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Excited-state absorption in erbium-doped calcium lithium niobium gallium garnet

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ABSTRACT

Excited-state absorption (ESA) spectra of Er^{3+} in the partially disordered calcium lithium niobium gallium garnet (CLNGG), recorded in the spectral range 400–900 nm, are presented and discussed. The use of a pump wavelength of 973 nm enables a complete separation of the ESA spectra from ground-state absorption (GSA) and stimulated emission. For the identification of various ESA transitions, the Er^{3+} energy levels above $^4S_{3/2}$ in CLNGG are determined using GSA spectra at low temperature. Excitation spectra for the population of ($^4S_{3/2}$, $^2H2_{11/2}$) levels by two-step sequential absorption with $^4I_{13/2}$ as an intermediate level are generated using the recorded ESA and GSA spectra.

1. Introduction

The partially disordered calcium lithium niobium gallium garnet (CLNGG) and its isomorph calcium niobium gallium garnet (CNGG) are interesting hosts for the laser active lanthanide ions due to their attractive combination of properties: the broadening of the absorption / emission lines of the doping ions on the one hand and good thermal conductivity on the other hand [1]. These properties make these rare-earth-doped crystals suitable for efficient diode laser pumping [2–4] and tunable/ultrashort laser emission [5–7].

Laser emission in Er^{3+}-doped CNGG and CLNGG was studied on transition $^4I_{11/2} \rightarrow {}^4I_{13/2}$ [8]. Research of the spectroscopic properties of these erbium-doped materials is in progress. Energy-levels and the presence of non-equivalent Er^{3+} centers were investigated [9,10], as well as the intensities of Er^{3+} transitions in Er:CNGG and Er:CLNGG [11–13]. Energy-transfer processes in Er:CNGG were addressed in a relatively recent paper [14]. However, there is still a need for spectroscopic data characterizing these Er^{3+}-doped crystals in order to enable the prediction – using mathematical modeling – of the laser performances of these systems on various transitions.

The excited-state absorption (ESA) processes can play an important role in Er^{3+} laser emission on various transitions. They can contribute to the population of the laser initial level by upconversion mechanisms [15] or constitute a loss mechanism by reabsorption of the laser photons [16].

In this paper, we investigate the excited-state absorption (ESA) processes taking place in Er:CLNGG in UV, visible and near infrared. To our knowledge, this is the first investigation of this subject. The high energy levels of Er^{3+} in CLNGG are also investigated for the first time in this paper, using low-temperature absorption spectra.

The experimental methods are detailed in Section 2.

Section 3 presents and discusses the experimental results. The positions of the energy levels of Er^{3+} in CLNGG are found from the low-temperature absorption spectra and the influence of the presence of various non-equivalent Er^{3+} on the absorption spectra is discussed (Section 3.1).

The ESA spectra of Er:CLNGG in the spectral range 400–900 nm, calibrated to absorption cross-sections, are presented (Section 3.2). The various transitions are identified using the data obtained in Section 3.1 about the energy levels of Er^{3+}:CLNGG.

The excitation spectra for the levels ($^4S_{3/2}$, $^2H2_{11/2}$) for upconversion pumping in two spectral ranges are generated in Section 3.3 using products of ground-state absorption (GSA) and ESA spectra.

2. Experimental

Bulk crystalline samples of Er:CLNGG, of concentrations 0.1 at.%, 2.46 at.%, and 5 at.% with respect to Ca^{2+} were used in the experiments. The samples were grown in our laboratory using the

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Czochralski method according to the congruent formula $Ca_3Li_{0.275}Nb_{1.775}Ga_{2.95}O_{12}$.

The GSA spectra at low temperature (10 K) were obtained using a closed-cycle cryostat (CTI-Cryogenics model 22) for the cooling of the samples. The light source was a tungsten–halogen lamp; after modulation with a mechanical chopper (Stanford Research Systems SR540), the light beam was analyzed using a 1-m 1000 M Horiba Jobin-Yvon monochromator and detected using a EMI photomultiplier with a S-20 (Na_2KSb-Cs) photocathode (wavelength range 300–800 nm); the signal was processed using a lock-in amplifier (SR830, Stanford Research Systems). The spectra of all transitions except $^4I_{15/2}\rightarrow{}^2H2_{11/2}$ and $^4I_{15/2}\rightarrow{}^4G_{11/2}$ were recorded using an Er(5 at.%):CLNGG sample; the spectra of these two hypersensitive transitions were recorded using a sample of Er:CLNGG of only 0.1 at.% concentration, to avoid the saturation of the very intense spectral lines.

The ESA spectra were obtained using a pump–probe method, in a double modulation scheme, with the sample at room temperature. The experimental setup is very similar to that described in Ref. [17]. The pump laser beam is emitted by a fiber-coupled laser diode DioMod 980/30/400, centered at the wavelength 973 nm (transition $^4I_{15/2}\rightarrow{}^4I_{11/2}$ of Er^{3+}); the beam is modulated with a mechanical chopper (Stanford Research Systems SR540) at 11 Hz. The probe beam is emitted by a tungsten–halogen lamp and modulated with a similar chopper at about 2 kHz. For the visible spectral range, the probe beam was spectrally analyzed using a Horiba Jobin-Yvon monochromator model 1000 M and detected using a EMI photomultiplier with the S-20 photocathode; the signal was processed using two lock-in amplifiers (SR830, Stanford Research Systems) with reference frequencies corresponding to the two modulation frequencies. The data – i.e., the outputs of both lock-in amplifiers, proportional respectively to GSA (high-frequency reference amplifier) and ESA (low-frequency reference amplifier) – were then acquired and processed by a personal computer connected to the RS232 port of the second lock-in amplifier.

