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NIR-to-VIS Upconversion of Er^{3+} in Host Materials with Low-Energy Phonons

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Abstract. Intense NIR-to-VIS upconversion luminescence is observed in Er^{3+} -doped heavier halide host materials such as chlorides and bromides. The multiphonon relaxation rate is found to be a crucial factor in the chemical tuning of the excited-state properties.

Upon laser excitation in the near IR, a series of trivalent rare-earth ions, especially Er^{3+} , emit light in the VIS or near UV. A schematic representation of this upconversion process, first found in 1966 by *Auzel* [1], is depicted in *Fig. 1*. In the so-called energy-transfer upconversion (ETU) mechanism on the left, two ions are pumped into an intermediate state in the near IR; one ion then transfers its energy by a radiationless process onto the other ion, thereby lifting it into a higher state in the VIS or UV. A competing upconversion process is based on excited-state absorption (ESA) on a single ion and is shown on the right-hand side in *Fig. 1*. The first stimulated emission from such an upconverted system was found 1971 by *Johnson and Guggenheim* [2], and in 1986, *Silversmith et al.* [3] reported the first cw upconversion laser. In the last years, there has been a renewed interest in upconversion processes and new materials due to the availability of diode lasers as highly efficient pump sources in the near IR. Potential applications of these processes are phosphors or lasers in the VIS and near UV with a multitude of possible applications [4][5].

Most of the work on upconversion has been done in rare-earth-ion-doped oxide and fluoride host lattices. Our approach is to use chlorides and bromides, which have received little attention so far. These heavier halides have lower phonon energies which lead to a significant reduction of multiphonon relaxation rates. Excited states with negligible population in an oxide or fluoride can thus become important in a chloride or bromide, both for radiative and nonradiative processes such as luminescence and upconversion, respectively. In *Fig. 2* we illustrate the effect on the upconversion luminescence of a very simple chemical substitution. Er^{3+} was doped with a concentration of 1% into the isostructural compounds RbGd_2Cl_7 and

RbGd_2Br_7 . Upon excitation at roughly 975 nm, the chloride crystals exhibit a strong green luminescence, whereas the luminescence of the bromide is in the blue. Er^{3+} -doped oxide and fluoride host lattices show the same behavior as the chloride. *Fig. 3* provides a straightforward explanation. In both cases, the 975-nm excitation leads to the population of $^4\text{F}_{7/2}$ by one of the upconversion processes in *Fig. 1*. In the chloride, as well as in fluorides and oxides, this $^4\text{F}_{7/2}$ state is immediately depopulated by a nonradiative multiphonon relaxation via $^2\text{H}_{11/2}$ into $^4\text{S}_{3/2}$. Green luminescence out of $^4\text{S}_{3/2}$ and the thermally populated $^2\text{H}_{11/2}$ is then observed. In the bromide, in contrast, the nonradiative depopulation of $^4\text{F}_{7/2}$ is not competitive and spontaneous blue emission is observed. Multiphonon processes are known to depend very critically on the electronic energy gap and on the highest-energy vibrations of the crystal [6]. These are of the order of $>550\text{ cm}^{-1}$, 350 cm^{-1} , 260 cm^{-1} , and 180 cm^{-1} for oxides, fluorides, chlorides, and bromides, respectively. The critical energy gap between $^4\text{F}_{7/2}$ and $^2\text{H}_{11/2}$ is about 1250 cm^{-1} . As a rule of thumb, multiphonon relaxation is competitive when the number of vibrational quanta required to bridge the gap is smaller than 5–6. This is the case for all but the bromides, which is nicely illustrated by our example. Other trends of the upconversion behavior along the halide series are discussed in [7] and [8].

