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Upconversion luminescence in K_2LaX_5:Er^{3+} (X=Cl, Br)

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Abstract

Upconversion (UC) luminescence was observed in Er^{3+} (1%) doped K_2LaCl_5 and K_2LaBr_5 crystals. The two lattices exhibit distinctly different behavior. Upon $^4I_{9/2}$ excitation, the UC luminescence spectra of both the chloride and bromide are dominated by $^2H_{9/2}$ transitions at low temperature. At room temperature $^4S_{3/2}$ and $^2H_{11/2}$ become dominant. For $^4I_{11/2}$ excitation, the chloride and bromide show completely different luminescences. The $^4F_{7/2}$ luminescence dominates the bromide spectrum at all temperatures, but in the chloride, it is relatively unimportant. The differences are attributed to different $^4F_{7/2} \rightarrow {}^2H_{11/2}$ multiphonon relaxation rates.

1. Introduction

There is considerable current interest in new near infrared (NIR) to visible (VIS) upconversion (UC) materials. Er^{3+} doped crystals and glasses can conveniently be excited by Ti:sapphire or semiconductor diode laser pumping. Among the host materials studied so far, oxide and fluoride lattices dominate [1]. With the exception of $CsCdBr_3$ [2], other halides have been largely neglected. This is understandable from a practical point of view, because oxides, and to a lesser degree fluorides, are not sensitive to moisture. Chloride, bromide and iodide materials, on the other hand, are usually hygroscopic and have to be protected. From another point of view, however, these heavier halide materials offer some distinct advantages. Due to the lower phonon frequencies, multiphonon relaxation processes are less competitive and, as a consequence, excited state dynamics and populations are distinctly different from oxide and fluoride lattices. Furthermore, upconversion processes can be enhanced by choosing host lattices with small separations of neighboring Er^{3+} ions. In the present study, we have chosen the two isostructural host lattices K_2LaCl_5 and K_2LaBr_5 [3]. The La^{3+} ions, partially substituted by Er^{3+}, occupy a site with C_s symmetry and are coordinated by seven halide ions. These polyhedra share two common edges and form chains of the composition $[LaX_3X_{4/2}]^{2-}$. Their Er^{3+} upconversion behavior changes dramatically as we go down the halide series, and we can rationalise the observed trend in terms of simple models.

2. Experimental details

The crystals of the congruently melting K_2LaX_5:1% Er^{3+} (X=Cl, Br) were grown by the Bridgeman technique. Starting materials were the binary halides KX, LaX_3 and ErX_3. The rare earth halides were prepared by the ammonium halide method [4] and all educts sublimed in tantalum containers for purification. Stoichiometric amounts were sealed into silica ampoules under vacuum and placed into a Bridgeman furnace. Crystals for spectroscopic measurements were selected under a polarisation microscope, those for absorption measurements cut and polished to a defined thickness. Their orientation was checked by X-ray back-scattering Laue exposures. All handling was done under strictly dry conditions in nitrogen filled dry boxes (less than 0.1 ppm H_2O), because the substances are sensitive to moisture.

Absorption spectra were measured on a Cary 5E at 12 K using a closed cycle helium refrigerator. The samples were mounted into gas tight copper cells with silica windows. For the luminescence and Raman measurements, the crystals were sealed into small silica tubes under 300 mbar helium pressure. Unpolarised luminescence and excitation spectra were recorded at 10 K and room temperature. The excitation was done by an argon ion laser pumped CW Ti-sapphire laser (SEO) into the $^4I_{11/2}$ and $^4I_{9/2}$ states of Er^{3+}. The samples were cooled by helium gas in silica flow tubes. The luminescence was dispersed by a Spex 1402 double monochromator and detected with a Hamamatsu R 3310-01 photomultiplier and a Stanford research SR400 photon counting system. The spectra were corrected

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for monochromator and detector response. Raman spectra were recorded at 20 K on the same setup by argon ion laser excitation at 514.57 nm.

