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Cooperative radiative and nonradiative effects in K_2NaScF_6 codoped with V^{3+} and Er^{3+}

Christine Reinhard, Karl Krämer, Daniel A. Biner, and Hans U. Güdel^{a)} Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3000 Bern 9, Switzerland

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K₂NaScF₆ crystals codoped with V³⁺ and Er³⁺ exhibit some novel cooperative near-IR to visible upconversion processes at cryogenic temperatures. V³⁺ mainly acts as a broadband sensitizer. The V^{3+ 3}T_{1g}→³T_{2g} excitation between 13 500 and 15 500 cm⁻¹, after fast relaxation to V^{3+ 1}T_{2g}, can be transferred to Er^{3+ 4}I_{11/2}, and then upconversion takes place. Four upconversion mechanisms are identified and characterized. For narrow-band laser excitation the overall efficiency of the upconversion processes is low. However, at 12 K for broadband excitation, such as in a lamp, between 12 000 and 14 500 cm⁻¹ the number of emitted visible photons is roughly doubled by codoping V³⁺ in addition to Er³⁺. © 2004 American Institute of Physics. [DOI: 10.1063/1.1640335]

I. INTRODUCTION

The phenomenon of photon upconversion, i.e., longwavelength excitation followed by shorter wavelength emission, has been widely observed and investigated in lanthanide containing materials.¹⁻³ Lanthanide ions in solids, thanks to the shielding of the 4f electrons, often exhibit more than one metastable excited f - f state. This is one of the conditions for upconversion. Another one is a sizeable absorption cross section at the excitation wavelengths, usually in the near-infrared (NIR).⁴ f-f transitions are usually weak and the corresponding absorption bands sharp. Laser excitation into the absorption maximum of, e.g., $Er^{3+4}I_{11/2}$ around 980 nm still leads to intense green ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ upconversion (UC) emission in many Er³⁺ containing materials.^{5,6} But higher UC yields can be obtained by sensitization. Yb³⁺ has proven to be an excellent UC sensitizer for the most important UC ions Er³⁺ (green) and Tm³⁺ (blue) in halide lattices.7,8

The idea in the present paper is to use broadband NIR sensitization of Er^{3+} and thus induce upconversion. This is driven by academic curiosity on the one hand, but also by the application potential of a device based on such a material. Present day lamps, particularly incandescent lamps, emit a great deal of their output in the NIR, where it is lost. If part of this output could be recycled by NIR to visible (VIS) upconversion, the lamp efficiency could potentially be improved. Spin-allowed d-d bands of transition-metal (TM) ions are broad, and properly situated in the spectrum, might suit the purpose of light absorption, followed by energy transfer (ET) to Er^{3+} , where the UC process could take place.9 There are a number of restrictions for the choice of the TM ion. Its first and hopefully metastable excited state must lie above $\text{Er}^{3+4}I_{11/2}$, so that ET to Er^{3+} must be possible. The TM ion must have negligible absorption in the green, around 550 nm, where the $\operatorname{Er}^{3+4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ emission takes place. And finally there must be a spin-allowed absorp-

The aim of the present paper is not the development of a material which can be used to increase the visible output of lamps. Rather, it represents a very first step towards this long term objective. The chemistry and upconversion photon physics of compounds codoped with a lanthanide and a TM ion is essentially unexplored.^{11,12} So we have to start with questions such as: Is the V^{3+}/Er^{3+} couple a suitable one? Can a fluoride containing both ions be synthesized? Does upconversion occur and with which efficiency and by which mechanisms? Figure 1 shows the energy level schemes of Er^{3+} and V^{3+} in an octahedral fluoride environment. The absorption and luminescence properties of V³⁺ doped K_2NaScF_6 have been studied and described in the literature.¹³ The broad absorption ${}^{3}T_{1g} \rightarrow {}^{3}T_{2g}$ is situated be-tween 13 500 and 15 500 cm⁻¹. The lowest energy excited state ${}^{1}T_{2a}$ from which emission takes place at low temperature is situated at 10413 cm⁻¹. Er³⁺ upconversion processes have been studied in many fluoride crystals and glasses.^{14,15} The origin of the ${}^{4}I_{11/2}$ excited state lies at about 10200 cm⁻¹ in such an environment, i.e., just about perfect for excitation transfer from $V^{3+1}T_{2g}$.

