LASERS

SELECTIVELY EXCITED Er\(^{3+}\) LUMINESCENCE IN CALCIUM LITHIUM NIOBIUM GALLIUM GARNET

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The presence of multiple Er\(^{3+}\) luminescent centres in calcium lithium niobium gallium garnet is investigated using selectively excited luminescence spectra of transitions \(^4S_{3/2} \rightarrow ^4I_{15/2}\) and \(^4I_{11/2} \rightarrow ^4I_{15/2}\) pumped in infrared \((^4I_{15/2} \rightarrow ^4I_{9/2})\) at low temperature (10 K). Three luminescent centres were identified and the positions of the lowest four sublevels of their \(^4I_{15/2}\) energy level could be estimated.

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1. INTRODUCTION

The rare-earth-doped partially disordered garnets CNGG (Calcium Niobium Gallium Garnet) and CLNGG (Calcium Lithium Niobium Gallium Garnet) are presently of great interest in laser physics due to their broad absorption and emission bands that make them suitable for efficient diode laser pumping [1–3] and tunable/ultrashort laser emission [4–6]. Their spectra are composed of inhomogeneously-broadened lines due to the distribution of the rare-earth-ions on sites with various neighbourhoods in the disordered crystal structure; thus, environments which differ in the first coordination spheres can cause major differences between the spectroscopic properties of the doping ions and make them behave as distinct non-equivalent centres, while environment differences in the more distant coordination spheres cause inhomogeneous broadening of the spectral lines of these centres by slightly altering their spectroscopic properties.

Although Nd\(^{3+}\) and Yb\(^{3+}\) ions are the most intensely studied rare-earth ions for these applications, erbium-doped CNGG and CLNGG were also studied for the possibilities of laser emission on transition \(^4I_{11/2} \rightarrow ^4I_{13/2}\) [7]; the energy-transfer processes in Er:CNGG were also investigated [8]. However, the structure of the optical spectra of Er\(^{3+}\) in CLNGG was not, to our knowledge, discussed in detail up to now.

In this paper, we investigate the multi-centre structure of the Er\(^{3+}\) spectra in CLNGG. The presence of multiple non-equivalent Er\(^{3+}\) centres in this garnet is put into evidence using two methods:

(i) Decomposition of spectral lines obtained at low temperature (10 K) into their Gaussian components. This method can be applied to absorption as well as luminescence spectra. It was applied here with good results to the spectrum of transition $^4S_{3/2} \rightarrow ^4I_{15/2}$ and to the spectrum of transition $^4I_{15/2} \rightarrow ^4I_{9/2}$ (which possesses a well-separated 0-0 line, corresponding to the transition between the lowest Stark levels of both multiplets).

(ii) Analysis of selectively-excited luminescence spectra. This method is based on short-pulse narrow-bandwidth pumping and recording of the luminescence spectra corresponding to various centres which are preferentially excited at a well-determined pump wavelength. The method was applied here to two transitions: $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4I_{11/2} \rightarrow ^4I_{15/2}$. The spectra of both these transitions consist, at 10 K, in eight lines, so that the contributions of the various luminescent centres in the selectively-excited spectra are relatively easily observed.

2. EXPERIMENTAL

The Er:CLNGG single crystal used in this work was grown by the Czochralski method using an ADL Inc. crystal growth equipment. The atomic concentration of erbium with respect to calcium was 5%.

The absorption spectra were recorded at 10 K using a tungsten-halogen lamp, a 1-m Jarrell-Ash monochromator and suitable detectors and filters. The optical signal was chopped using a mechanical chopper (SR540) and analysed using a lock-in amplifier (SR830) from Stanford Research Systems. For the cooling of the samples, a closed-cycle He cryostat CS202-X1.AL (IDB) was used.

The luminescence spectra were recorded at 10 K, using a setup similar to the one used for the absorption spectra.

The selective excitation of the luminescence on transition $I_{11/2} \rightarrow ^4I_{15/2}$ was accomplished using a pulsed Ti:Sapphire laser Solar TII model CF131A (pulse duration 8-20 ns). For the excitation, pumping on transition $^4I_{15/2} \rightarrow ^4I_{9/2}$ was used.

3. RESULTS AND DISCUSSION

The luminescence spectrum of transition $^4S_{3/2} \rightarrow ^4I_{15/2}$ at 10 K, pumped in UV using a broad-band Xe-Hg arc lamp, is presented at the bottom of Fig. 1. The lines of the broad-band-pumped emission spectrum are separated in the two groups of lines characteristic to garnets [9]. The simplest model that could fit this spectrum was composed of 10 Gaussian lines, 2 lines more than the number of the Stark levels of $^4I_{15/2}$ [10], with centres at: 17839 cm$^{-1}$, 17866 cm$^{-1}$, 17948 cm$^{-1}$, 17990...
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This fact denotes the presence of at least two Er\(^{3+}\) non-equivalent centres in Er:CLNGG. From the superposition of this luminescence spectrum and the absorption spectrum \(4I_{15/2} \rightarrow 4S_{3/2}\), and using the position of the hotbands observed in low-temperature absorption spectra, we could deduce the energy values for the Stark levels of \(4I_{15/2}\) for these two centres: (i) \(0, 22-26\) cm\(^{-1}\), \(58\) cm\(^{-1}\), \(79\) cm\(^{-1}\), \(399\) cm\(^{-1}\), \(525\) cm\(^{-1}\) and (ii) \(0, 22-26\) cm\(^{-1}\), \(70\) cm\(^{-1}\), \(414\) cm\(^{-1}\), \(524\) cm\(^{-1}\) [10].