3. Results and discussion

Polarised absorption spectra of K_2LaCl_5:1% Er^{3+} were measured in the NIR and VIS region for light propagation along all the three axes of the orthorhombic unit cell. All the pairs of spectra for which the electric vector had the same direction were found to be identical. We conclude that the f–f transitions gain their intensity by an electric dipole mechanism. The K_2LaBr_5:1% Er^{3+} absorption spectra were found to be very similar. Figure 1 shows the relevant sections of the K_2LaCl_5:1% Er^{3+} absorption spectrum. The $^4I_{9/2}$ excitation is more intense than the $^4I_{11/2}$ excitation. This is opposite to all the other host lattices reported so far. We have no clear understanding for this contrasting behavior at present, but in view of some practical applications, it may be an important observation.

The $^4I_{11/2}$ and $^4I_{9/2}$ excitations were used for the upconversion luminescence experiments. The corresponding excitation schemes are depicted in Figs. 2(a) and (b), respectively. Figures 3(a) and (b) show the experimental results obtained at room temperature for the chloride and bromide lattices, respectively, and $^4I_{11/2}$ excitation. The contrast between Figs. 3(a) and (b) is dramatic, and it shows what a minor chemical variation can do to the physical properties. Upconversion luminescence is observed in both lattices, but it originates from completely different excited states. We conclude that the UC excitation step shown in Fig. 2(a) occurs in both cases, but the secondary relaxation processes are completely different. In the chloride, most of the initial $^4F_{7/2}$ population is lost by multiphonon relaxation to $^2H_{11/2}$ and $^4S_{3/2}$. A Boltzmann equilibrium is established between these. This is very reminiscent of the behavior observed in fluoride lattices [5]. In the bromide, by contrast, the $^4F_{7/2} \rightarrow {}^4I_{15/2}$ luminescence just above 20 000 cm^{-1} is absolutely dominant. A smaller feature around 14 000 cm^{-1} is due to the $^4F_{7/2} \rightarrow {}^4I_{13/2}$ transition. This is reminiscent of the behavior observed in the $CsCdBr_3$ host lattice [2]. We conclude that in the bromide, the $^4F_{7/2} \rightarrow {}^2H_{11/2}$ multiphonon relaxation processes cannot compete. In order to get an idea about the phonon frequencies in the two lattices, we measured their unpolarised Raman spectra at 20 K. The result is shown in Fig. 4. The highest energy vibrational modes in K_2LaCl_5 and K_2LaBr_5 are 232 cm^{-1} and 164 cm^{-1}, respectively. If we take the highest energy modes to be the most efficient accepting modes in the non-radiative process, 5.3 and 7.5 quanta, respectively, are required to bridge the $^4F_{7/2} \rightarrow {}^2H_{11/2}$ energy gap of about 1230 cm^{-1}. From the observed behavior, we conclude that this step from 5.3 to 7.5 quanta slows down the non-radiative rate constant by one to two orders of magnitude.

