ELSEVIER

Journal of Alloys and Compounds 275–277 (1998) 191–195

Journal of ALLOYS AND COMPOUNDS

NIR to VIS upconversion in $LaCl_3$: 1% Er^{3+} One- and two-color excitations around 1000 and 800 nm

Karl W. Krämer[a,]*, Hans U. Güdel[a], Robert N. Schwartz[b]

[a]*Universität Bern, Departement für Chemie und Biochemie, Freiestr. 3, CH-3000 Bern 9, Switzerland*
[b]*Hughes Research Laboratories, 3011 Malibu, CA 90265-4799, USA*

Abstract

$LaCl_3$: 1% Er^{3+} shows visible luminescence upon near infrared excitation. In a first step the $^4I_{15/2}\rightarrow{}^4I_{11/2}$ or $^4I_{15/2}\rightarrow{}^4I_{9/2}$ transitions of Er^{3+} are excited by infrared laser radiation around 980 or 810 nm, respectively. In a second step the $^4F_{7/2}$ (490 nm), $^4F_{3/2}$ (445 nm) or $^2H_{9/2}$ (405 nm) levels are populated via excited state absorption from the $^4I_{11/2}$ or $^4I_{9/2}$ levels. The excitation wavelengths for the second step are again around 810 or 980 nm, respectively. The mechanisms of one- and two-color excitations were determined by polarized excitation spectroscopy. Efficient luminescence from those highly excited states is obtained in the blue, green and red spectral regions. The upconversion efficiency can be strongly enhanced by two-color excitation. Pure blue $^4F_{5/2}\rightarrow{}^4I_{15/2}$ and red $^4F_{5/2}\rightarrow{}^4I_{13/2}$ upconversion luminescence was detected for the first time upon NIR excitation of Er^{3+}. © 1998 Elsevier Science S.A.

Keywords: Laser spectroscopy; Low-phonon materials; Rare-earth halides; Upconversion

1. Introduction

Near infrared (NIR) to visible (VIS) upconversion is a process for the generation of visible luminescence or laser action in rare-earth-doped materials upon NIR excitation [1]. The process is nonlinear, with two or more low-energy excitation photons converted into one high-energy photon. The current interest in upconversion materials and upconversion processes is mainly motivated by the potential of these systems as phosphor or laser materials. Er^{3+}-doped crystals and glasses are particularly suited for upconversion processes because of its favorable energy level structure. There are two levels in the NIR, $^4I_{11/2}$ and $^4I_{9/2}$ around 980 and 810 nm, respectively, which can conveniently be excited by diode lasers. Both lie approximately halfway between the ground state and an excited state in the VIS/UV. Green luminescence is thus commonly observed in Er^{3+} compounds upon NIR excitation. The main object in the present paper is an evaluation of the various NIR excitation schemes, and the system to be used is $LaCl_3$: 1% Er^{3+}.

$LaCl_3$ was used as the host material for fundamental spectroscopic studies of the rare-earth ions more than 30 years ago [2]. Due to its low phonon energies and not excessive hygroscopicity it is a particularly interesting host lattice for upconversion studies. Furthermore, the high symmetry of the rare-earth site of $LaCl_3$ gives rise to selection rules for dipole transitions which provide useful information for the identification of spectroscopic transitions. In a recent study we reported in detail the energy levels and line-strength calculations of $LaCl_3$: 1% Er^{3+} [3].

2. Experimental

Crystals of $LaCl_3$: 1% Er^{3+} were grown in evacuated silica ampoules from $LaCl_3$ and $ErCl_3$ by the Bridgman technique. The chlorides were prepared from the oxides La_2O_3 and Er_2O_3 (both 99.999%) by the ammonium chloride method [4] and purified by vacuum sublimation in silica ampoules. $LaCl_3$ crystallizes in the UCl_3 structure with space group $P6_3/m$ and La^{3+} on site (2c) with site symmetry C_{3h} [5]. Er^{3+} can be doped into $LaCl_3$ up to about 2% and substitutes randomly for La^{3+} on its regular site. Suitable single crystals were cut and polished in a nitrogen filled dry box with $H_2O<1$ ppm. A crystal cut parallel to the *c*-axis was used for spectroscopic investigations. It was mounted in an air-tight copper cell with silica windows to protect against moisture.

---

*Corresponding author. Fax: +41 31 631 4399.

