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Blue emission of Pr^{3+} ions in $LaCl_3$ crystal triggered by U^{3+}

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Abstract

An anti-Stokes emission in $LaCl_3$:Pr^{3+} was found after excitation by a laser line resonant with the $^3H_6 \rightarrow ^3P_0$ transition. The intensity of the blue emission was enhanced by three orders of magnitude when U^{3+} was added into the crystal. A mechanism for the up-conversion observed is discussed as well as the possibility of an avalanche process in Pr^{3+} triggered by U^{3+} ions. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Up-conversion; Actinides; Rare earths; Avalanche; Energy transfer

1. Introduction

Among other excitation sources the diode lasers offer coherent emission, which matches well most of the rare earth absorption lines. The efficiency of a diode laser is high and more over they are relatively cheap. But, the cheap laser diodes emit in the red or in the near infrared region. Therefore all processes, which convert excitation light into shorter wavelength emission, are carefully investigated. Among them energy transfer up-conversion and APTE [1]. Recently an avalanche of photons attaches the scientists' attention.

The avalanche phenomenon discovered by Case and co-workers [2] was later proved to be sufficiently efficient for laser action to be observed in $YLiF_4$:Nd^{3+} at low temperature. Güdel et al. investigating $CsCdCl_3$ doped with Ni^{2+} showed in 1992 evidence of avalanche emission in transition metal elements [3].

In this paper, we present the results of an investigation of the anti-Stokes Pr^{3+} emission in $LaCl_3$:Pr^{3+} triggered by U^{3+} ions. The results are compared with those observed in $LaCl_3$:Pr^{3+} crystal without U^{3+}. We have already observed the anti-Stokes emission in $LaCl_3$:Pr^{3+}, U^{3+} crystal, preliminary reports have been presented in 1997 [4,5].

The $LaCl_3$ crystal serves as a host for many rare earth ions and actinides. The intruder substitutes the La^{3+} sites with C_{3h} point group symmetry. It is a material, which is easy to obtain and because of low vibronic transitions (see for example work of Richman et al. [6]) the nonradiative transition rate is low. The empirical energy level scheme of $LaCl_3$ doped wit Pr^{3+} was reported by Rana and Kaseta [7] and later by Hargreaves [8]. Energy levels of Pr^{3+} in $LaCl_3$ under pressure were reported by Tröster et al. [9]. The study of radiative and nonradiative transitions in $LaCl_3$:Pr^{3+} and $PrCl_3$ were presented in Ref. [10].

Crosswhite and co-workers published in 1980 an article on spectroscopic properties of U^{3+} in $LaCl_3$ [11], they found that the emitting levels are the $^2H_{11/2}$ at 19737 cm^{-1}, the $^2K_{15/2}$ at 18556 cm^{-1}, the $^4F_{9/2}$ at 14 674 cm^{-1} and the $^4G_{7/2}$ at 13 233 cm^{-1}. A detailed study of energy levels of $LaCl_3$:U^{3+} was published by Carnal et al. [12]. Investigation of up-conversion in $LaCl_3$:U^{3+} was presented in 1996 [4] and in 1997 [5,13].

2. Experimental

Crystals of $LaCl_3$ were grown by the Bridgman technique. Good quality crystals (5 cm long, 0.6 cm diameter) doped with 0.1% of U^{3+} and 0.1% of U^{3+} co-doped with 1% of Pr^{3+} were obtained. The samples were mounted in quartz tubes, with the *c* axis parallel to the tube. The tube was filled with helium to a partial pressure of 400 mm Hg to provide good thermal contact with the crystal. The samples were mounted inside an Oxford helium cryostat. Laser light was directed at the sample by a mirror arrangement and fluorescence was focused by a set of lens through suitable filters on to the slit of a Jobin Yvon 1 m monochromator model THR 1000. A 1200 gr/mm grating provided a resolution of 0.01 nm. The signal was detected