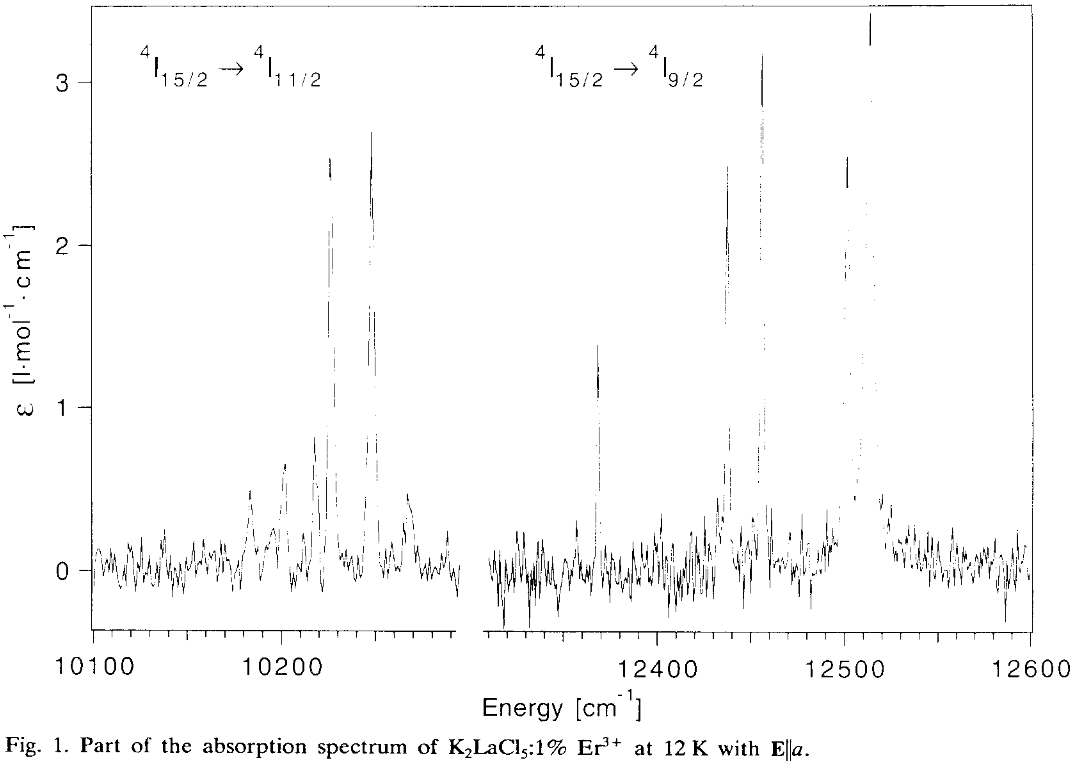

Fig. 1. Part of the absorption spectrum of K_2LaCl_5:1% Er^{3+} at 12 K with E∥*a*.

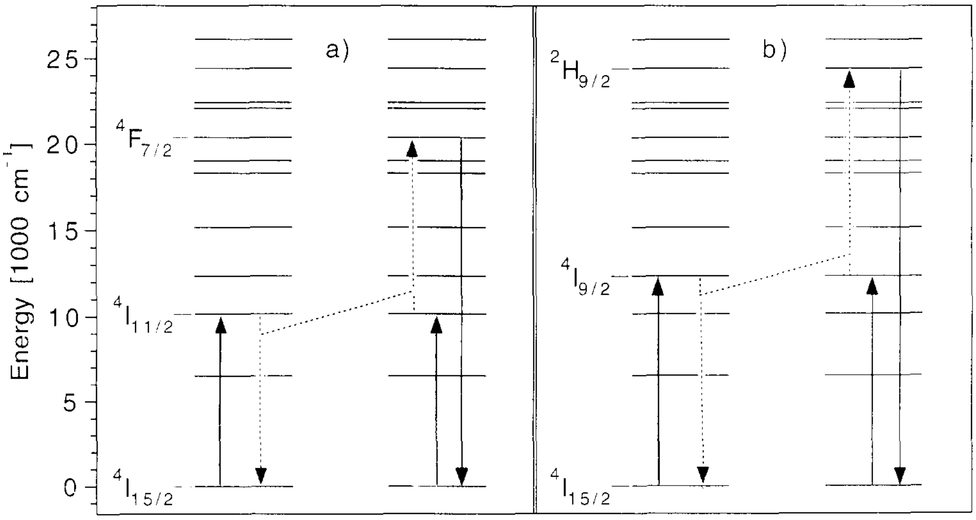

Fig. 2. Schematic upconversion excitation schemes used in this study.