For the measurement of ESA spectra in the infrared, a 1-m Jarrell-Ash monochromator and a EMI photomultiplier with the S-1 (AgOCs) photocathode (wavelength range 300–1100 nm) were used in a similar setup. A KG3 filter was used in front of the entrance slit of the monochromator in order to prevent the scattered pump radiation from entering the monochromator.

The main advantage of our working method is that, due to the infrared pump wavelength, only the two lowest excited states of Er^{3+} are significantly populated: $^4I_{11/2}$ and $^4I_{13/2}$. This excludes the stimulated emission from our spectra. Another important advantage is that the pumping in IR makes possible the use of a fiber-coupled diode laser array, with a significantly lower cost than other lasers used previously for pump, and a better superposition of the pump and probe beams in the sample.

3. Results and discussion

3.1. Preliminary data

In order to enable an accurate identification of the ESA and GSA transitions in the ESA spectra, we studied the high-energy levels (above $^4S_{3/2}$) of Er^{3+} in CLNGG. The procedure was similar to that applied in Ref. [9]: the absorption spectra were recorded at 10 K and processed using the same approach based on fitting with the minimum number of Gaussian functions that reproduce the spectrum in all its details. The results, completing the energy level scheme outlined in Ref. [9], are presented in Fig. 1 and Table 1.

The comparison between the number of peaks of each transition on one hand, and the number of peaks predicted for the same transition by the multiplicity of the initial and final multiplets on the other hand, can give an idea about the number of non-equivalent Er^{3+} centers that manifest themselves in the transition. Assuming that only the lowest Stark level of $^4I_{15/2}$ is populated at 10 K, the number of peaks present in the spectrum of any GSA transition should be given – for each Er^{3+} center – by the multiplicity of the final level. This assumption is justified by the following: (i) the next lowest Stark level of $^4I_{15/2}$ being placed at least at 22 cm^{-1} [9], thus its population at 10 K being less than 4% of the population of the lowest Stark level; (ii) the absence of hot bands from the recorded spectra.

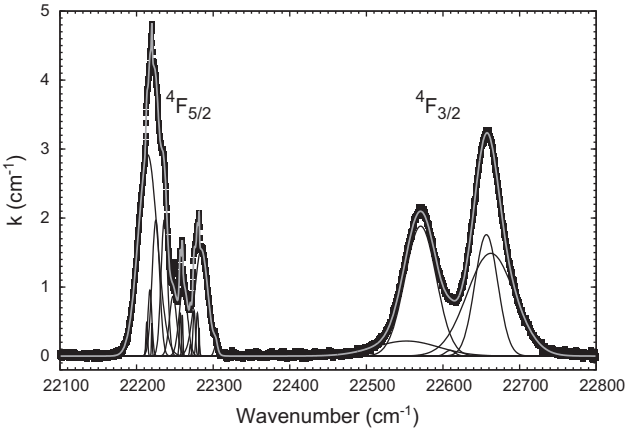

Fig. 1. Absorption spectrum of transition $^4I_{15/2}\rightarrow(^4F_{5/2},{}^4F_{3/2})$ at 10 K; black symbols: experimental data; gray line: sum of fitting functions; black line: Gaussian fitting functions.

For the $^4I_{15/2}\rightarrow{}^2H2_{11/2}$ transition, the presence of 11 peaks in its spectrum instead of 6 indicates – in the limits of our minimalistic approach – the presence of at least two non-equivalent Er^{3+} centers in CLNGG.

The absorption spectrum of transition $^4I_{15/2}\rightarrow{}^4F_{7/2}$ presents 10 Gaussian peaks instead of 4 (indicated by the multiplicity of $^4F_{7/2}$), which indicates the presence of at least three non-equivalent Er^{3+} centers in CLNGG.

The presence of 16 peaks instead of 3 in the spectrum of transition $^4I_{15/2}\rightarrow{}^4F_{5/2}$ (Fig. 1, left) indicates the presence of at least six non-equivalent Er^{3+} centers that contribute to this spectrum. To our knowledge, this is the greatest number of centers put into evidence in CLNGG up to now; a close number of five centers was found for Nd^{3+} in CLNGG [18,1]. The spectrum of $^4I_{15/2}\rightarrow{}^4F_{3/2}$ presents only 5 rather wide Gaussian peaks, thus sensing the presence of only three non-equivalent centers (Fig. 1, right).

Twelve Gaussian peaks could be separated in the spectrum of transition $^4I_{15/2}\rightarrow{}^2H2_{9/2}$, indicating the presence of at least three Er^{3+} centers in CLNGG, while the spectrum of transition $^4I_{15/2}\rightarrow{}^4G_{11/2}$ is clearly influenced by the presence of only two centers (it allowed the separation of 9 Gaussian peaks).

Finally, the spectrum of transition $^4I_{15/2}\rightarrow(^4G_{9/2},{}^2K_{15/2},{}^4G_{7/2})$ could be separated into 15 peaks (instead of 17); this transition could not be used to obtain information about the non-equivalent Er^{3+} centers in CLNGG due mainly to the difficulty of the separation of transitions between the Stark levels of the three thermalized manifolds.

At low temperatures, the transitions that are most likely to assure a good separation of the spectral lines belonging to different non-equivalent centers are those with a low multiplicity of the final level. However, the effects of the neighborhood of one center on its various transitions can be very different: the lines belonging to the same center can be different in intensity and linewidth for different transitions and also the splitting of each