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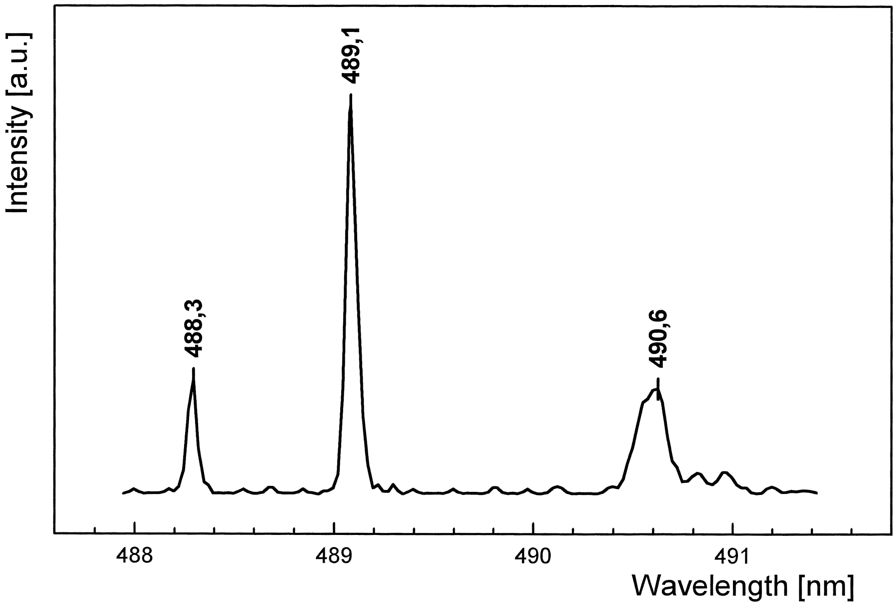

Fig. 1. The $^3P_0 \rightarrow ^3H_4$ emission after excitation by 616 nm, $T=15$ K.

using an R928 Hamamatsu photomultiplier and collected in an IBM clone PC computer. Lambda Physik performed laser excitation with a Lumonics Dye laser model HD 300-B, which has a line half-width of 0.04 cm^{-1}, excited by an excimer laser. The decay time profiles of the observed fluorescence were recorded both on a photon counter system by Standford Research System model SR400 and on a 9350 M digital oscilloscope by Lecroy.

3. Results and discussion

The blue $^3P_0 \rightarrow ^3H_4$ emission (see Fig. 1) was observed at 11 K after excitation of the $LaCl_3$:Pr^{3+} crystal by a laser line, the energy of which was resonant with the $^3H_6 \rightarrow ^3P_0$ transition.

The decay profile of the 10 K emission observed is shown in Fig. 2. It is one exponential decay with a decay constant equal to 14.5 μs, no rise time is observed. Fig. 3 presents the decay profile of the emission from the $^2K_{15/2}$ (U^{3+}) level in $LaCl_3$:U^{3+}, Pr^{3+} crystal. The curve in Fig. 3a was obtained by direct excitation of the $^2K_{15/2}$ (U^{3+}) level and the decay time is very short ($\tau=90$ ns). Fig. 3b shows decay profile while the $^2K_{13/2}$ (U^{3+}) was excited and now the behaviour of the $^2K_{15/2}$ emission is different, the beginning of the decay profile is as steep as in Fig. 3a, but then a tail with decay time equal 14.5 μs is observed.

When $LaCl_3$:Pr^{3+} crystal co-doped with U^{3+} was investigated the intensity of the $^3P_0 \rightarrow ^3H_4$ emission increased by three orders of magnitude. Fig. 4 presents an excitation spectrum of the $LaCl_3$:U^{3+}, Pr^{3+} crystal monitored at $^3P_0$ emission. A broad peak at 616 nm is observed,

Fig. 2. The $^3P_0 \rightarrow ^3H_4$ emission decay curve after 615,424 nm excitation, $T=10$ K.