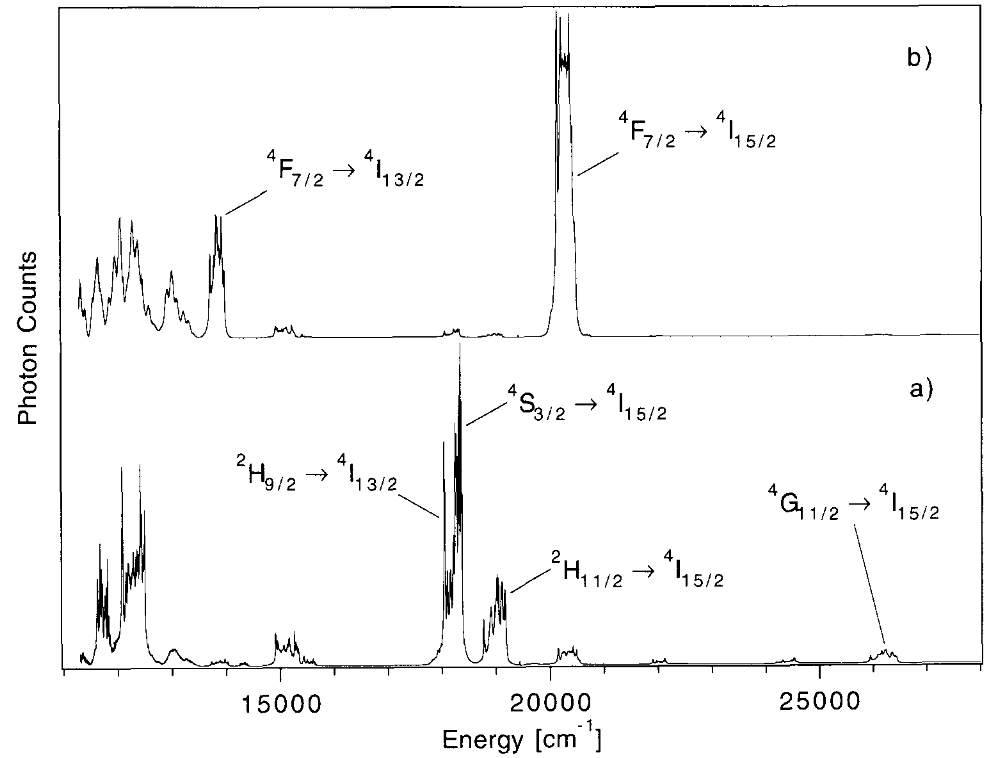

Fig. 3. Unpolarised room temperature upconversion luminescence spectra of K_2LaCl_5:1% Er^{3+} (a) and K_2LaBr_5:1% Er^{3+} (b) upon $^4I_{15/2} \rightarrow {}^4I_{11/2}$ excitation at 10 178 cm^{-1} and 10 164 cm^{-1}, respectively.

Figure 5 shows the low temperature UC luminescence spectra of the bromide for both $^4I_{11/2}$ (Fig. 5(a)) and $^4I_{9/2}$ (Fig. 5(b)) excitation. Except for the sharpening and resolution of the fine structure, Fig. 5(a) is very similar to the corresponding room temperature spectrum in Fig. 3(b). Interestingly, the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition shows up with higher intensity at 10 K. The spectrum in Fig. 5(b) essentially consists of transitions originating in the $^2H_{9/2}$ excited state. The $^2H_{9/2} \rightarrow {}^4I_{13/2}$ transition, which lies very close to the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition and should not be mistaken for the latter, is the dominant transition in the green. The $^2H_{9/2} \rightarrow {}^4I_{15/2}$ transition in the UV at around 24 000 cm^{-1} carries about the same intensity.