II. EXPERIMENTAL SECTION

A. Crystal growth

 $K_2NaScF_6:Er^{3+}$: The appropriate stoichiometric amounts of Sc_2O_3 (REacton[®] Alfa Aesar 99.99%), Er_2O_3

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tion band in the red/NIR part of the spectrum. V^{3^+} in a fluoride or chloride environment fulfills the conditions, and we have already demonstrated the principal feasibility of the concept in V^{3^+} and Mo^{3^+} doped Cs_2NaYCl_6 .¹⁰ In the present study we choose Er^{3^+} , one of the most efficient and best studied UC ions, and we choose a fluoride instead of chloride, because fluorides are generally much less air sensitive than chlorides. For the particular combination of V^{3^+} as a sensitizer and Er^{3^+} as an upconverter a fluoride lattice has the essential advantage that $V^{3^+ 1}T_{2g}$ lies above $Er^{3^+ 4}I_{11/2}$, in contrast to the other halides.

^{a)}Author to whom correspondence should be addressed. Fax: +41 31 631 43 99; Electronic mail: hans-ulrich.guedel@iac.unibe.ch



FIG. 1. Energy level scheme for Er^{3+} and V^{3+} in an octahedral fluoride environment with some relevant excitation and relaxation processes. Straight and wavy arrows indicate radiative and nonradiative processes, respectively.

(Johnson Mattey & Brandenberger), KCl (Merck Suprapur®), and NaCl (Merck Suprapur®) were dissolved in hot HCl (30% Suprapur). The solution was evaporated, and the resultant white solid was ground and dried. The white $K_2NaScCl_6:Er^{3+}$ powder was fluorinated at 550 °C in a HF gas stream for 64 h. The HF gas stream was produced by decomposing KHF₂ (Fluka, puriss p.a.) at 420 °C. The $K_2NaScF_6:Er^{3+}$ powder was enclosed in a tantalum ampoule, which had been sealed into a quartz ampoule. Crystal growth of $K_2NaScF_6:Er^{3+}$ was achieved by melting the powder at a furnace temperature of 1050 °C and slow cooling to room temperature over a period of two weeks. The Er^{3+} concentration in the starting mixture was 0.5%, but only 0.05% were actually incorporated into the crystal, as estimated from absorption spectra.

VF₃: Dark green VF₃ was obtained by fluorination of VCl₃ (Atomergic Chemetals 99%) in a HF gas stream for 14 h at 400 °C.

 $K_2NaScF_6:Er^{3+}$; V^{3+} : First, the same procedure was followed as for $K_2NaScCl_6:Er^{3+}$, except for the fluorination step. The white $K_2NaScCl_6:Er^{3+}$ powder was mixed with the appropriate amount of VF₃ and fluorinated in a HF gas stream at 400 °C for 24 h. Single crystals with an average size of $1\times1\times0.5$ mm were obtained, with the method described for the growth of $K_2NaScF_6:Er^{3+}$. The elpasolite structure was verified by powder X-ray diffraction. The V³⁺ and Er^{3+} concentration in the starting mixture was 2.5% and 0.5%, respectively, but only 0.2% and 0.05%, respectively, were actually incorporated. This was estimated from the *d*-*d* and *f*-*f* absorptions in the VIS/NIR.

B. Spectroscopy

Absorption spectra were measured on a Cary 5E (Varian) spectrometer. Samples for absorption were embedded in po-

lymerizable resin and then cut and polished. The samples were mounted in an open copper cell and cooled with a closed cycle cryostat.

Continuous-wave luminescence and excitation spectra were performed using a tunable Ti:sapphire laser (Spectra Physics 3900S), pumped by a frequency doubled Nd³⁺:YVO₄ laser (Spectra Physics Millenia Xs), as an excitation source. Wavelength control was achieved by using an inchworm driven (Burleigh PZ-501) birefringent filter, and the wavelength was monitored with a wavemeter (Burleigh WA2100). The visible sample upconversion luminescence was dispersed by a 0.85 m double monochromator (Spex 1402) with 500 nm blazed 1200 grooves/mm gratings. The visible luminescence was detected by a cooled photomultiplier tube (Hamamatsu 3310-01) using a photon counting system (Stanford Research SR400). The laser beam (diameter: 1 mm) was focused on the sample with a f=53mm focal lens.

The near-infrared sample luminescence was dispersed by a 0.75 m single monochromator (Spex 1702) equipped with a 750 nm blazed 600 grooves/mm grating. It was measured with a liquid nitrogen cooled Ge detector (ADC 403L). The detector signal was processed by a lock-in amplifier (Stanford Research DS 345).

The spectra represent the number of photons versus wave numbers. All the luminescence spectra were corrected for the wavelength dependent response of the monochromator and detection system, and for the refractive index of air (vacuum correction). The upconversion excitation spectrum was corrected linearly for the wavelength dependent output power of the Ti:sapphire laser. The luminescence spectra measured using near-infrared and visible sensitive detectors were scaled to each other by measuring the sample luminescence around 10 000 cm⁻¹ with both detectors.

