Red excited-state absorption and up-conversion in Er^{3+} : $Ca_3Al_2Ge_3O_{12}$

X. Zhang[a,b], J.-P. Jouart[a,*], G. Mary[a], X. Liu[b], J. Yuan[b]

[a]Laboratoire d'Energétique et d'Optique, UTAP, Université de Reims, BP 1039, 51687 Reims cédex 2, France

[b]Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021, China

Abstract

A spectroscopic study of the green ($^4S_{3/2} \rightarrow {}^4I_{15/2}$) and blue ($^2P_{3/2} \rightarrow {}^4I_{11/2}$) emissions from Er^{3+}:$Ca_3Al_2Ge_3O_{12}$, induced by a red tunable laser excitation is reported. The green emission is due to either an excited-state energy transfer or an excited-state absorption, depending on whether the laser excitation wavelength is tuned on $^4I_{15/2} \rightarrow {}^4F_{9/2}$ or $^4I_{13/2} \rightarrow {}^4F_{5/2}$. The blue emission mainly results from a three-step absorption process.

Keywords: Up-conversion; Er; Garnet; Excited-state absorption

Rare-earth doped compounds exhibiting a good overlap between ground-state absorption (GSA) and excited-state absorption (ESA) at the pump wavelength are promising candidates for the single-wavelength pumped up-conversion lasers [1]. A different approach consists in searching for new compounds working on the base of an avalanche effect [2]. In that case, the overlap between GSA and ESA at the pump wavelength should be avoided [3]. We report here the results of a spectroscopic study of the red ($^4F_{9/2} \rightarrow {}^4I_{15/2}$), green ($^4S_{3/2} \rightarrow {}^4I_{15/2}$) and blue ($^2P_{3/2} \rightarrow {}^4I_{11/2}$) emissions from Er^{3+}-doped calcium aluminum germanate garnet Er^{3+}:$Ca_3Al_2Ge_3O_{12}$ (CAGG) induced by a red tunable dye laser excitation.

The polycrystalline samples were prepared using a high-temperature reaction from a mixture of

CaO, Al_2O_3, GeO_2 and ErF_3 with the stoichiometric ratio. The samples were checked by the X-ray diffraction to verify the cubic garnet structure. The luminescence measurements were performed at 300 and 100 K. Five samples doped with 0.5, 1, 2, 5, and 10 at% ErF_3 were studied.

The emission spectrum of CAGG:1 at% Er^{3+} at 100 K, observed between 12 000 and 21 500 cm^{-1}, following the red laser excitation, consists of eight groups of lines, with, in particular, the red, green and blue emissions. This spectrum was used to establish the energy level diagram given in Table 1.

The excitation spectra for the blue (21 114 cm^{-1}) and green (18 490 cm^{-1}) emission lines of CAGG:1% Er^{3+} were recorded, at 100 and 300 K, between 15 200 and 15 800 cm^{-1} (Fig. 1). The local surrounding effect on the energy levels is such as both ESA ($^4I_{13/2} \rightarrow {}^4F_{5/2}$ and $^4S_{3/2} \rightarrow {}^4G_{7/2}$) overlap between 15 600 and 15 700 cm^{-1}, whereas the GSA $^4I_{15/2} \rightarrow {}^4F_{9/2}$ ranges on the low energy side,

* Corresponding author. Fax: 26 05 32 50.

from 15 200 to 15 500 cm^{-1}. Two optimum excitation wave numbers (15 677 and 15 423 cm^{-1}) were selected, both inducing a strong green emission with comparable intensities. The red emission is about five times (under 15 423 cm^{-1}) and 30 times (under 15 677 cm^{-1}) weaker than the green one. The blue emission only grows appreciable under 15 677 cm^{-1}.

