ELSEVIER

Journal of Alloys and Compounds 323–324 (2001) 312–314

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Concentration effect on the up-conversion luminescence of neodymium activated calcium gallium germanium garnet crystal

J.J. Romero*, D. Jaque, J. García-Solé, U. Caldiño G.[1]

Departamento de Física de Materiales C-IV, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain

Abstract

In this work, we report on the infrared (pump) to visible luminescence of Nd^{3+} ion in $Ca_3Ga_2Ge_3O_{12}$ for different Neodymium concentrations. Three visible structured emission bands centred at 541, 601 and 677 nm are observed, which are related to emissions mainly from the excited state $^4G_{7/2}$. The relative intensity between the red band (677 nm) and the other bands changes with both concentration and excitation intensity for Nd^{3+} contents >2 at.%. In addition, a new up-conversion emission band in the blue region (centred about 460 nm) was detected in these samples. These results can be explained because of a pump induced thermalisation of the $^4G_{11/2}$ excited state from which additional emissions appear.

Keywords: Luminescence; Solid state lasers; Disordered materials

1. Introduction

Nd^{3+} doped crystals have been demonstrated to be excellent for diode pumping lasers due to their intense absorption peaks around 800 nm, where most commercial laser diodes emit. Thus, during the last few years, there has been increased interest in these laser crystals as regards a variety of technological applications, such as communications, laser prints, very bright displays and several optoelectronic devices.

Although YAG:Nd is still the most common laser crystal for diode pumping, it has some disadvantages: (a) its growth process is relatively expensive because of a high melting point (1960°C), and (b) the Nd^{3+} concentration inside the crystal without quenching is limited to 1 at.% [1]; this induces a long absorption length for pump light increasing, hence, the internal losses (which are proportional to the crystal length).

Very recently, it was possible to obtain laser action in the region of 1 μm in the Nd^{3+} doped $Ca_3Ga_2Ge_3O_{12}$ garnet (CGGG:Nd) by Ti-Sapphire end pumping [2]. Furthermore, CGGG:Nd emerges as an interesting laser crystal because of the following advantages: (a) its lower melting point, about 1400°C, which can be easily reached with silicon carbide common ovens; (b) crystals with Nd concentrations of ~16 at.% have been grown with relatively good optical quality [3]; (c) an accurate temperature stabilisation of the diode pump source is not as necessary as for YAG:Nd because of its considerably broader absorption bands; this peculiar characteristic of its bands is due to the formation of a variety of Nd^{3+} centres [4]; and (d) the contribution of excited state absorption of pump radiation to the up-conversion luminescence, which can lead to considerable losses in the laser gain, has been found to be much smaller than that of up-conversion energy transfer [5]. Since it seems to be that the dynamics of the up-converted luminescence changes with Nd concentration [5], in this work we report on the concentration effect in the up-conversion luminescence.

2. Experimental

CGGG:Nd crystals were grown from the melt by the Czochralski technique. The Nd concentration in the melt was changed from 0.5 to 16 at.%.

Emission and excitation spectra were obtained using a cw-argon pumped Ti-sapphire tunable laser (Spectra Physics 3900). The emitted light was dispersed by a 500M SPEX monochromator and finally detected by a cooled photomultiplier (Hamamatsu R636). Finally, a lock-in amplifier ERS (model SR830 DSP) was used to increase

*Corresponding author.

[1]On sabbatical leave from Departamento de Física, Universidad Autónoma Metropolitana, Iztapalapa.

0925-8388/01/$ – see front matter
PII: S0925-8388(01)01076-3

the signal-to-noise ratio. An infrared filter was used to avoid both the pump radiation and the infrared luminescence. All spectra were obtained at room temperature.

3. Results and discussion

Fig. 1 displays the emission spectrum recorded for different Nd concentrations (0.5, 1, 2, 8 and 16 at.%) when the CGGG:Nd crystal is pumped within the $^4I_{9/2} \rightarrow {}^4F_{5/2}$ transition (at 805 nm). Three structured bands in the green, yellow and red regions of the electromagnetic spectrum, centred at 541, 601 and 677 nm, respectively, are seen. These up-converted emissions have been assigned to the $^4G_{7/2} \rightarrow {}^4I_{9/2}$, $^4G_{7/2} \rightarrow {}^4I_{11/2}$ and $^4G_{7/2} \rightarrow {}^4I_{13/2}$ transitions, respectively [5]. The emission associated with the $^4G_{7/2} \rightarrow {}^4I_{15/2}$ transition was not observed, since it overlaps the 805-nm excitation.

It has been previously demonstrated that the $^4G_{7/2}$ excited state is predominantly populated by up-conversion energy transfer [5], in which two nearby Nd^{3+} ions are both initially excited to the $^4F_{3/2}$ state. Because of their interaction, one ion goes to a lower state, releasing some energy, while the second ion uses this energy and goes to the higher excited state $^4G_{7/2}$ (Fig. 2, left side).