For luminescence lifetime measurements in the NIR, rectangular pulses of the Ti:sapphire were generated by using an acousto-optic modulator (Coherent 305) connected to a function generator (Stanford Research DS 345). The temporal behavior of the luminescence intensity was detected using a multichannel scaler (Stanford Research SR430) for decay curves. For all the luminescence measurements, cooling of the crystals was achieved using the helium-gas flow technique.

III. RESULTS

Figure 2(a) shows the 12 K luminescence spectrum of $K_2NaScF_6:Er^{3+}$ excited into the maxima of the ${}^4I_{9/2}$ absorption band at 12 525 cm⁻¹ for the visible and at 12 534 cm⁻¹ for the near-IR part, with a laser power of 121 mW. We observe the dominant NIR emissions ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$ and ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ located around 10 000 and 6500 cm⁻¹, respectively. In addition, the ${}^2H_{9/2} \rightarrow {}^4I_{15/2}$, ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ emissions are observed in the VIS part of the spectrum, but with smaller intensities. The ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$ origins are located at 10 198 and 6503 cm⁻¹, respectively. The photon ratio of the ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$ and ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ emissions is 44/56 at this temperature.

Figure 2(b) shows the 12 K luminescence spectrum of $K_2NaScF_6:Er^{3+}$; V^{3+} excited into the ${}^3T_{2g}$ absorption band



FIG. 2. (a) 15 K luminescence spectra of K₂NaScF₆:Er³⁺ excited into ${}^{4}I_{9/2}$ at 12 525 cm⁻¹ for the visible and at 12 534 cm⁻¹ for the near-IR part (laser power 121 mW). (b) 15 K luminescence spectra of K₂NaScF₆:Er³⁺; V³⁺ excited into V³⁺³T_{2g} at 14 175 cm⁻¹ (laser power 150 mW). Note the scaling factors of the VIS part. The asterisk (*) denotes a peak which is due to the second order of the pump laser.

at 14 175 cm⁻¹ with a laser power of 150 mW. In the near IR around 10 000 cm⁻¹ we observe a superposition of $V^{3+1}T_{2g} \rightarrow {}^{3}T_{1g}$ emission, with an origin at 10 413 cm⁻¹, and a weak $Er^{3+4}I_{11/2} \rightarrow {}^{4}I_{15/2}$ emission with an origin at 10 198 cm⁻¹. Besides this dominant feature there is a strong $Er^{3+4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ emission around 6500 cm⁻¹ and very weak ${}^{2}H_{9/2} \rightarrow {}^{4}I_{15/2}$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ emissions in the VIS.

Figures 3(b) and 3(c) show 15 K NIR excitation spectra of K₂NaScF₆:Er³⁺ monitoring the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ UC luminescence at 18 315 cm⁻¹ and the ${}^{4}I_{11/2} \rightarrow {}^{4}I_{15/2}$ NIR luminescence at 10 081 cm⁻¹, respectively. The ${}^{4}I_{15/2} \rightarrow {}^{4}I_{11/2}$ and ${}^{4}I_{15/2} \rightarrow {}^{4}I_{9/2}$ multiplets are seen in both spectra, but with clear differences in the fine structure. For future reference, Fig. 3(a) shows a section of the single-crystal absorption spectrum of K₂NaScF₆:Er³⁺. The proper *x* axis is shown at the top. It is shifted with respect to the *x* axis of the Figs. 3(b) and 3(c) by 10 198 cm⁻¹, the origin of Er³⁺⁴I_{11/2} in this lattice.

Figures 4(b) and 4(c) show 15 K excitation spectra of $K_2NaScF_6:Er^{3+}$; V^{3+} monitoring the $Er^{3+} {}^4S_{3/2} {}^{+}I_{15/2}$ UC emission at 18 315 cm⁻¹ and the $V^{3+} {}^1T_{2g} {}^{+}3T_{1g}$ NIR emission at 10 198 cm⁻¹, respectively. They both show bands corresponding to $Er^{3+} {}^4I_{15/2} {}^{+}4I_{11/2}$ (around 10 300 cm⁻¹) and ${}^4I_{15/2} {}^{+}4I_{9/2}$ (around 12 500 cm⁻¹) excitations, but with very different relative intensities and fine structures. Above 13 500 cm⁻¹ the excitation spectrum of the $V^{3+} {}^1T_{2g} {}^{-}3T_{1g}$ emission in Fig. 4(c) shows the onset of the ${}^3T_{1g} {}^{-}3T_{2g}$ absorption. In the UC excitation spectrum in Fig. 4(b) there are relatively strong sharp features above 14 000 cm⁻¹ superimposed on a broadband shown in gray. Our Ti:saphhire laser is tunable up to 14 500 cm⁻¹, and we were