The fitting of the spectrum was accomplished using a Levenberg-Marquardt method implemented by the program fityk [11].

The simple decomposition into Gaussian components is not able to reveal all the spectral lines belonging to non-equivalent Er\(^{3+}\) centres; there are Gaussian lines in this decomposition which are visibly larger than the others and can mask two or even more Gaussian lines of smaller line width. In order to put into evidence more clearly the multi-centre nature of the luminescence spectrum of \(4S_{3/2} \rightarrow 4I_{15/2}\), we recorded the spectra of the same transition pumped selectively by upconversion at the wavelengths 810.7 nm, 811 nm, 811.5 nm, 812 nm, and 812.5 nm; the sample was the same and its temperature was also 10 K. These spectra, presented in Fig. 1, prove that the structure of the luminescence spectrum of \(4S_{3/2} \rightarrow 4I_{15/2}\) is due to the presence of multiple luminescent centres Er\(^{3+}\) occupying sites with different neighbourhood in the partially disordered CLNGG. The change of the luminescence spectrum with the pump wavelength is obvious and is due to the excitation of different non-equivalent luminescent centres at different pump wavelengths. The selectively pumped luminescence spectra also put into evidence spectral lines that are not present in the simple Gaussian decomposition:

- The spectrum obtained by pumping at 812.5 nm presents a line at 17787 cm\(^{-1}\) that is masked in the previous decomposition by the large Gaussian line at 17839 cm\(^{-1}\);
- The spectrum obtained by pumping at 811.5 nm presents a line at 17941 cm\(^{-1}\) that could not be identified in the simple decomposition of the luminescence spectrum, possibly being obscured by the large Gaussian line at 17948 cm\(^{-1}\);
- The spectrum obtained by pumping at 811 nm contains a line at 17972 cm\(^{-1}\) which could not be identified by the simple decomposition of the broadband-pumped luminescence spectrum.

The presence of multiple non-equivalent Er\(^{3+}\) centres in CLNGG is also visible in the low-temperature absorption spectrum of transition \(4I_{15/2} \rightarrow 4I_{9/2}\). The 0-0 transition of this spectrum, recorded at 10 K, is presented in Fig. 2. This line, which is the least affected by homogeneous broadening, could be decomposed into (at least) three Gaussian components [10], which denotes the presence of at least three non-equivalent Er\(^{3+}\) centres in CLNGG.
Fig. 1 – Lines: emission spectra of transition $^{4}S_{3/2} \rightarrow ^{4}I_{15/2}$ in Er(5 at. %):CLNGG at 10 K, pumped selectively at the indicated wavelengths. Bottom, points: the same, pumped by a broad-band Xe arc lamp; the dashed lines represent the decomposition of the broad-band-pumped spectrum into Gaussian components; the vertical grid lines mark the centres of the Gaussian components.
Fig. 2 – Part of the absorption spectrum of transition $^4I_{15/2} \rightarrow ^4I_{9/2}$ in Er(5 at. %)CLNGG at 10 K, representing the transition between the lowest Stark levels of both multiplets. The vertical lines indicate the wavenumbers used for the selective pumping of $^4I_{11/2}$: 12300 cm$^{-1}$ (813 nm), 12306 cm$^{-1}$ (812.6 nm), and 12338 cm$^{-1}$ (810.5 nm).

Fig. 3 – Part of the luminescence spectrum of transition $^4I_{11/2} \rightarrow ^4I_{15/2}$ selectively excited at 810.5 nm, 812.6 nm and 813 nm (see the grid lines in Fig. 2), respectively, at 10 K. Letters indicate the various luminescent centres to which the spectral lines are attributed.
The line in Fig. 2 was used for selective pumping of level $^4I_{11/2}$ (by absorption on $^4I_{9/2}$ and subsequent multiphonon decay to $^4I_{11/2}$), whose luminescence emission by transition $^4I_{11/2} \rightarrow ^4I_{15/2}$ was recorded. The pump wavelength was varied inside the line profile; of all the pump wavelengths used, we retained as the most interesting the wavelengths marked by vertical grid lines in Fig. 2: 810.5 nm, 812.6 nm, and 813 nm. The spectra obtained for these three pump wavelengths, normalized at their maximum intensity, are represented in Fig. 3. As the lines corresponding to transitions between the lowest Stark component of $^4I_{11/2}$ (which is the only populated at 10 K) and the upper four Stark components of $^4I_{15/2}$ are weaker than the other lines in the spectrum of $^4I_{11/2} \rightarrow ^4I_{15/2}$, these lines could not be used for the identification of various luminescent Er$^{3+}$ centres. The only lines represented in Fig. 3 correspond to transitions between the lowest Stark level of $^4I_{11/2}$ and the lowest four Stark levels of $^4I_{15/2}$.