0925-8388/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII: S0925-8388(98)00301-6

Polarized continuous wave excitation and upconversion luminescence spectra were obtained by argon-ion laser (Spectra Physics 2045) pumped Ti-sapphire laser (Schwartz Electrooptics) excitation of Er^{3+}. For the two-color experiments a tunable monomode CW diode laser (SDL 8630) was used as the second light source. For measurements at 78 K the sample was cooled in an Oxford Instruments MD 4 cryostat. The polarization was controlled by a polarization rotator and calcite polarizers in front and behind the sample. The luminescence passed a polarization scrambler before it entered the monochromator to prevent artifacts. The luminescence was dispersed by a 0.85 m double monochromator (Spex 1402) with gratings blazed at 500 nm (1200 grooves mm^{-1}) and detected by a cooled photomultiplier (RCA 31034) using a photon counting system (Stanford Research 400).

For the time resolved measurements the 10 ns pulses of the second harmonic of a Nd:YAG (Spectra Physics DCR-3) were used to pump a dye laser (Lambda Physik FL 3002) with Rhodamin B or Pyridin 1 dyes. The dye laser output was shifted into the NIR by a H_2 Raman shifter (Spectra Physics RS-1). The luminescence was dispersed by a single monochromator (Spex 1702), detected by a cooled photomultiplier (RCA 31034) and recorded by a Stanford Research 430 multichannel scaler. Instrument control and data acquisition were performed by a personal computer. The luminescence spectra were corrected for the wavelength dependence of the monochromator and detector sensitivity. Their ordinates were converted to units of emitted photons per unit time. The data were analyzed using the software package Igor (Wave Metrics).

3. Results and discussion

3.1. Excitation

The efficiency of excitation by NIR lasers is one of the limiting factors in the development of new visible phosphor and laser materials based on the upconversion principle in lanthanide-doped compounds. In the present paper we explore a variety of NIR excitation mechanisms which lead to VIS and UV luminescence in $LaCl_3$: 1% Er^{3+}. Both one-color and two-color excitation schemes are considered, and in the following we refer to Fig. 1A. The two intermediate states most suitable for NIR diode laser excitation are $^4I_{11/2}$ (980 nm) and $^4I_{9/2}$ (810 nm). As it happens the $^4I_{15/2}\rightarrow{}^4I_{11/2}$ energy is similar to $^4I_{11/2}\rightarrow{}^4F_{7/2}$ (scheme (a)), and $^4I_{15/2}\rightarrow{}^4I_{9/2}$ is similar to $^4I_{9/2}\rightarrow{}^2H_{9/2}$ (scheme (c)). Since $^4F_{3/2}$ is about halfway between $^4F_{7/2}$ and $^2H_{9/2}$ we can combine a 980 and 810 nm light source to reach $^4F_{3/2}$ (schemes (b1) and (b2)). Whereas one-color excitations based on (a) and (c) are usual schemes for obtaining NIR to VIS upconversion with resulting yellow-green emission in Er^{3+} systems, schemes (b) have not been considered before. The host material $LaCl_3$ investigated here belongs to the family of low-phonon energy hosts. As we have pointed out for several host lattices, excited state dynamics and steady state populations of Er^{3+} are completely different in these materials than in fluorides and oxides [6–8]. This is due to the reduced efficiency in multiphonon relaxation. In fluorides and oxides, on the other hand, a distinction of the four excitation paths in Fig. 1 is meaningless, because they