From Fig. 1, it can also be seen that the red emission intensity gradually increases with Nd concentration in relation to the green and yellow bands, becoming dominant for 8 and 16 at.%. In addition, the shape and intensity of this band also change with the excitation power for Nd concentrations >2 at.%. Fig. 3 displays the up-converted emissions for different excitation intensities into the sample doped with Nd 16 at.%. It can be observed that the intensity of the red band increases in relation to the other bands and its shape changes when the pump power is increased. At low pump power (560 mW), the shape of this band is very similar to that observed for the samples with Nd concentrations ≤2 at.%. This behaviour of the red band with the excitation intensity was also detected for the sample doped with Nd 8 at.%. Taking into account that the red band shape changes with increasing excitation intensity, it is reasonable to presume that transitions from some additional state participate in this emission. This state might be the $^4G_{11/2}$ state, which can be populated via the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4G_{11/2}$ transitions of two close ions or directly by pump induced thermalisation from the $^4G_{7/2}$ state (Fig. 2). In the first mechanism the $^4G_{11/2}$ state undergoes multiphonon relaxation to the $^4G_{7/2}$ emitting state. Therefore, both mechanisms lead to emissions from

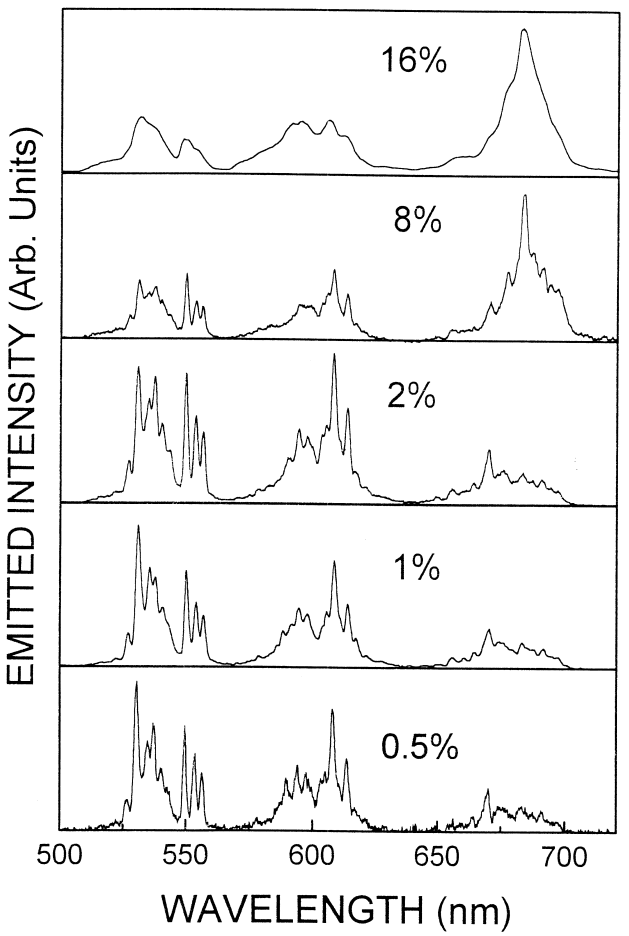

Fig. 1. Up-conversion emission spectra displayed by CGGG:Nd crystals with different Nd concentrations.

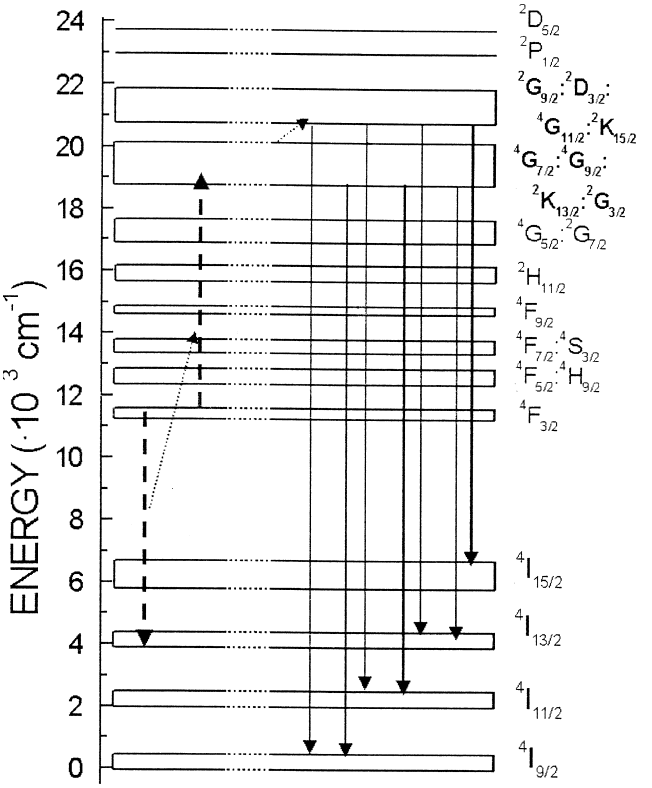

Fig. 2. Energy state diagram showing the energy transfer up-converted emissions in CGGG:Nd crystals with high Nd concentrations (8–16 at.%) and under intense excitation.