For pumping at 813 nm, the luminescence spectrum presents four distinct peaks of much greater intensity than the others, which can be attributed to a single luminescent centre, denoted as centre A. The energy of the lowest Stark levels of $^4I_{15/2}$ in this centre could be calculated using the positions of these lines: 0, 18 cm$^{-1}$, 51 cm$^{-1}$, 79 cm$^{-1}$. The positions of the four lines were found by fitting the spectrum with Gaussian lines; there are also other four Gaussian lines present in this spectrum, which were used only for improving the quality of fitting. These positions are close to the values found for Er:YAG [9].

The spectrum recorded for pumping in the opposite margin of the pump line (810.5 nm) also has a simpler structure. Although it could be fitted with acceptable precision using no less than 10 Gaussian lines, elimination of lines corresponding to previously identified centre A leaves fewer peaks of significant intensity to be allocated to other centres. The peak at 10255 cm$^{-1}$ is present only in this spectrum; peaks at 10181 cm$^{-1}$ and 10200 cm$^{-1}$ are also characteristic to this spectrum; the energy intervals between these three peaks are close to the ones found in YAG [9]. The fourth peak should be placed between the peak at 10255 cm$^{-1}$ and the one at 10200 cm$^{-1}$ and the energy difference between it and the peak at 10255 cm$^{-1}$ has to be around 20 cm$^{-1}$. The only peak in the spectrum that satisfies this condition is the peak at 10231 cm$^{-1}$. Thus, these four peaks may be attributed to another luminescent centre, which we denote by letter C. The energy of the lowest Stark levels of $^4I_{15/2}$ calculated for this centre are: 0, 24 cm$^{-1}$, 55 cm$^{-1}$, 75 cm$^{-1}$; these values are close to those found above by the decomposition of the broadband-pumped spectrum of transition $^4S_{3/2} \rightarrow ^4I_{15/2}$.

Pumping at 812.6 nm (in the centre of the absorption line of $^4I_{9/2}$) yielded a spectrum with a more complicated structure, due not to the number of Gaussian components (it could be fitted with good precision using 11 Gaussian functions), but mainly to the placing of all peaks in a narrower spectral range. Elimination
of the lines corresponding to previously identified luminescent centres makes the identification of other centres easier. It can be easily seen that the peaks at 10192 cm\(^{-1}\) and 10211 cm\(^{-1}\) are not present in the other two luminescence spectra. The other two peaks that are placed at the correct energy intervals around these two are at 10163 cm\(^{-1}\) and 10236 cm\(^{-1}\). Thus, the energy of the lowest four Stark levels of \( ^4I_{15/2} \) for this centre (denoted by letter B) were calculated: 0, 25 cm\(^{-1}\), 44 cm\(^{-1}\), 73 cm\(^{-1}\).

The spectra also present Gaussian components that could not be attributed to a distinct luminescent centre and peaks much broader than the others, that could hide two or more lines under their envelope; however, this simple method allowed us to identify three distinct luminescent centres. This number of centres was also found in [10] by a simple Gaussian decomposition of absorption spectra of Er:CLNGG at 10 K. Other works identified non-equivalent luminescent centres in CLNGG doped with other rare-earth ions; for example, the use of Eu\(^{3+}\) as a probe led to the identification of three different centres [12]; however, the multi-centre structure seemed more complex in the case of Nd\(^{3+}\) [12,13]. Our results obtained for Er\(^{3+}\) are in agreement with the previous results regarding the multi-centre structure of rare-earth-doped CLNGG: three non-equivalent centres were identified, while there still remains the possibility of the presence of at least a supplementary one (a few peaks were not yet attributed to any centre).

4. CONCLUSIONS

The presence of at least three distinct Er\(^{3+}\) centres in CLNGG, indicated by a simple analysis of the luminescence and absorption spectra at 10 K, was closer investigated using selectively-pumped luminescence on transitions \( ^4S_{3/2} \rightarrow ^4I_{15/2} \) and \( ^4I_{11/2} \rightarrow ^4I_{15/2} \) at 10 K. The luminescence spectrum of transition \( ^4S_{3/2} \rightarrow ^4I_{15/2} \) presents changes with the change of the pump wavelength, thus proving the presence of multiple non-equivalent Er\(^{3+}\) centres in CLNGG. The study of the luminescence spectrum of transition \( ^4I_{11/2} \rightarrow ^4I_{15/2} \) allowed us to separate the lines that correspond to three different such centres and to determine the four lowest Stark energy levels of \( ^4I_{15/2} \) for each centre.

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