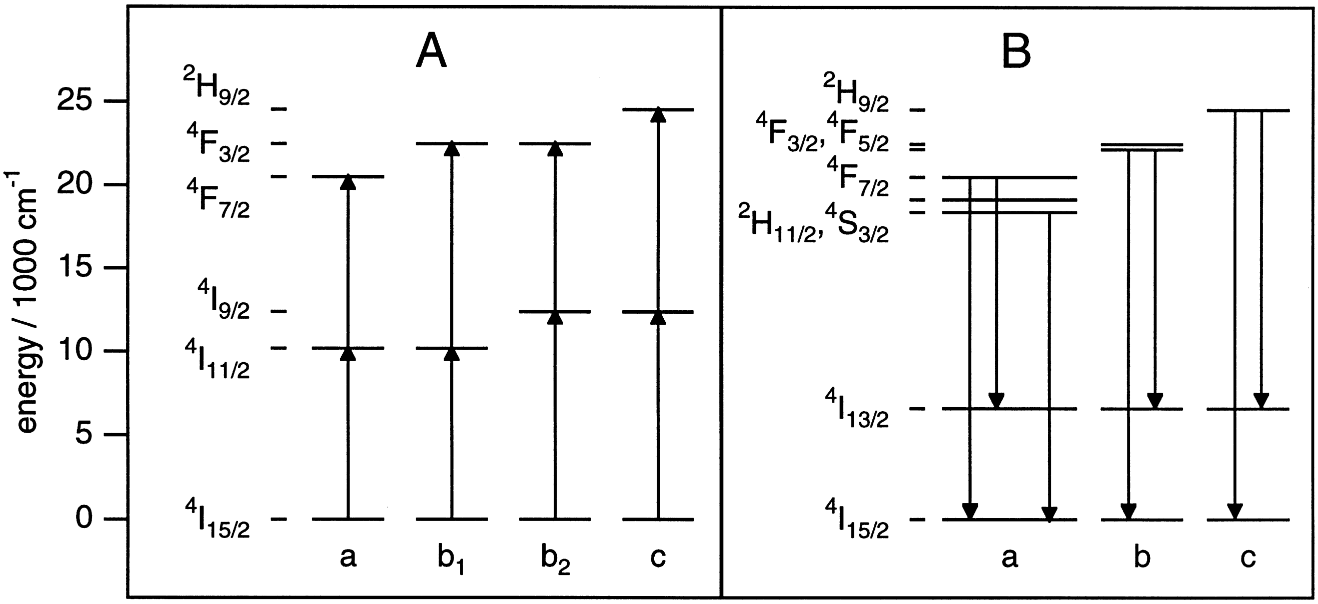

Fig. 1. Excitation (left) and luminescence (right) paths in $LaCl_3$: 1% Er^{3+} on NIR excitation around 980 and/or 810 nm.

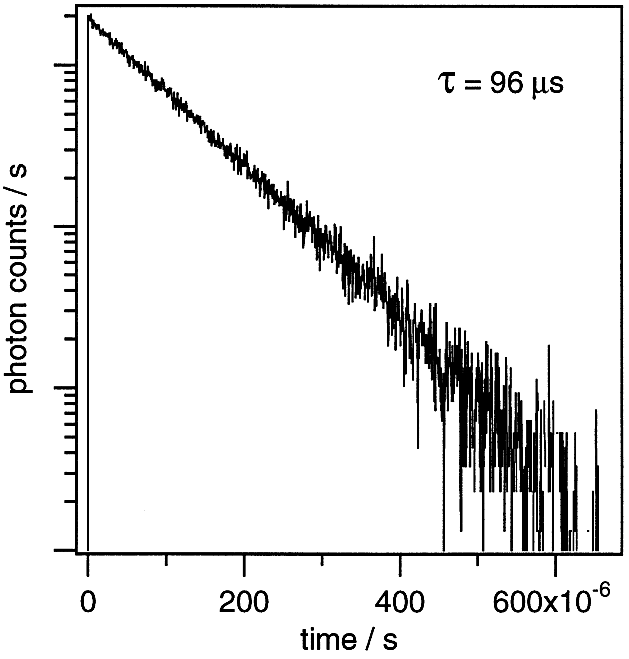

Fig. 2. Decay curve of the $^4F_{7/2}$ luminescence (20 382 cm^{-1}) of $LaCl_3$: 1% Er^{3+} on excitation at 10 280 cm^{-1} ($E\|a$) at 78 K in a semilogarithmic representation.

are all followed by efficient multiphonon relaxation to $^4S_{3/2}$.

Accurate determination of the relevant crystal-field levels is essential for elucidation of the upconversion excitation mechanisms in Fig. 1A. These were reported and analyzed in terms of a crystal-field model calculation in Ref. [3]. Another important property is the time dependence of the upconversion luminescence after an excitation pulse. As pointed out in detail elsewhere [7,8] the time dependence shown in Fig. 2 for a one-color excitation according to scheme (a) in Fig. 1 is typical of an excited-state absorption (ESA) mechanism. In contrast to energy transfer upconversion the transient shows no rise time, because both the ground and the excited state absorption steps occur within the laser pulse. All the upconversion mechanisms discussed here occur by ESA.