Table 1
Positions of the Stark sublevels of Er^{3+} in CAGG

Level	Energy (in cm^{-1})
$^4I_{15/2}$	0, 50, 93, 131, 147, 420, 524, 580
$^4I_{13/2}$	6614, 6667, 6675, 6693, 6776, 6831, 6919
$^4I_{11/2}$	10 264, 10 303, 10 369, 10 384, 10 416, 10 423
$^4I_{9/2}$	12 324, 12 522, 12 594, 12 719, 12 785
$^4F_{9/2}$	15 307, 15 319, 15 325, 15 473, 15 536
$^4S_{3/2}$	18 415, 18 490
$^2H_{11/2}$	19 110, 19 116, 19 132, 19 142, 19 182
$^4F_{5/2}$	22 291, 22 312, 22 360
$^2P_{3/2}$	31 498, 31 617
$^4G_{7/2}$	34 092, 34 108, 34 114

Fig. 2. Excitation spectra (at 100 K) for the green and blue emissions of CAGG:1% Er^{3+}. The spectra are not normalized with respect to the sensitivity of the apparatus. For clarity, the spectrum for the blue emission is shifted along the intensity axes.

The green emission intensity varies as I^2 (I being the excitation power) and the blue one as I^3 (Fig. 2). The filling mechanism of the $^2P_{3/2}$ level consists of three absorptions exciting successively the Er^{3+} ion from $^4I_{15/2}$ to a vibronic sideband of $^4F_{9/2}$, from $^4I_{13/2}$ to $^4F_{5/2}$ and from $^4S_{3/2}$ to $^4G_{7/2}$ [4]. After each absorption, the Er^{3+} ion relaxes to a metastable level which is the starting point of the next one. Under 15 677 cm^{-1}, ESA ($^4I_{13/2} \rightarrow {}^4F_{5/2}$) contributes to the $^4S_{3/2}$ filling, whereas an energy transfer between two Er^{3+} ions excited in the $^4I_{11/2}$ state happens under 15 423 cm^{-1}. When the Er^{3+} concentration increases, the GSA peaks are reinforced compared to the ESA ones, thus indicating that the energy transfer is more efficient at high concentration and that the avalanche effect is not operating in this compound.

References

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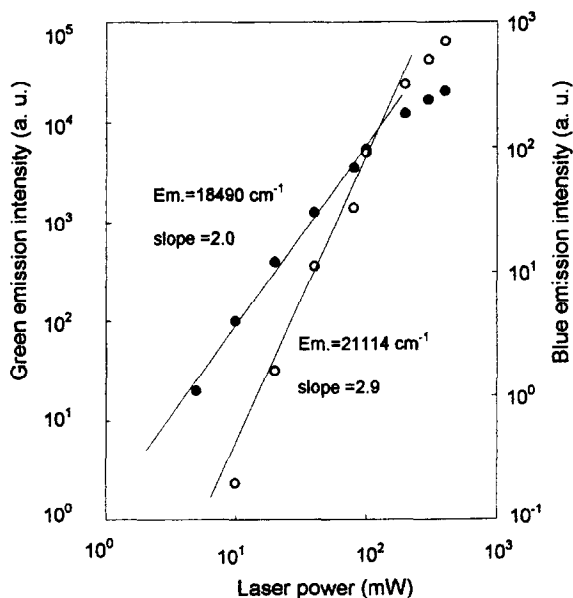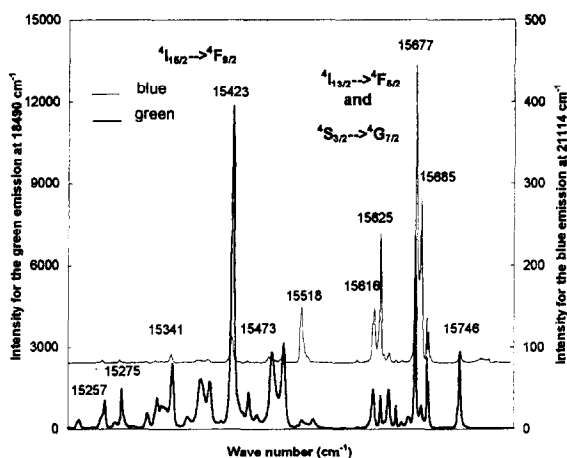[4] J.P. Jouart, M. Bouffard, X. Zhang and G. Mary: Ann. Phys. (France) 20 (1995) 119–120.

Fig. 1. Dependence (at 100 K) of the green and blue emission intensities of CAGG:1% Er^{3+} on the laser power (the excitation wave number is tuned on 15 677 cm^{-1}).