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Excited state absorption and gain measurements in Cr doped LiNbGeO_5 and $\text{K}_3\text{Nb}_3\text{Si}_2\text{O}_{13}$ single crystals

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1. Introduction

Crystals doped with tetravalent chromium Cr^{4+} ions now motivate a great number of researches 1) from a fundamental point of view, since it is not quite sure that this kind of ions is the only one responsible for all the optical properties of the materials and, even if it was the case, because it is still difficult to describe quantitatively these properties within the framework of the existing models, 2) for their potential applications, since these crystals give rise to very interesting broad-band and high gain tunable solid-state lasers emitting in the near infrared domain and/or saturable absorbers for passive mode locking and Q switching.

Chromium doped LiNbGeO_5 (LNG) belongs to this kind of materials, and preliminary spectroscopic studies (absorption, emission, fluorescence lifetime as a function of temperature)[1] strongly indicate that tetravalent chromium substitutes in the crystal for Ge^{4+} ions in sites of quasi-tetrahedral symmetry and that it is responsible for most of the optical and laser properties of the system.

Here we report on complementary data such as excited-state absorption spectra in the visible as well as in the infrared domains and laser gain measurements. ESA spectra in the visible domain were recorded more particularly to try to locate one of the excited energy level (${}^3T_{1b}$) of the Cr^{4+} ion which does not appear, because it corresponds to a two-electron jump transition, in the regular ground state absorption spectrum.

We also report for the first time on a similar study made on another very interesting chromium doped crystal with formula $\text{K}_3\text{Nb}_3\text{Si}_2\text{O}_{13}$ (KNS).

2. Experimental results

The table 1 gives the observed and calculated mean transition energies of the ground state (GSA) and excited state (ESA) absorptions found in $\text{LiNbGeO}_5:\text{Cr}$. The assignments and the calculations are made by using the data of Ref. 1 and by assuming that the active center in this material is a Cr^{4+} ion in a tetrahedral environment and according to the following Racah and crystal field parameters:

$$Dq = 810 - 950 \text{ cm}^{-1}, B \approx 750 \text{ cm}^{-1}, C/B \approx 4.5$$

These results show that the triplet state ${}^3T_1(t_2^2)$ (or ${}^3T_{1b}$) should be located between about 22000 and 24000 cm^{-1} , a wavelength region ($\approx 450 \text{ nm}$) where there is no clear GSA bands. Correlatively they also predict a spin and electric

dipole allowed ESA transition ${}^3T_2 \rightarrow {}^3T_{1b}$ between about 13000 and 16000 cm^{-1} .

Figure 1 shows the results of a pump-probe experiment in which the system was excited by the pulsed radiation of a YAG:Nd laser at 1.06 μm (pulse of 15 ns duration) and ESA was probed with the aid of an externally triggered and adequately delayed xenon flash lamp with 5 μs pulse duration. I_p and I_u stand for the transmitted intensities of the probe light throughout the crystal when it is and it is not pumped, respectively. They are related to the GSA and ESA cross sections σ_{gsa} and σ_{esa} by the usual expression:

$$\ln(I_u/I_p) = (\sigma_{\text{esa}} - \sigma_{\text{gsa}}) N_1 d$$

where N_1 and d represent the excited state population density and the length of the crystal.

Figure 1 indicates the existence of a strong ESA band in the blue range which is probably due to a transition to a charge transfer state. It also indicates the existence of ESA bands around 700 - 900 nm since the observed features do not follow exactly the shapes of the GSA bands [1]. Thus, in this wavelength domain, GSA bleaching as well as ESA probably occur together.

A deconvolution of the ESA cross section σ_{esa} has been attempted then by assuming various values of N_1 . The most relevant results are shown in the figure 2. A strongly polarized ESA band appears clearly between about 600 and 900 nm (11000 - 16000 cm^{-1}), in a domain where it was actually expected.

Figures 3, 4 and 5 shows the luminescence properties of Cr doped $\text{K}_3\text{Nb}_3\text{Si}_2\text{O}_{13}$ (KNS). It is a uniaxial system that we have studied very recently. It belongs to the space group D_{3h}^4 and the lattice parameters are $a = 9.03$ Å and $c = 8.04$ Å. The absorption and emission spectra resemble very much those of Cr doped LNG and other systems in which Cr^{4+} can enter the lattice in sites of tetrahedral symmetry. Also, since the Si^{4+} ions in KNS site in environments of T_d symmetry, it is likely that the active center in KNS:Cr is again a Cr^{4+} replacing a Si^{4+} ion.

In the end we show in Figures 6a and 6b the room temperature gain cross section curves for LNG:Cr and KNS:Cr that we have obtained in a pump-probe experiment in which the pump beam was the same as above and the probe beam was that of the Raman shifted radiation (a hydrogen Raman cell is used) of a pulsed dye laser. These results indicate that LNG:Cr could be operated between 1.2 and 1.55 μm with a peak gain cross-section of about $0.8 \times 10^{-19} \text{ cm}^2$ whereas KNS:Cr could lase between 1.25 and 1.65 μm , but with a much lower gain cross section.

3. Conclusion

ESA measurements have been conducted on a Cr doped crystal LiNbGeO_5 in which the Cr ions were assumed to substitute, in a tetravalent state, for the tetrahedrally coordinated Ge^{4+} ions and the observed ESA bands, their positions as well as their intensities, strongly supported this interpretation. Subsequently the luminescence properties of a new Cr doped

crystal of formula $K_3Nb_3Si_2O_{13}$ have been studied and interpreted again in terms of Cr^{4+} ions in tetrahedral environments. In the end we have reported the laser gain characteristics of both systems and have shown the superior potentials of $LiNbGeO_5:Cr$ over $K_3Nb_3Si_2O_{13}:Cr$.

References

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Transition	Observed (cm ⁻¹)	Calculated (cm ⁻¹)
$^3A_2 \rightarrow ^3T_2 (t_2 e)$	8100 - 9100	8100 - 9100
$^3T_1 (t_2 e)$	11800 - 14600	13220 - 14630
$^1E (e^2)$	-	12380
$^3T_1 (t_2^2)$	-	22300 - 23900
$^3T_2 \rightarrow ^3T_1 (t_2^2)$	11000 - 16000	13000 - 16000

Table 1: Observed and calculated mean transition energies in $LiNbGeO_5:Cr^{4+}$

Figure 1: Polarized difference absorption spectra recorded in LNG:Cr after pulsed laser excitation at 1.06 μm

Figure 2: GSA and ESA cross section spectra of LNG:Cr for light polarized E//a, E//b and E//c

Figure 3: Room temperature polarized absorption spectra of $K_3Nb_3Si_2O_{13}:Cr$

Figure 4: Low temperature polarized emission spectra of $K_3Nb_3Si_2O_{13}:Cr$

Figure 5: Thermal variation of the infrared fluorescence lifetimes ($1/e$ time constants because of non-exponential decays) in KNS:Cr

Figure 6: Room temperature gain cross section curves of (a) LNG:Cr and (b) KNS:Cr