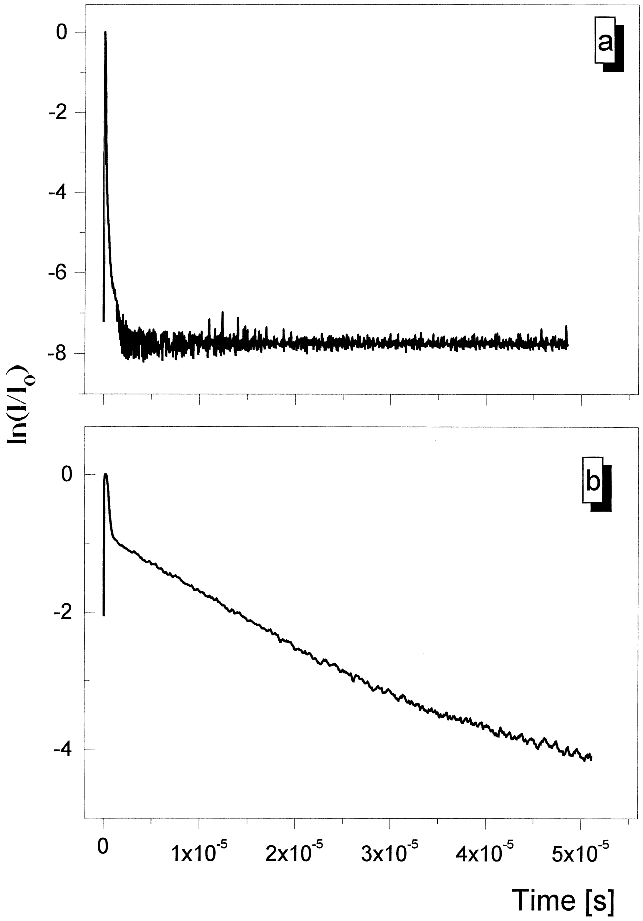

Fig. 3. The 10 K decay curves of U^{3+} emission. (a) $^2K_{15/2}\rightarrow{}^4I_{9/2}$ transition in $LaCl_3$:U^{3+}, Pr^{3+} excited at 536 nm (the $^2K_{15/2}$ absorption line). (b) $^2K_{15/2}\rightarrow{}^4I_{9/2}$ transition in $LaCl_3$:U^{3+}, Pr^{3+} excited at 615 424 nm (the $^2K_{13/2}$ absorption line).

it corresponds to the $^4I_{9/2}\rightarrow{}^2K_{13/2}$ transition of the U^{3+} ions in $LaCl_3$. On the slope of this peak, a narrow line appears at 615.424 nm. This narrow line was assigned to the $^3H_6\rightarrow{}^3P_0$ excited state absorption.

The fluorescence output of the blue praseodymium emission versus incident pump power in the vicinity of critical pump power density is shown in Fig. 5. The dependence of the intensity of the blue praseodymium emission versus excitation power for the co-doped crystal is 2.3. Similar results were observed for $LaCl_3$:Pr^{3+}, but to obtain the blue emission in $LaCl_3$:Pr^{3+} we had to pump the crystal with the 20 mW laser line. Below this value the anti-Stokes emission was not observed, while for co-doped crystal at already 2 mW the blue Pr^{3+} emission was observed.

We concluded from the data collected that the emission from the Pr^{3+} ions does not show a significant rise time, which could indicate direct excitation of the $^3P_0$ level from the excited $^3H_6$ level. The changes in the decay profile of the $^2K_{15/2}\rightarrow{}^4I_{9/2}$ transition of U^{3+} in $LaCl_3$:Pr^{3+}, U^{3+} crystal with changes of excitation wavelength indicate back transfer from Pr^{3+} to U^{3+} ions, because the long lived part of the decay curve is the same as the decay of Pr^{3+}. The possibility of up-conversion in $LaCl_3$:U^{3+} we have discussed in Refs. [4,13].

