifetime studies are reported for a K_2ErF_5 crystal in [27]. In [15], the up-conversion luminescence of Er^{3+} impurity ions in a Tm^{3+}:K_2YF_5 crystal has been studied and recently some data on the up-conversion luminescence in K_2YF_5 doubly doped with Er^{3+} and Yb^{3+} have been reported [28]. Relatively scarce information about this crystal is related to the difficulty of its synthesis.

2. Experimental

Crystals of orthorhombic K_2YF_5 and K_2YbF_5 doped with Er^{3+} as well as K_2ErF_5 and K_2YbF_5 were grown under hydrothermal conditions. For hydrothermal experiments, copper insert lined autoclaves having a volume of about 40 cm^3 were utilized and the inserts were separated into synthesis and crystallization zones by perforated diaphragms. The fluoride crystals were synthesized by a direct temperature-gradient method as a result of the reaction of the aqueous solutions containing 40–50 mol% KF with oxide mixtures $(1-x-y)Y_2O_3$–xEr_2O_3–yYb_2O_3 at a temperature of about 750 K in the synthesis zone, a temperature gradient along the reactor body of up to 3 K/cm, and a pressure of about 100 MPa. The purity of the utilized oxides was more than 99.99%. Under these conditions, spontaneously nucleated crystals up to 0.5 cm^3 in size were grown in the upper crystallization zone of the autoclave for 200 h.

The structure type and phase purity of synthesized samples were characterized with conventional powder X-ray diffraction (XRD) technique and powder XRD patterns were obtained by using a Bruker D8 Advance X-Ray powder diffractometer with Cu Kα radiation.

Absorption spectrum was measured for a 10 at% Er^{3+}:K_2YF_5 crystal with a Varian CARY 5000 spectrophotometer (the spectral bandwidth, SBW, was 0.1 nm).

Up-conversion luminescence (UCL) was excited by continuous-wave radiation of InGaAs laser diodes emitting at $\sim$960 nm (excitation to the Er^{3+} $^4I_{11/2}$ state) or at 980 nm (excitation to the Yb^{3+} $^2F_{5/2}$ state). Excitation light was focused on the sample in a $\sim$100 µm spot; the maximum power density was $\sim$40 kW/cm^2. Luminescence was also excited at $\sim$355 and $\sim$520 nm (excitation to the $^2G_{9/2}$ and $^2H_{11/2}$ states of Er^{3+}, respectively) and a ns optical parametric oscillator (OPO) Lotis TII LT-2214 was used. Luminescence spectra were measured with a lock-in amplifier, a

monochromator MDR-23 (SBW $\sim$0.1 nm) as well as sensitive Hamamatsu S5345 and C5460-01 photodetectors. The spectral sensitivity of the set-up was accurately determined with a halogen lamp with calibrated spectral power density. The monochomator itself was calibrated with Pb and Xe lamps.

For the studies of luminescence decay, OPO with the pulse duration of $\sim$20 ns was tuned to 355 or 960 nm. Luminescence was collected by a wide-aperture lens and re-imaged to the input slit of a monochromator MDR-12 (SBW$\sim$1 nm); then it was detected with fast Hamamatsu S5345 or C5460 photodetectors (response time, $<$100 ns) and a 500 MHz Textronix TDS-3052B digital oscilloscope.

The CIE chromaticity coordinates of phosphors were calculated by using the photo luminescence data. All spectroscopic studies were performed at room temperature.

3. Results and discussion

Some as-grown crystals are shown in Fig. 1 and, as one can see, crystals demonstrate good optical quality. The XRD patterns of K_2YF_5, K_2ErF_5 and K_2YbF_5 are shown in Fig. 2 and they confirm that synthesized crystals have the orthorhombic lattice with similar unit cell dimensions, $a=10.820$ Å, $b=6.613$ Å, $c=7.249$ Å (for K_2YF_5), $a=10.813$ Å, $b=6.609$ Å, $c=7.245$ Å (for K_2ErF_5) and $a=10.765$ Å, $b=6.514$ Å, $c=7.203$ Å (for K_2YbF_5), see ICDD PDF Card-01-072-2387 [14,29]. Similar XRD patterns have been obtained for K_2YF_5 and K_2YbF_5 containing different Er^{3+} concentrations by confirming that all the compounds also crystallize into the pure orthorhombic phases, and Erbium doping does not lead to the formation of another crystal phase.

By using a 1 mm-thin plate made of the as-grown crystal, an absorption spectrum has been measured for 10 at% Er^{3+}:K_2YF_5 and it is shown in Fig. 3. Similar absorption characteristics are observed for Er^{3+}:K_2YbF_5 crystal which agrees with very similar
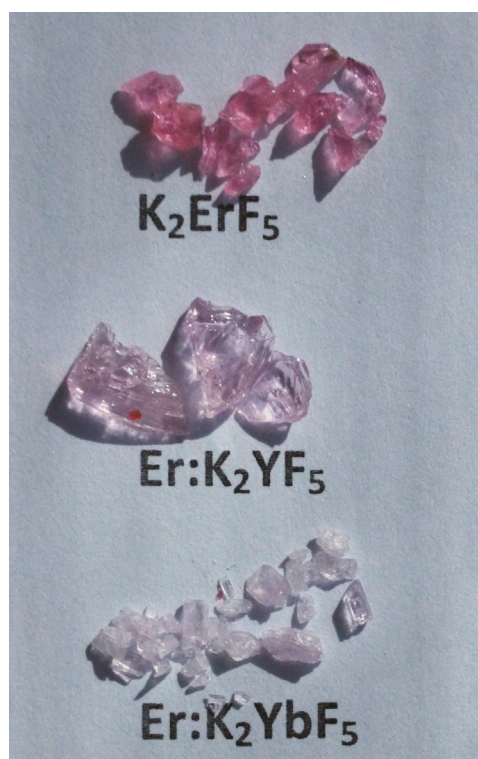

Fig. 1. Images of the studied Er-doped K_2YF_5 and K_2YbF_5 crystals.