Fig. 3 shows polarized excitation spectra of the $^4F_{7/2}\rightarrow{}^4I_{15/2}$ luminescence at 78 K. In σ and π polarization the electric vector of the excitation light is perpendicular and parallel to the *c*-axis, respectively. All three spectra correspond to excitation scheme (a) in Fig. 1. The bottom trace is a one-color excitation spectrum, whereas for the other two spectra two lasers were used, one fixed at the arrow position and the other scanned. We observe

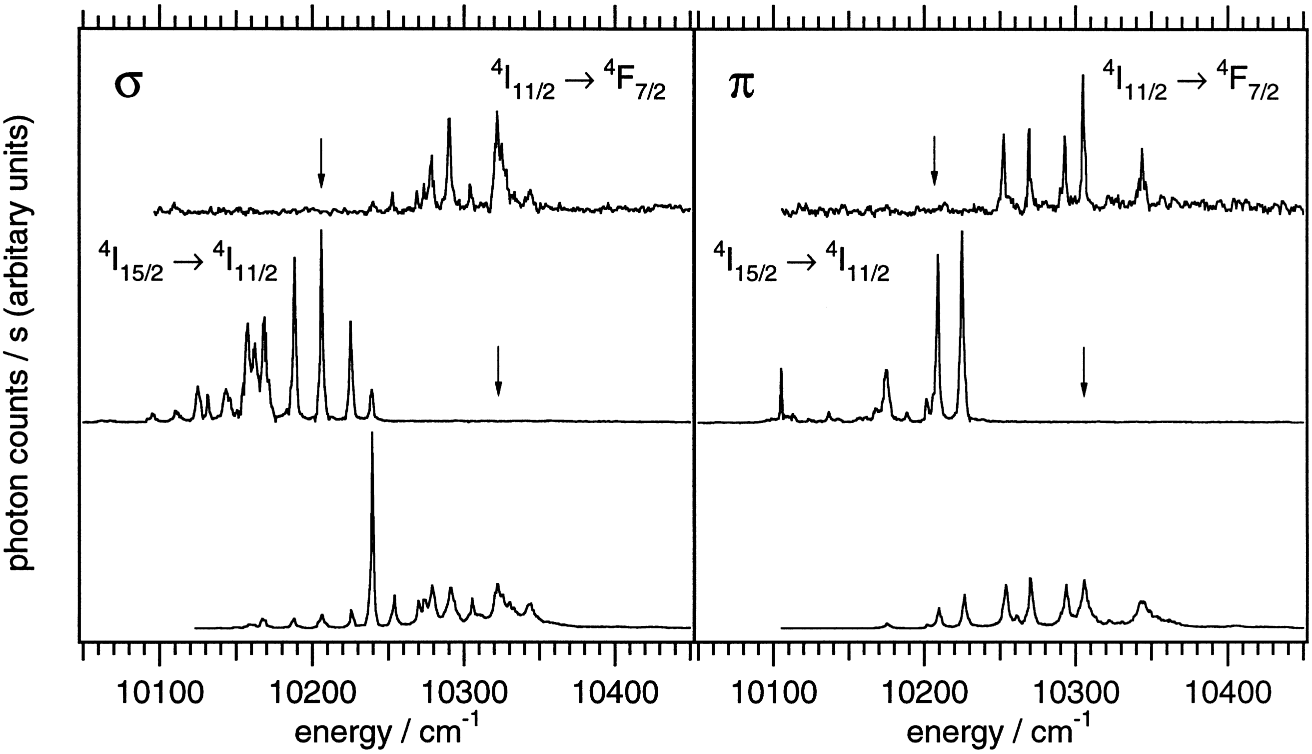

Fig. 3. One- and two-color excitation spectra of the $^4F_{7/2}$ luminescence of $LaCl_3$: 1% Er^{3+} at 78 K. The excitation was σ polarized ($E\|a$) for the spectra on the left-hand side and π polarized ($E\|c$) on the right-hand side. The upper two traces show two-color excitations with one excitation energy fixed at the arrow and the second energy scanned. The one-color excitation spectra are shown in the bottom traces.

distinctly different spectra for the two polarizations. This is due to the fact that in the point group C_{3h} there are distinct selection rules for the transitions between crystal-field levels [3]. We also notice that the overlap between the $^4I_{15/2} \rightarrow ^4I_{11/2}$ ground-state absorption (GSA) and the $^4I_{11/2} \rightarrow ^4F_{7/2}$ ESA excitation at 78 K is extremely small in σ polarization and virtually absent in π polarization. The small overlap in σ polarization occurs at 10 239 cm^{-1}. The GSA transitions are at lower energy and the ESA transitions at higher energies. Due to this energy displacement a one-color excitation is bound to be inefficient, because it is essentially determined by the convolution of the upper two traces. This is fully confirmed by experiment. The outstanding peak at 10 239 cm^{-1} in the one-color excitation spectrum at the bottom corresponds to the small overlap of the upper two spectra at this energy. At this position the GSA $^4I_{15/2}(1) \rightarrow ^4I_{11/2}(6)$ and the ESA transition $^4I_{11/2}(6) \rightarrow ^4F_{7/2}(1)$ coincide to within 3 cm^{-1}, where the numbers in parentheses designate the respective crystal-field levels [3]. These two transitions are σ polarized, in excellent agreement with the absence of an excitation peak at 10 239 cm^{-1} in π polarization. Fig. 3 also points the way to achieving a more efficient excitation. By combining two exciting lasers and tuning their energies to the maxima of the upper and middle spectra in Fig. 3, respectively, the efficiency of the $^4F_{7/2}$ population should be significantly increased compared with the one-color experiment. Initial preliminary experiments have shown an increase of at least an order of magnitude.