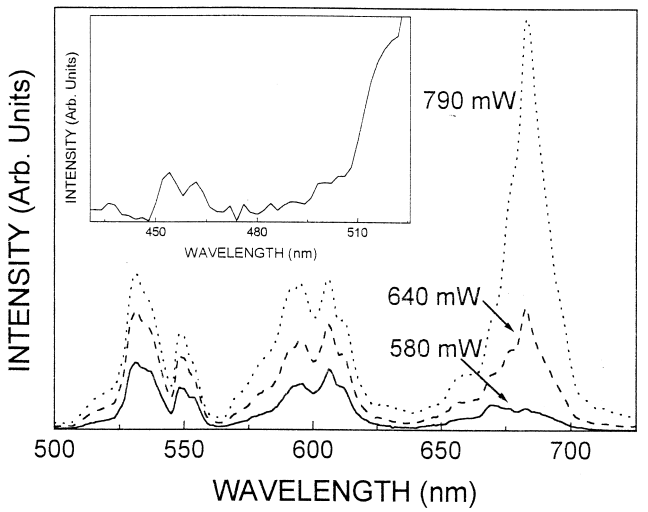

Fig. 3. Up-conversion emission spectra obtained under excitation at 805 nm as function of the pump source power for the CGGG:Nd(16 at.%) crystal. The inset shows the blue emission obtained under a 790-mW pump source power.

the $^4G_{11/2}$ state which is thermally populated from the $^4G_{7/2}$ state. In fact, a substantial crystal heating was detected under intense excitation. Moreover, a higher Nd concentration induces a larger crystalline field splitting of the $^4G_{11/2}$ and $^4G_{7/2}$ states, reducing their separation, and therefore a not very high temperature is required to populate the $^4G_{11/2}$ state. Thus, such a thermalisation effect is favoured in the samples with high Nd^{3+} concentrations (8 and 16 at.%) and under high intensity excitation.

The transitions departing from the $^4G_{11/2}$ state permit observation of a red emission to the $^4I_{15/2}$ terminal state, which overlaps the $^4G_{7/2}\rightarrow{}^4I_{13/2}$ red transition, and a new emission in the blue region (about 460 nm) corresponding to the $^4G_{11/2}\rightarrow{}^4I_{9/2}$ transition (Fig. 2). The excitation spectrum monitored at 460 nm displays the absorption lines corresponding to the $^4I_{9/2}\rightarrow{}^4F_{5/2}$ transition. Therefore, this blue up-converted emission, which is shown in the inset of Fig. 3, is a clear evidence of the $^4G_{11/2}$ state thermalisation from the $^4G_{7/2}$ state. From Fig. 2 it can also be observed that the other emissions associated with the $^4G_{11/2}\rightarrow{}^4I_{13/2}$ and $^4G_{11/2}\rightarrow{}^4I_{11/2}$ transitions overlap the $^4G_{7/2}\rightarrow{}^4I_{11/2}$ (yellow) and $^4G_{7/2}\rightarrow{}^4I_{9/2}$ (green) transitions, respectively.

In summary, CGGG:Nd crystals doped with high Nd concentrations (8–16 at.%) can generate infrared to visible up-converted luminescence in four regions of the spectrum under intense excitation (instead of the three transitions usually observed [5]): blue (450–467 nm), green (530–557 nm), yellow (587–617 nm) and red (660–697 nm). The pump induced thermalisation of the $^4G_{11/2}$ excited state from the $^4G_{7/2}$ state explains the additional up-converted emissions appearing in these crystals, as well as the red emission intensity increasing with the pump source power.

Acknowledgements

This work has been supported by the Comisión Interministerial de Ciencia y Tecnología (CICYT) under Project No. PB 97-0033 and by Comunidad Autónoma de Madrid (project No. 07N/0029/98). U. Caldiño acknowledges the CONACyT (México) for his sabbatical year Grant no. 990511.

References

[1] A.A. Kaminskii, Laser Crystals, Springer, Berlin, 1981.
[2] D. Jaque, G.U. Caldiño, J.J. Romero, J. García-Solé, J. Appl. Phys. 86 (1999) 6627.
[3] A.A. Kaminskii, B.V. Mill, A.V. Buthashin, Phys. Status Solidi (a) 78 (1983) 723.
[4] G.U. Caldiño, M. Voda, F. Jaque, J. García-Solé, A.A. Kaminskii, Chem. Phys. Lett. 213 (1993) 84.
[5] F. Ramos-Lara, D. Jaque, J. García-Solé, G.U. Caldiño, J. Phys. Condens. Matter. 12 (2000) L441.