The question arises of how the $^3H_6$ level is populated. Two processes should be considered (see Fig. 6). One is a cross relaxation in U^{3+} ions that could be described as follows:

$$(^4F_{9/2},\ ^4I_{9/2}) \rightarrow (^4F_{5/2},\ ^4I_{11/2}) + 126\ \mathrm{cm}^{-1} \qquad (1)$$

then the energy is transferred to the $^3H_6$ level.

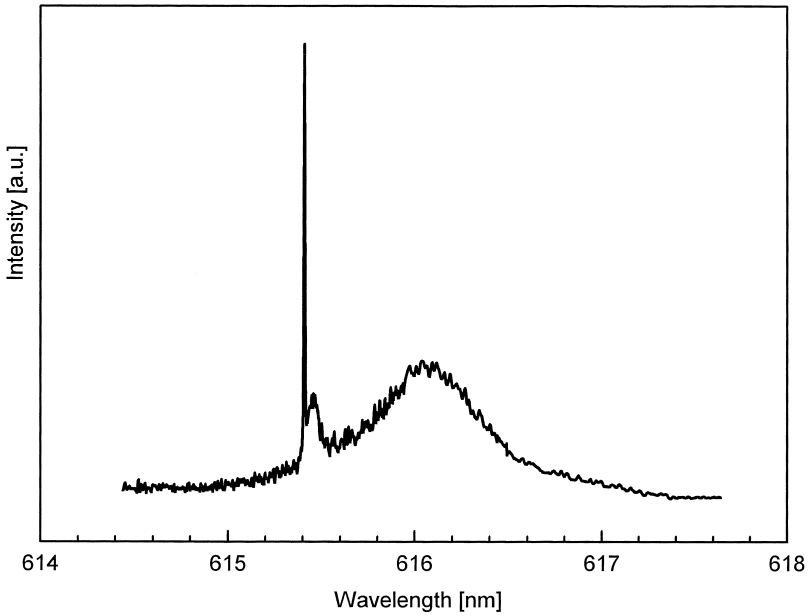

Fig. 4. The 10 K excitation spectrum of $LaCl_3$:U^{3+}, Pr^{3+} monitored at Pr^{3+} emission.

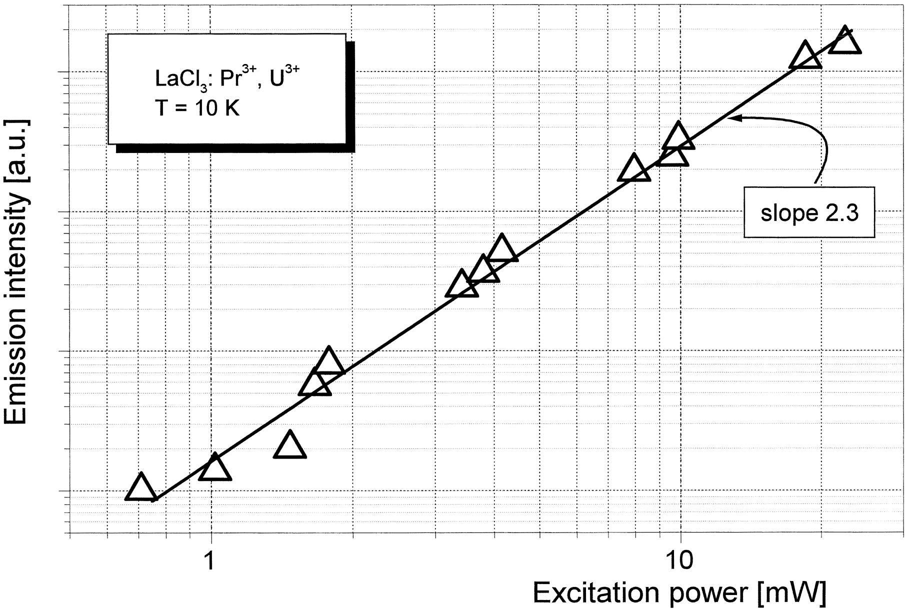

Fig. 5. The dependence of the intensity of the $^3P_0 \rightarrow {}^3H_4$ emission on excitation power.