FIG. 3. (a) 7 K absorption spectrum of K₂NaScF₆:Er³⁺ in the region of the ${}^{4}F_{7/2}$, ${}^{4}F_{5/2}$, and ${}^{4}F_{3/2}$ transitions. The true energy axis of this absorption spectrum is at the top of the graph. The energy axis at the bottom represents a redshift of 10 198 cm⁻¹, the energy of the ${}^{4}I_{11/2}$ origin in the absorption spectrum. (b) 15 K excitation spectrum of K₂NaScF₆:Er³⁺ monitoring the Er^{3+ 4}S_{3/2} \rightarrow ⁴ $I_{15/2}$ upconversion luminescence at 18 315 cm⁻¹. (c) 15 K excitation spectrum of K₂NaScF₆:Er³⁺ monitoring the Er^{3+ 4} $I_{11/2}$ \rightarrow ⁴ $I_{15/2}$ NIR luminescence at 10 081 cm⁻¹. The excitation spectra are corrected linearly for the output of the Ti:sapphire laser. The *y* scales are different for the energy ranges to the left and right of the dotted line. The letters A, B, C, and D stand for the excitations ${}^{4}I_{15/2} \rightarrow {}^{4}I_{11/2}$, ${}^{4}I_{11/2} \rightarrow {}^{4}F_{7/2}$, ${}^{4}I_{15/2} \rightarrow {}^{4}I_{9/2}$ and ${}^{4}I_{9/2} \rightarrow {}^{4}F_{3/2}$ respectively, see Fig. 6(a).

thus able to catch the most important part of the excitation spectrum. Figure 4(a) shows a section of the single-crystal absorption spectrum of $K_2NaScF_6:Er^{3+}$. The proper *x* axis is shown at the top. It is shifted with respect to the *x* axis of the Figs. 4(b) and 4(c) by 6503 cm⁻¹, the origin of $Er^{3+4}I_{13/2}$ in this lattice.

In Fig. 5 we compare the excitation spectrum of K_2NaScF_6 : Er^{3+} in the region of the ${}^4I_{15/2} \rightarrow {}^4I_{11/2}$ absorption with the $V^{3+} {}^1T_{2g} \rightarrow {}^3T_{1g}$ emission spectrum of K_2NaScF_6 : Er^{3+} ; V^{3+} at 15 K. The spectral overlap is seen to be very good. The inset of Fig. 5 shows the temperature dependence of the $V^{3+}T_{2g}$ lifetime.

IV. DISCUSSION

A. V³⁺ and Er³⁺ luminescences

Our primary goal in this study is the search for cooperative new processes in V^{3+} and Er^{3+} codoped K_2NaScF_6 crystals. Before doing so, see Sec. IV B, we have to briefly characterize and discuss the "normal" luminescence processes of V^{3+} and Er^{3+} , respectively, in this lattice.

The host lattice K_2NaScF_6 is cubic with a lattice constant of 8.47 Å. It belongs to the family of cubic facecentered elpasolites and contains discrete $[ScF_6]^{3-}$ units. The ionic radii of Sc^{3+} , V^{3+} , and Er^{3+} for octahedral coordination are 0.75, 0.64, and 0.89 Å, respectively.¹⁶ We at-



FIG. 4. (a) As in Fig. 3, but with a shift of 6503 cm⁻¹, the ${}^{4}I_{13/2}$ origin, between the top and bottom axes. (b) 15 K upconversion excitation spectrum of K₂NaScF₆:Er³⁺; V³⁺ monitoring the Er³⁺⁴S_{3/2} \rightarrow ⁴ $I_{15/2}$ luminescence at 18 315 cm⁻¹. (c) 15 K excitation spectrum of K₂NaScF₆:Er³⁺; V³⁺ monitoring the NIR luminescence at 10 198 cm⁻¹. Spectra (b) and (c) are corrected for the linear output power of the Ti:sapphire laser. The *y* scales are different for the energy ranges left and right of the dotted line. The letters refer to excitations defined in Fig. 6.

tribute the fact that only small amounts of both V^{3+} and Er^{3+} could be incorporated to the differences in ionic radius between host and guests.

The $V^{3+1}T_{2g} \rightarrow {}^{3}T_{1g}$ luminescence spectrum of $K_2 \text{NaScF}_6: \text{Er}^{3+}; V^{3+}$ shown in Fig. 2(b) is slightly contaminated by the underlying $\text{Er}^{3+4}I_{11/2} \rightarrow {}^{4}I_{15/2}$ emission. It is very similar in line positions and relative intensities to the published spectrum of $K_2 \text{NaScF}_6$: V^{3+} .¹³ There is a significant difference in the 15 K lifetimes, however, we determine τ_{15K} = 68 ms, whereas a value τ_{15K} = 25 ms was reported for this temperature in Ref. 13. Since the presence of Er^{3+} in our crystal cannot possibly lead to a longer ${}^{1}T_{2g}$ lifetime, we conclude that the sample used in Ref. 13 was suffering from nonradiative loss processes not present in our sample. The steep drop of τ between 15 and 80 K, see inset of Fig. 5, was also observed in Ref. 13. It is thus typical of V^{3+} in this lattice and not primarily resulting from the presence of Er³⁺ in our codoped crystals. In Ref. 13 this thermal quenching was attributed to thermally activated multiphonon relaxation processes.