3.2. Emission

Fig. 4a,b,c show the 78 K luminescence spectra of $LaCl_3$: 1% Er^{3+} obtained by the upconversion excitation modes a, b and c, respectively, in Fig. 1A. Their assignment to transitions originating in $^4F_{7/2}$, $^4F_{5/2}$ and $^2H_{9/2}$, as shown in Fig. 1B, is straightforward. In Fig. 4a there is a weak $^4S_{3/2}$ emission resulting from a partial nonradiative $^4F_{7/2} \rightarrow ^4S_{3/2}$ relaxation. In other chlorides this mul-

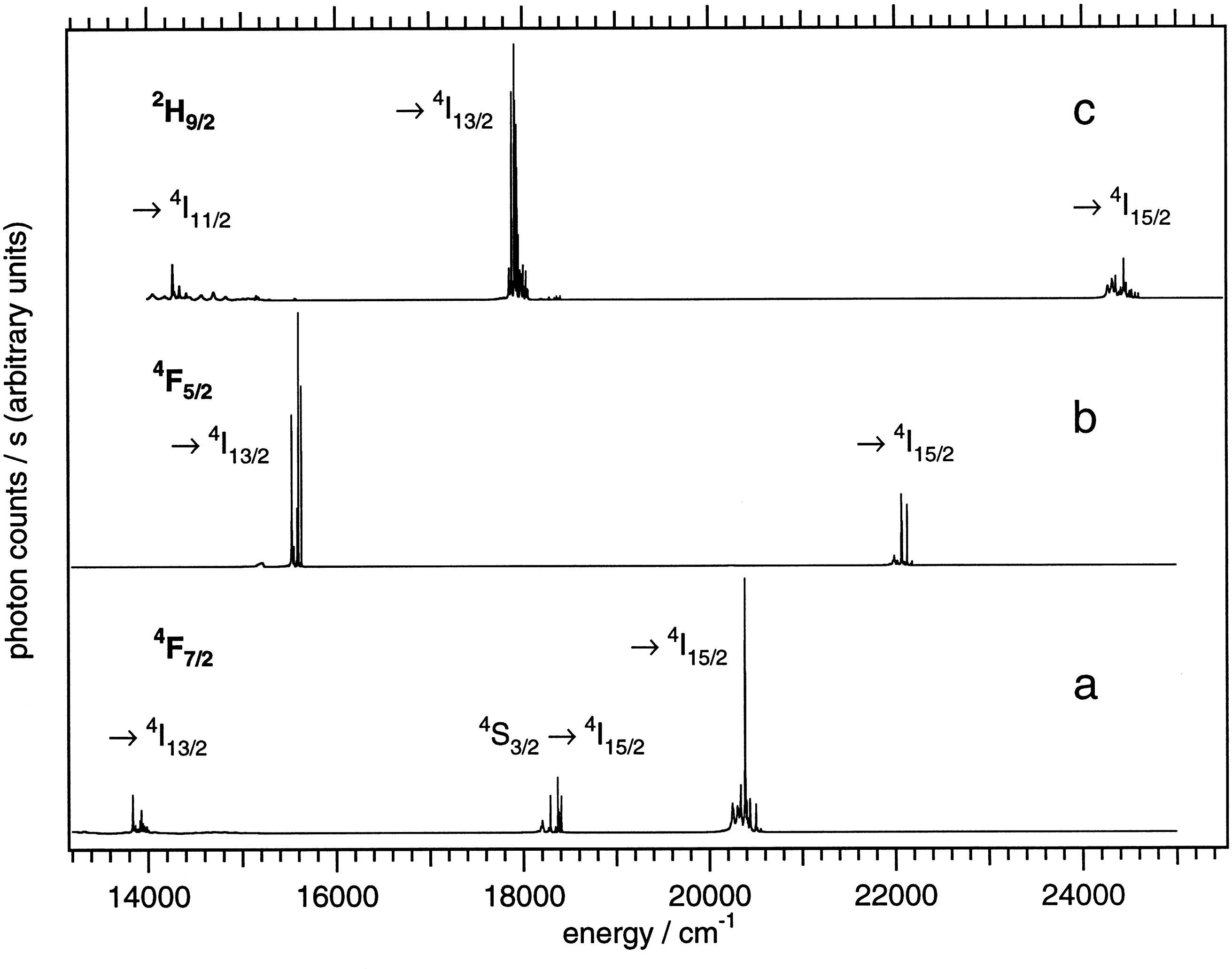

Fig. 4. Luminescence spectra of $LaCl_3$: 1% Er^{3+} at 78 K excited by schemes (a), (b) and (c) in Fig. 1A (from bottom to top). The luminescence was σ, π and unpolarized (from top to bottom) and scaled to be equal for the strongest transitions.

tiphonon relaxation is more efficient than in $LaCl_3$, which behaves more like a bromide in this respect.

Whereas $^2H_{9/2}$ and $^4F_{7/2}$ populations can also be achieved by one-color excitation around 810 and 980 nm, respectively, excitation into the $^4F_{3/2}/^4F_{5/2}$ doublet is only possible by the two-color schemes (b1) and (b2) in Fig. 1A. Accordingly, upconverted pure $^4F_{5/2}$ emission has not been observed so far. We see two multiplets, one in the deep blue at about 22 100 cm^{-1} and one in the red around 15 600 cm^{-1} corresponding to the $^4F_{5/2}\rightarrow{}^4I_{15/2}$ and $^4I_{13/2}$ transitions, respectively. The energy gap between the $^4F_{3/2}$ and the $^4F_{5/2}$ multiplet is only 319 cm^{-1}, and nonradiative $^4F_{3/2}\rightarrow{}^4F_{5/2}$ relaxation is very fast. The transitions are listed in Table 1.