In the low temperature K_2LaCl_5:1% Er^{3+} UC luminescence spectrum excited into $^4I_{9/2}$, which is not shown here, the transitions originating in $^2H_{9/2}$ are also dominant. In addition, there are relatively intense $^4G_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions. The energy gap between $^2H_{9/2}$ and $^4F_{3/2}$ of approximately 1940 cm^{-1}

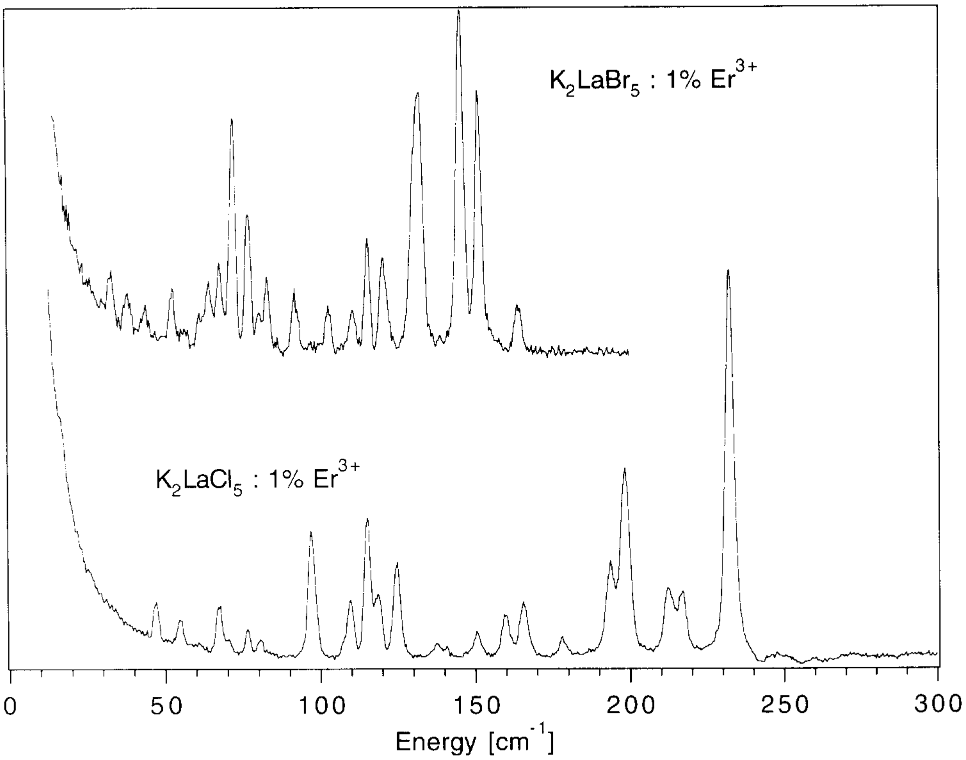

Fig. 4. Unpolarised Raman spectra of K_2LaX_5:1% Er^{3+} (X=Cl, Br) at 20 K upon excitation at 514.57 nm by an Argon ion laser.