There are hundreds of papers in the literature dealing with NIR to VIS upconversion in Er^{3+} doped fluorides.^{17,18} In upconversion phosphor and laser materials, in which sharp line excitation is used, $\text{Yb}^{3+2}F_{7/2} \rightarrow {}^2F_{5/2}$ excitation around 10 307 cm⁻¹ (970 nm) is often used as an efficient sensitizer. As shown in Figs. 2 and 3 excitation into ${}^4I_{15/2} \rightarrow {}^4I_{11/2}$ between 10 200 and 10 500 cm⁻¹ and ${}^4I_{15/2} \rightarrow {}^4I_{9/2}$ between 12 300 and 12 800 cm⁻¹ leads, in addition to ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$



FIG. 5. Luminescence spectrum at 15 K of K₂NaScF₆:Er³⁺; V³⁺ excited at 14 175 cm⁻¹ (bottom, V³⁺¹T_{2g} \rightarrow ³T_{1g}) and 15 K excitation spectrum of K₂NaScF₆:Er³⁺ monitoring the ⁴I_{11/2} \rightarrow ⁴I_{15/2} emission at 10 081 cm⁻¹ (top). The areas below the curves are normalized to one. The inset shows the V³⁺ ¹T_{2g} luminescence lifetime in K₂NaScF₆:Er³⁺; V³⁺ as a function of temperature.

and ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ emission in the NIR, to efficient upconversion emission in K₂NaScF₆:Er³⁺ at 15 K. The dominant UC bands are due to ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ (green) and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ (red) transitions, with a very small intensity also in the violet ${}^{2}H_{9/2} \rightarrow {}^{4}I_{15/2}$ emission, when excited into ${}^{4}I_{15/2} \rightarrow {}^{4}I_{9/2}$. They are all due to two-photon and three-photon processes as evidenced by their power dependence, which was experimentally determined.

Figure 6(a) shows a scheme with the UC mechanism in $K_2NaScF_6:Er^{3+}$ for ${}^4I_{15/2} \rightarrow {}^4I_{11/2}$ and ${}^4I_{15/2} \rightarrow {}^4I_{9/2}$ excitation, respectively. These were determined from the excitation spectra in Fig. 3. A sequence of ground-state absorption [GSA, steps A and C in Fig. 6(a)] and excited-state absorption steps [ESA, steps B and D in Fig. 6(a)] lead to ${}^4F_{7/2}$ and ${}^4F_{3/2}$ population upon ${}^4I_{15/2} \rightarrow {}^4I_{11/2}$ and ${}^4I_{15/2} \rightarrow {}^4I_{9/2}$ laser excitation, respectively. In our $K_2NaScF_6:Er^{3+}$ we see from a comparison of Figs. 3(a) and 3(c) an energetic coincidence of the multiplets A and B. A similar coincidence occurs for transitions C and D. These are well established processes in Er^{3+} doped fluorides.^{5,19} As a result of these mechanisms the actual excitation multiplets around 10 400 and 12 600 cm⁻¹ in Fig. 3(b) correspond to the products of the profiles A*B and C*D, respectively. This explains the difference to Fig. 3(c), in which the pure GSA steps A and C are probed.

From the relative photon counts in the various emission bands in Fig. 2(a) we get important information about nonradiative relaxation processes. The integrated photon ratio for the ${}^{4}I_{11/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ emissions at 15 K upon ${}^{4}I_{15/2} \rightarrow {}^{4}I_{9/2}$ excitation is 44/56. The most likely nonradiative ${}^{4}I_{11/2} \rightarrow {}^{4}I_{13/2}$ process is multiphonon relaxation. The energy gap between the ${}^{4}I_{11/2}$ and ${}^{4}I_{13/2}$ multiplet is about 3700 cm⁻¹. The highest phonon energy in K₂NaScF₆ is estimated to be 560 cm⁻¹.^{13,20} Thus six quanta of the highest energy vibration are needed to bridge this energy gap. Since the ${}^{4}I_{15/2} \leftrightarrow {}^{4}I_{11/2}$ oscillator strength is very small, the