In conclusion, we find that by combining two NIR excitation energies for $LaCl_3$: 1% Er^{3+} the upconversion efficiency for visible emission can be enhanced significantly with respect to a one-color excitation. The two lasers are tuned to the maximum intensity of the GSA and ESA steps, respectively. Er^{3+}-doped crystals with similar chemical composition exhibit widely varying upconversion efficiencies upon one-color NIR excitation. This variation is likely due to some accidental coincidences in the GSA and ESA steps. One such coincidence has been identified in the present work on $LaCl_3$: Er^{3+}. At 10 239 cm^{-1} there is simultaneous GSA and ESA absorption at 78 K, leading to a sharp maximum in the corresponding one-color excitation spectrum. The use of two colors opens new excitation pathways besides enhancing the efficiency of established ones.

Table 1
Relative branching ratios of the visible luminescence of $LaCl_3$: 1% Er^{3+} at 78 K

	$\rightarrow{}^4I_{15/2}$	$\rightarrow{}^4I_{13/2}$	$^4S_{3/2}\rightarrow{}^4I_{15/2}$	Luminescence
$^2H_{9/2}$	1	2	0	$E\|\|a$
$^4F_{5/2}$	1	2	0	$E\|\|c$
$^4F_{7/2}$	7	1	1.5	Unpolarized

Acknowledgements

This work was supported by the Swiss National Science Foundation and the Priority Program Optics of the Board of the Swiss Federal Institute of Technology. Financial support from the Hans-Sigrist Stiftung is gratefully acknowledged.

References

[1] W. Lenth, R.M. Macfarlane, Opt. Photon News 3 (1992) 8.
[2] F. Varsani, G.H. Dieke, J. Chem. Phys. 36 (1962) 2951.
[3] K.W. Krämer, H.U. Güdel, R.N. Schwartz, Phys. Rev. B 56 (1997) 13830.
[4] G. Meyer, Adv. Synth. React. Solids 2 (1994) 1.
[5] W.H. Zachariasen, Acta Crystallogr. 1 (1948) 265.
[6] T. Riedener, K. Krämer, H.U. Güdel, Inorg. Chem. 34 (1995) 2745.
[7] M.P. Hehlen, G. Frei, H.U. Güdel, Phys. Rev. B 50 (1994) 16264.
[8] T. Riedener, H.U. Güdel, J. Chem. Phys. 107 (1997) 2169.