Another scheme could be described as follows:

$$({}^4F_{9/2}, {}^3H_4) \rightarrow ({}^2H_{9/2}, {}^3F_2) - 10\ \mathrm{cm}^{-1} \tag{2}$$

Second process is more probable because it is nearly resonant; lattice vibrations could easily compensate the 10 cm^{-1} energy mismatch.

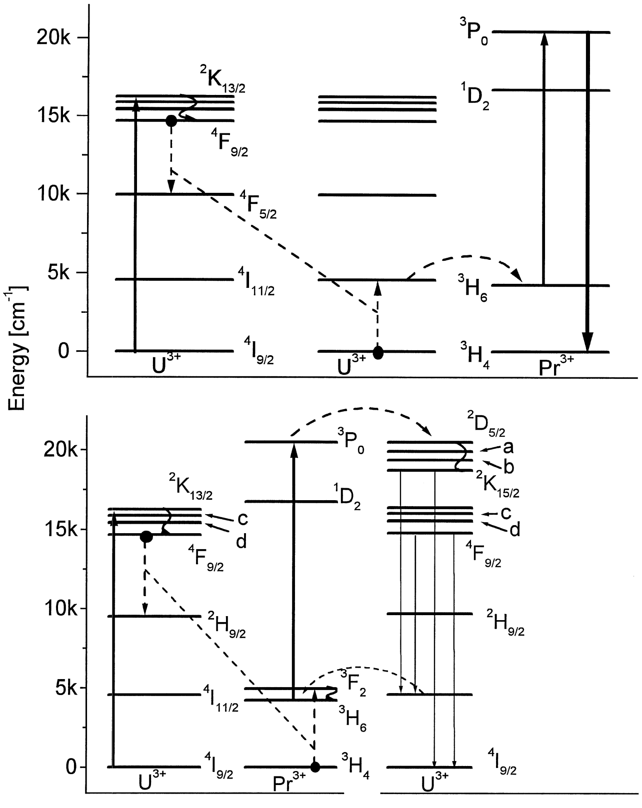

Fig. 6. Schematic energy level diagram of U^{3+} and Pr^{3+} levels in LaCl$_3$ crystal. Only levels involved in the looping mechanism are shown.

The presence of U^{3+} ions triggered anti-Stokes emission at 2 mW, while anti-Stokes emission in pure LaCl$_3$:Pr^{3+} is observed at an excitation energy almost 10 time higher. Chivian et al. [2] triggered the avalanche process by using a second laser, which populates the $^3H_5$ state. Auzel [14] also showed a triggered avalanche emission in a glass sample doped with erbium ions.

We believe that instead of using a second laser, suitable ions can be introduced into the lattice to populate the intermediate state. The excitation energy, which is resonant with the $^3H_6 \rightarrow {}^3P_0$ transition is partially absorbed by the $^2K_{13/2}$ (U^{3+}) absorption line. After being absorbed the energy is transferred then to the $^3H_6$ level by cross-relaxation described above and the next photon populates resonantly the $^3P_0$ level. From this level some of the energy is transferred resonantly to the $^2D_{5/2}$ (U^{3+}) level and also some of the emitted energy from $^3P_0$ level is absorbed by U^{3+} ions. Thus, populated in this way the $^4F_{9/2}$ (U^{3+}) level will repopulate the $^3H_6$ (Pr^{3+}) one by cross relaxation. The scheme described above is similar to the looping mechanism described by Brenier et al. [15].

4. Conclusions

We found that the blue $^3P_0 \rightarrow {}^3H_4$ emission is present in the LaCl$_3$ crystal after excitation by a red laser line which is resonant with the $^3H_6 \rightarrow {}^3P_0$ transition. The intensity of the blue emission of Pr^{3+} is higher by three orders of magnitude in the presence of U^{3+} ions in the crystal. The explanation of the phenomenon observed is based on the looping mechanism.

Some preliminary results with continuous excitation support our supposition, that an avalanche could be triggered by U^{3+} ions. These results will be present in the next paper.

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