FIG. 6. Schematic representation of the relevant upconversion mechanisms in $K_2NaScF_6:Er^{3+}$ (a) and $K_2NaScF_6:Er^{3+}$; V^{3+} (b)–(d). The relevant GSA and ESA transition steps are labeled by the letters A–G. Straight and wavy arrows stand for radiative and nonradiative processes, respectively.

nonradiative ${}^{4}I_{11/2} \rightarrow {}^{4}I_{13/2}$ deactivation by multiphonon relaxation is competitive. Looking at the VIS part of Fig. 2(a), we see that the ${}^{2}H_{9/2} \rightarrow {}^{4}I_{15/2}$ emission is extremely weak. In this case multiphonon relaxation down to ${}^{4}S_{3/2}$ is absolutely dominant, since the largest gap between ${}^{2}H_{9/2}$ and ${}^{4}F_{3/2}$ is only 2300 cm⁻¹. In Er³⁺ containing UC phosphors the green (${}^{4}S_{3/2}$) and red (${}^{4}F_{9/2}$) photon ratio can be tuned by varying the Er³⁺ (and Yb³⁺) concentrations as well as the temperature. Besides multiphonon relaxation there are processes such as cross-relaxation that are likely to contribute to ${}^{4}S_{3/2} \rightarrow {}^{4}F_{9/2}$ relaxation.

For 121 mW laser excitation into ${}^{4}I_{9/2}$ at 15 K we obtain a ratio of integrated VIS (${}^{4}S_{3/2} + {}^{4}F_{9/2}$) to NIR (${}^{4}I_{11/2} + {}^{4}I_{13/2}$) emitted photons of 13%. This is a high ratio, comparable to the best known Er³⁺ based UC phosphors.²¹

B. Cooperative processes in V³⁺ and Er³⁺ codoped K_2NaScF_6

1. V³⁺ to Er³⁺ energy transfer

Excitation into the spin-allowed $V^{3+3}T_{1g} \rightarrow {}^{3}T_{2g}$ absorption band between 13500 and 15500 cm⁻¹ in the codoped K₂NaScF₆:Er³⁺; V³⁺ crystal leads, in addition to the normal V³⁺ emission around 10000 cm⁻¹, to Er³⁺ emission both in the NIR and the VIS. This is seen in Fig. 2(b). The Er³⁺⁴I_{11/2} $\rightarrow {}^{4}I_{15/2}$ band strongly overlaps with the V³⁺¹T_{2g} $\rightarrow {}^{3}T_{1g}$ band, see Figs. 2(a) and 2(b). The Er³⁺⁴I_{13/2} $\rightarrow {}^{4}I_{15/2}$ emission around 6500 cm⁻¹, on the other hand, is well separated.

From the measured integrated photon counts at 15(200) K in the various emission bands we derive the ratios shown in Fig. 7. At 15 K we can assume that there is no multiphonon relaxation from $V^{3+1}T_{2g}$ to ${}^{3}T_{1g}$. We then find that 58% of the V^{3+} excitation is emitted as ${}^{1}T_{2g}$ to ${}^{3}T_{1g}$ and 42% is transferred to Er^{3+} . This is subdivided into 19% ${}^{4}I_{11/2} \rightarrow {}^{4}I_{15/2}$ and 23% ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$. At 200 K multiphonon relaxation processes become much more important. The total of emitted photons decreases substantially, and the ratios change. The total loss of V^{3+} excitation due to nonradiative processes is reflected in the decreasing lifetime of the ${}^{1}T_{2g} \rightarrow {}^{3}T_{1g}$ luminescence between 10 and 200 K shown in the inset of Fig. 5. The decrease is about one order of mag-

nitude. This is mainly due to $V^{3+1}T_{2g} \rightarrow {}^{3}T_{1g}$ multiphonon relaxation processes. The part which is transferred to Er^{3+} all ends up on ${}^{4}I_{13/2}$, because $Er^{3+}{}^{4}I_{11/2} \rightarrow {}^{4}I_{13/2}$ multiphonon relaxation also dominates the ${}^{4}I_{11/2}$ depletion at this temperature. The net result is a photon ratio of 22/78 for $V^{3+}({}^{1}T_{2g})/Er^{3+}({}^{4}I_{13/2})$, respectively, at 200 K. From the above numbers we conclude that V^{3+} to Er^{3+} energy transfer is competitive with the other relaxation processes of $V^{3+}{}^{1}T_{2g}$, particularly at lower temperatures.