The principle of chemical variation to tune the optical spectroscopic properties turns out to be very successful in this research. We are also developing tech-

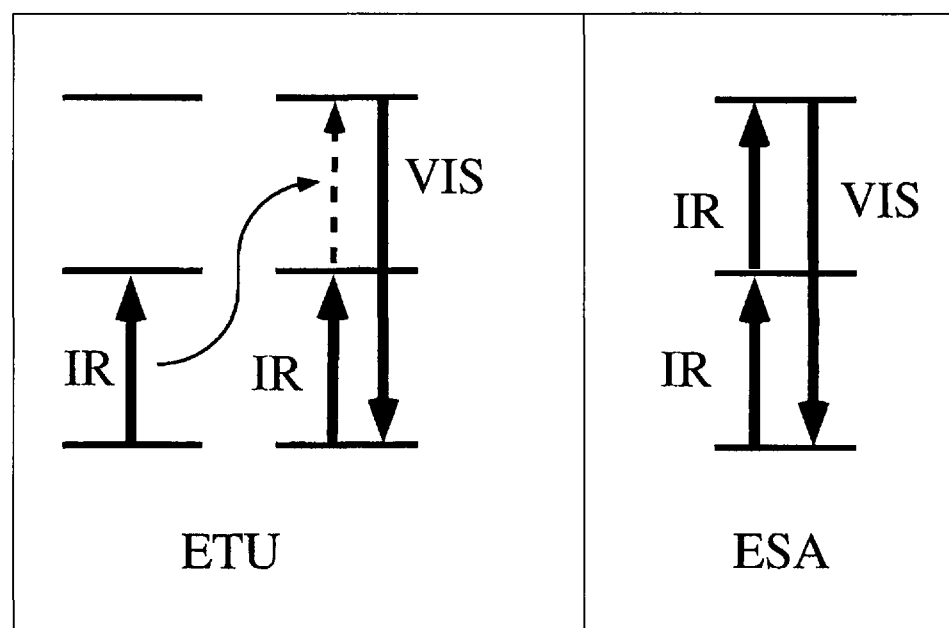


Fig. 1. Schematic representation of the energy transfer (ETU) and the excited-state absorption (ESA) upconversion processes

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^{a)} These results were presented as an oral contribution at the autumn meeting of the New Swiss Chemical Society (NSCS) in Basel, Switzerland, on November 21, 1996.