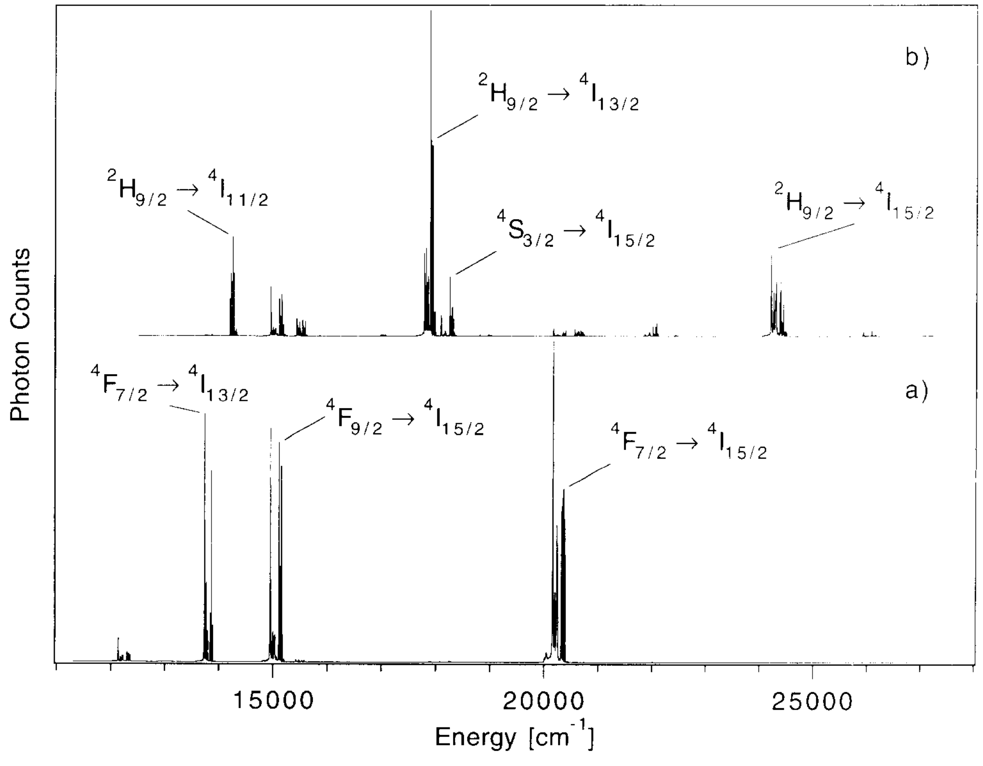

Fig. 5. Low temperature upconversion luminescence spectra of K_2LaBr_5:1% Er^{3+} upon $^4I_{15/2} \rightarrow {}^4I_{11/2}$ (a) and $^4I_{15/2} \rightarrow {}^4I_{9/2}$ (b) excitation at 10 222 cm^{-1} and 12 483 cm^{-1}, respectively.

requires about 8 and 12 quanta of the highest energy vibrations for the chloride and bromide, respectively. Multiphonon relaxation processes can thus not compete with the $^2H_{9/2}$ luminescence in either lattice. The occurrence of $^4G_{11/2}$ luminescence in the low temperature spectra of the chloride cannot be explained by the excitation schemes in Fig. 2. At least three infrared photons are needed to bring the system up to $^4G_{11/2}$. In K_2LaCl_5:1% Er^{3+}, at 10 K we find a relatively strong $^4F_{9/2} \rightarrow {}^4I_{15/2}$ luminescence. We do not believe that the $^4F_{9/2}$ population occurs by multiphonon relaxation from $^4F_{7/2}$ via $^4S_{3/2}$, because at room temperature, it has almost vanished. Cross relaxation processes such as $^4I_{11/2} + {}^4F_{7/2} \rightarrow {}^4F_{9/2} + {}^4F_{9/2}$ are more likely.

In conclusion, we find that the Er^{3+} upconversion luminescence behavior in the two host lattices studied here is distinctly different. The properties of the K_2LaCl_5:1% Er^{3+} crystal are comparable to the properties reported for Er^{3+} doped fluoride lattices such as $LiYF_4$ [5] or $BaYb_2F_8$ [6] when we excite into $^4I_{11/2}$. Multiphonon $^4F_{7/2} \rightarrow {}^2H_{11/2}$ relaxation efficiently quenches the $^4F_{7/2}$ luminescence. The behavior is exactly opposite in K_2LaBr_5:1% Er^{3+}. The radiative $^4F_{7/2}$ transitions dominate the non-radiative processes. For $^4I_{9/2}$ excitation, the behavior of the two materials is similar, but in contrast to fluoride lattices. $^2H_{9/2}$ transitions dominate the UC luminescence spectrum in both our host lattices at low temperatures, whereas in fluorides, non-radiative relaxation down to $^4S_{3/2}$ is competitive [5]. All these observations can be rationalised by simple considerations based on the energy gap law for multiphonon relaxation processes.

Acknowledgments

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