The energy transfer occurs from $V^{3+1}T_{2g}$, after fast ${}^{3}T_{2g} \rightarrow {}^{1}T_{2g}$ multiphonon relaxation. The accepting state is $\mathrm{Er}^{3+4}I_{11/2}$. The relevant spectral overlap is thus between the $V^{3+1}T_{2g} \rightarrow {}^{3}T_{1g}$ emission profile and the $\mathrm{Er}^{3+4}I_{15/2} \rightarrow {}^{4}I_{11/2}$ excitation profile. These experimental profiles, both normalized to one, at 15 K are shown in Fig. 5. The overlap is substantial and this explains the observed phenomena. From the $V^{3+1}T_{2g}$ branching ratio $k_{ET}/k_{rad} = 42/58$ and $k_{ET} = k_{tot} - k_{rad}$, see Fig. 7 and the measured $V^{3+1}T_{2g}$ lifetime at 15 K of 68 ms ($k_{tot} = 14.7 \mathrm{ s}^{-1}$) we derive a value for the macroscopic energy transfer rate constant $k_{ET} = 6.2 \mathrm{ s}^{-1}$.



FIG. 7. Schematic representation of the relevant radiative (straight arrows) and non-radiative (wavy arrows) processes in $K_2NaScF_6:Er^{3+}$; V^{3+} . The numbers represent the measured emission photon ratios relevant at 15 and (200) K.

This is a small value considering the almost optimal spectral overlap, and we ascribe it to the low concentration of both dopant ions in this lattice.

2. Cooperative upconversion mechanisms

Figure 2(b) shows that upconversion emission can be induced in K₂NaScF₆:Er³⁺; V³⁺ by exciting into the V^{3+ 3} T_{1g} \rightarrow ³ T_{2g} absorption band in the far red. There is no Er³⁺ absorption at the laser wavelength used in this experiment, and a control experiment with the singly Er³⁺ doped crystal does not show any upconversion emission. The three emission bands in the near UV, green and red spectral regions are very similar to the UC bands in the singly doped sample [Fig. 2(a)] and assigned to ${}^{2}H_{9/2} \rightarrow {}^{4}I_{15/2}$, ${}^{4}S_{3/2}$ $\rightarrow {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transitions, respectively. The power dependence of the ${}^{4}H_{9/2} \rightarrow {}^{4}I_{15/2}$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ upconversion emission intensity was found to be very close to quadratic, confirming the two-photon character of the process.

We note that the Er³⁺ bands in Fig. 2(b) are not as well resolved as in Fig. 2(a). The individual lines are broader, and this is ascribed to an inhomogeneous broadening due to the relatively high V³⁺ doping on the one hand and to small shifts and splittings of the Er³⁺ levels due to V³⁺-Er³⁺ exchange interactions on the other. The green emission is visible by eye at temperatures up to 200 K for 96 mW laser excitation at 14 175 cm⁻¹ into V^{3+ 3}T_{2g}. But, as seen in Fig. 2(b), the visible emissions are very weak compared to the NIR emission bands. A comparison of Figs. 4(b) and 4(c) confirms that V^{3+ 3}T_{1g}→³T_{2g} broadband excitation above 13 500 cm⁻¹ is most efficient in inducing Er³⁺ NIR (⁴I_{11/2} →⁴I_{15/2} +⁴I_{13/2} →⁴I_{15/2}) emission. Direct Er^{3+ 4}I_{15/2} →⁴I_{11/2} excitation, on the other hand, is unimportant.

The absorption and upconversion excitation spectra shown in Fig. 4 allow for an unambiguous identification and characterization of three distinct mechanisms. They are schematically represented in Figs. 6(b), 6(c), and 6(d) and will now be discussed in this order. The first step is the $V^{3+3}T_{1g} \rightarrow {}^{3}T_{2g}$ excitation. It is common to all three mechanism, and we label it G in Fig. 4 and 6. The onset of the ${}^{3}T_{1g}$ to ${}^{3}T_{2g}$ absorption band is around 13 500 cm⁻¹, and we can follow it up to about 14 500 cm⁻¹, the limit of our Ti:sapphire tuning range. In Fig. 4(c) it can be seen that we reach about the maximum of the absorption band. This is in good agreement with the absorption spectrum of V^{3+} in K₂NaScF₆ in Ref. 13, in which this absorption band extends from 13 500 to about 15 500 cm⁻¹. In the mechanism depicted in Fig. 6(b), this $V^{3+3}T_{1g} \rightarrow {}^{3}T_{2g}$ excitation relaxes to ${}^{1}T_{2g}$ and is then transferred to $Er^{3+4}I_{11/2}$ (Sec. IV B 1). The next step is an excited-state absorption (ESA) ${}^{4}I_{11/2}$ to ${}^{2}H_{9/2}$ on Er^{3+} [process F in Fig. 6(b)]. The experimental evidence for this is the peak labeled G*F in the upconversion excitation spectrum Fig. 4(b). Its position corresponds to the energy difference between the ${}^{2}H_{9/2}$ levels and 10 198 cm⁻¹ the lowest ${}^{4}I_{11/2}$ level of Er^{3+} . The ${}^{4}I_{15/2} \rightarrow {}^{2}H_{9/2}$ GSA is very weak, see Fig. 3(a), but the ${}^{2}H_{9/2}$ position in a fluoride environment is well established.²² We conclude that for excitation energies between 14300 and 14500 cm^{-1} this is the main UC mechanism. Since there are two radiative excitation

steps involved, one (G) on V^{3+} and the other one (F) on Er^{3+} , the excitation profile corresponds to the product G*F of the two profiles.