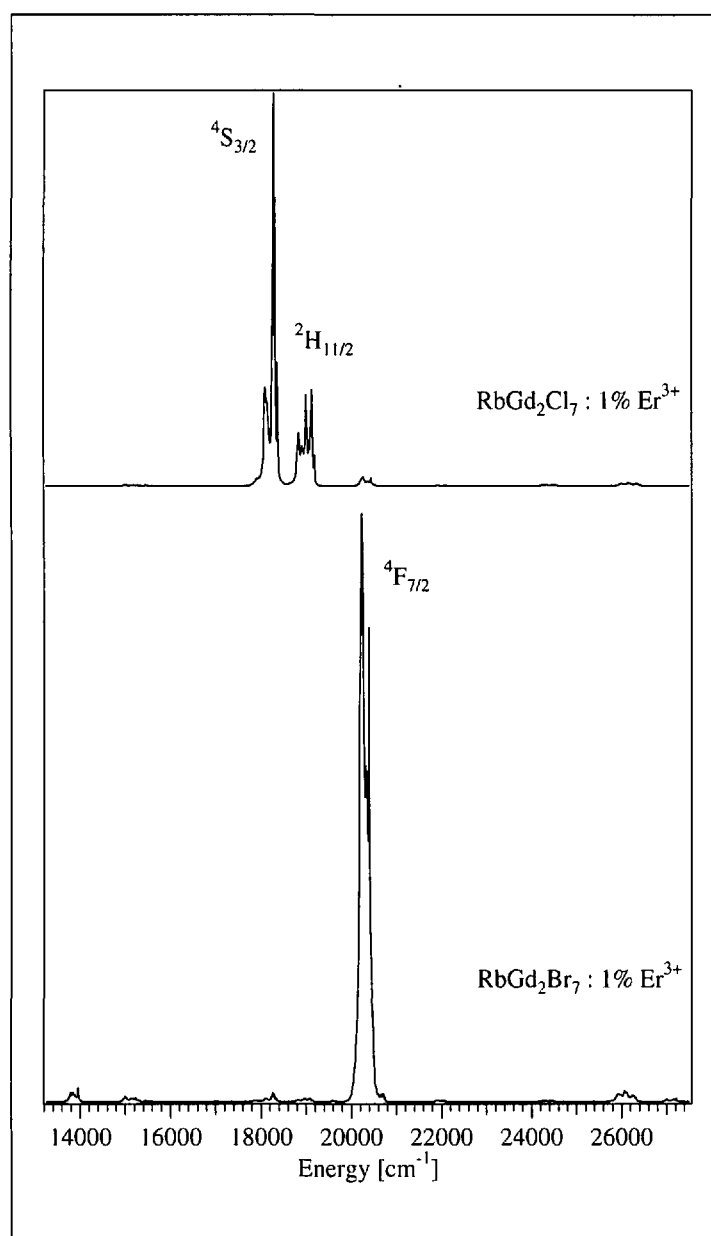


Fig. 2. Upconversion luminescence spectra at r.t. of $\text{RbGd}_2\text{X}_7: 1\% \text{Er}^{3+}$. Excitation at 10255 cm^{-1} ($\text{X} = \text{Cl}$) and 10229 cm^{-1} ($\text{X} = \text{Br}$).

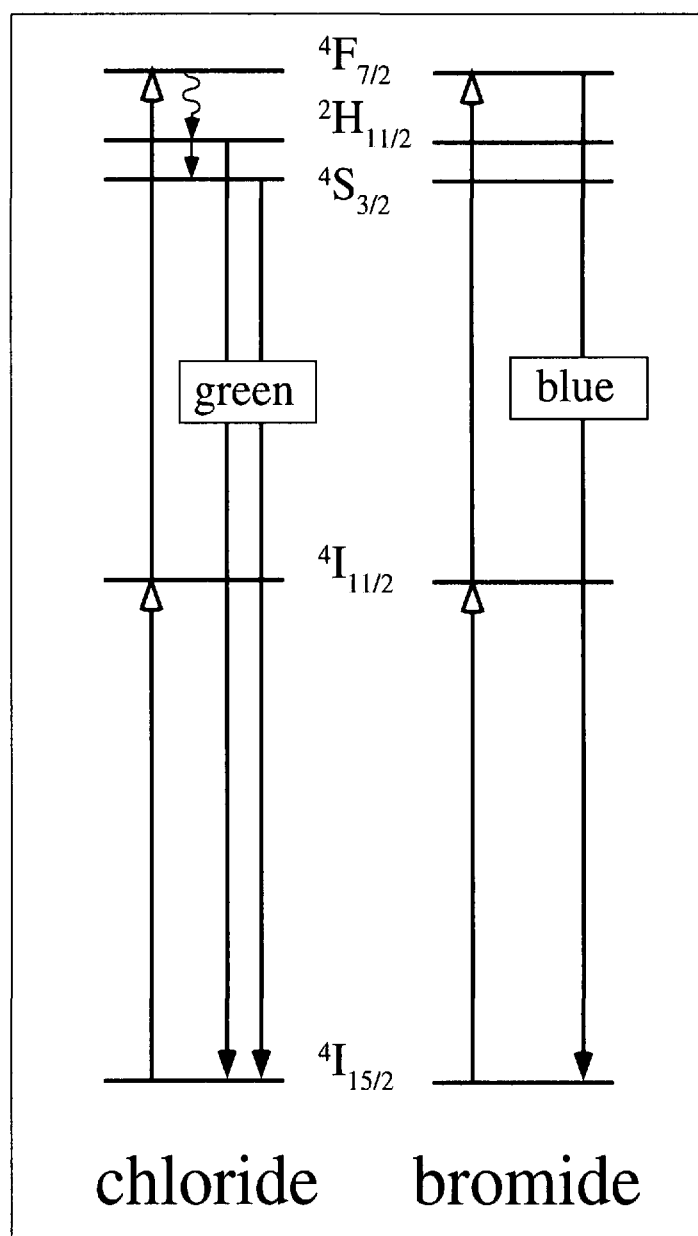


Fig. 3. Schematic representation of the radiative (filled arrows) and nonradiative transitions (curly arrows) in $\text{RbGd}_2\text{Cl}_7: 1\% \text{Er}^{3+}$ (left) and $\text{RbGd}_2\text{Br}_7: 1\% \text{Er}^{3+}$ (right) after an upconversion process (empty arrows) into $4\text{F}_{7/2}$.

niques to differentiate between the two upconversion mechanisms in Fig. 1 [9][10], and we are exploring the usefulness of theoretical models to understand the rather complex experimental situations [11][12]. These Er^{3+} -doped halides have a potential as laser materials [13], and we are exploring ways to overcome their softness and sensitivity to moisture.

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