The second mechanism, which experimentally manifests itself in the structured peak labeled G*E in Fig. 4(b), is more unusual and novel. It is a truly cooperative mechanism, in which both ions are involved in the upconversion step itself. We use a simple V^{3+} -Er³⁺ dimer picture to represent it in Fig. 6(c). While the first step G is not unusual, the second step E is. It is a radiative step with $V^{3+1}T_{2g}$ as the initial and $Er^{3+2}H_{9/2}$ as the final state. This follows from the energies of the peaks in the G*E band in Fig. 4(b). They correspond to energy differences between the $Er^{3+2}H_{9/2}$ levels and 10 413 cm⁻¹, the metastable lowest excited state of V³⁺. In the dimer picture the intermediate state in the upconversion process is a dimer state mainly localized on V^{3+} , whereas the upper emitting state is a dimer state with predominant Er³⁺ character. In a number of mixed lanthanide or mixed transition metal/lanthanide systems we have recently identified similar cooperative upconversion processes, and in all of these we ascribed them to an exchange mechanism.^{23,24} In the present case we have no direct contact between V^{3+} and Er^{3+} through a common bridging ligand, and the situation is less clear. We also considered another possible and less exotic mechanism, namely G on V³⁺, followed by energy transfer to $\text{Er}^{3+4}I_{11/2}$ and relaxation to ${}^{4}I_{13/2}$ and then ${}^{4}I_{13/2} \rightarrow {}^{4}F_{7/2}$ on Er^{3+} as the second excitation step. Adding 6503 cm^{-1} , the Er^{3+} origin, to the peak positions in the band system labeled G*E in Fig. 4(b), we do not get the known energies of the ${}^{4}F_{7/2}$ level, see also Fig. 4(a). In Fig. 6(d) we show the sensitization and upconversion scheme responsible for the underlying broad band between 13 500 and 14 500 cm⁻¹ in Fig. 4(b). Two quanta of $V^{3+1}T_{2g}$ excitation are consecutively injected by energy transfer into Er^{3+} . The resulting excitation spectrum corresponds to G*G and is thus broadband.

Let us finally return to the original question: is the title compound a broadband sensitizing upconverter? The answer is yes, but with an extremely low efficiency, particularly at temperatures of 200 K and above. At 15 K for narrow-band laser excitation with 150 mW into the V^{3+ 3}T_{2g} absorption we get a VIS:NIR photon ratio of about 0.1%. For broadband excitation, such as in a lamp, the situation would be much more favorable. Figure 4(b) shows that excitation peaks labeled C*D and the sum of G*E, G*F and G*G are of comparable intensity. This is mainly the result of the high absorption cross section G across the ${}^{3}T_{1g} \rightarrow {}^{3}T_{2g}$ absorption profile.

V. CONCLUSIONS

K₂NaScF₆ codoped with Er³⁺ and V³⁺ is a candidate for broadband sensitized upconversion from the far red and near-infrared into the green and red. The present study proves the principal feasibility. At 15 K broadband excitation between 12 000 and 14 500 cm⁻¹ will roughly double the visible light output in an Er³⁺ and V³⁺ codoped crystal of K₂NaScF₆ compared to single Er³⁺ doping. Even though green Er^{3+ 4}S_{3/2}→⁴I_{15/2} luminescence can be observed by eye upon V^{3+ 3}T_{1g}→³T_{2g} excitation in the full temperature range 15–200 K, the overall upconversion efficiency is very low. At temperatures above 50 K efficient multiphonon relaxation processes, mainly on the V³⁺, open up efficient loss channels. These are intrinsic processes of V³⁺ in an octahedral fluoride environment.¹³ In higher halides such as chlorides and bromides, multiphonon relaxation would be less efficient, but in these materials the V³⁺¹ T_{2g} state lies below $Er^{3+4}I_{11/2}$ and the sensitization cannot work. In addition, we are limited in the amounts of V³⁺ and Er³⁺ ions that can be incorporated into this lattice. This is ascribed to differences in the ionic radii between host and guests. The inability to incorporate a higher concentration of V³⁺ ions is particularly detrimental to our objective of using this ion as a sensitizer. Lattices based on Ga³⁺ such as GaF₃ would provide a better fit for V³⁺ but might be problematic for Er³⁺.

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