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Spectroscopy and laser action of Cr^{3+} , Nd^{3+} codoped crystal with Ca-Gallogermanate structure

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Energy transfer between Cr^{3+} and Nd^{3+} ions has been investigated in the 4.2K-300K temperature range by using steady-state and time-resolved laser spectroscopy. Nonradiative energy transfer has been studied from the time-resolved emission spectra and the donor fluorescence decays. The transfer efficiency was calculated as a function of temperature by using the Cr^{3+} lifetimes of the single doped and codoped samples.

Laser experiments were carried out in a diffusive cavity by pumping with Xenon flashlamps a codoped rod 54 mm long and 5 mm wide. The output laser spectrum was measured for different input energies above threshold. The laser spectral emission shows a complex structure which varies as a function of pump energy.

I. INTRODUCTION

Trigonal laser crystals with Ca-Gallogermanate structure ($\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ space group P321) have attracted attention because of their potential applications as laser hosts for transition-metal and lanthanide activators (1,2). In order to understand both the lasing properties of Nd^{3+} ions and the efficiency of the $\text{Cr}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer, a detailed spectroscopic study relating optical properties with characteristic features of the host crystal is required. In this work we present a detailed study of the energy transfer between Cr^{3+} and Nd^{3+} ions, in the 77K-300K temperature range, by using steady-state and time-resolved laser spectroscopy and the stimulated emission properties of Nd^{3+} ions pumped by flashlamps.

II. SPECTROSCOPIC RESULTS

a) Absorption and steady-state emission

Conventional absorption spectra at room temperature were recorded with a Cary 5 spectrophotometer for a codoped crystal with Cr^{3+} (0.3 at%) and Nd^{3+} (5 at%). Figure 1 includes this spectrum in the 300-900nm range which shows the narrow Nd^{3+} transition superimposed to the broad absorption bands of Cr^{3+} .

Figure 2 shows the steady-state emission spectrum obtained at 77K by exciting at 633nm into the $4\text{A}_2 \rightarrow 4\text{T}_2$ absorption band of Cr^{3+} . The fluorescence was analyzed with a 0.22m SPEX monochromator, and the signal was detected by a Hamamatsu R7102 extended IR photomultiplier and finally amplified by a standard lock-in technique. The presence of the Nd^{3+} fluorescence at 900nm ($4\text{F}_{3/2} \rightarrow 4\text{I}_{9/2}$) and at 1060nm ($4\text{F}_{3/2} \rightarrow 4\text{I}_{11/2}$) shows that energy transfer from Cr^{3+} to Nd^{3+} occurs, because only Cr^{3+} ions are excited at 633nm.

b) Time-resolved measurements

Time-resolved measurements were performed with a tunable dye laser (1ns pulse width), pumped by a pulsed nitrogen laser, and the emission detected with a Hamamatsu R7102 photomultiplier. The data were processed by a EGG-PAR boxcar integrator.

The decays of Cr^{3+} emission in a single doped crystal and in the codoped crystal were performed with a tunable dye laser (1ns pulse width), exciting the samples at the $^4\text{A}_2 \rightarrow ^4\text{T}_2$ absorption band and collecting the luminescence at 990nm, as a function of temperature. The decrease in the lifetime of Cr^{3+} in the presence of Nd^{3+} indicates nonradiative $\text{Cr}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer. The kinetics of the nonradiative Cr^{3+} to Nd^{3+} energy transfer can be understood within the Foster-Dexter's theory with a dipole-dipole interaction mechanism (3). The obtained value for the critical transfer distance for dipole-dipole interaction was 5.9Å. The transfer efficiency was estimated according to the expression $\eta = 1 - \tau/\tau_0$ with τ and τ_0 being the Cr^{3+} mean decay times with and without Nd^{3+} ions. Figure 3 shows the transfer efficiency as a function of temperature. As can be seen the transfer efficiency slightly increases with temperature.

The time-resolved emission spectra were obtained exciting the codoped sample at the $^4\text{A}_2 \rightarrow ^4\text{T}_2$ absorption band (650nm) and collecting the luminescence at different time delays after the laser pulse. Figure 4 shows these spectra at 77K which are vertically shifted and scaled to have a similar height. These spectra show superimposed to the Cr^{3+} emission, the Nd^{3+} emissions. These results show that even at quite a short time, nonradiative energy transfer occurs. As time increases there is a decrease of the Cr^{3+} emission, due to the faster decay of Cr^{3+} ions.

Fig.1.- Room-temperature absorption spectrum.

Fig.2.- Steady-state emission spectrum obtained at 77K.

Fig. 3.- Transfer efficiency as a function of temperature

Fig. 4.- Time-resolved emission spectra.

III. FLASH-LAMP PUMPED LASER EXPERIMENTS

Laser experiments were carried out with a 5 mm diameter and 54 mm long rod, of the codoped crystal. The pumping device was a laboratory made compact diffusive reflecting cavity with two Xenon flash-lamps. Experiments with a one meter confocal resonator with high reflecting mirrors show a low threshold input energy, about 5 Joules in condenser, and a good optical quality of the crystal.

Laser action was also achieved, using a one meter resonator with a 4 m radius concave high reflector and a flat 90% reflectivity output coupler. Threshold input discharge energy was 20 Joules and the maximal output laser energy was more than 50 mJ with a slope efficiency of 0.15% as is shown in Figure 5.

The spectrum of the laser output was recorded for several pumping energies, by using a 0.25 m Jovin-Yvon monochromator with variable slits and a Hamamatsu extended IR photomultiplier (resolution was 0.1 nm). At each selected wavelength an average of 24 pulses was made. The resulting energy as a function of the emission wavelength is shown in Fig. 6 for three different input energies. The center of the spectrum hardly changes, but the width increases assymetrically with the pump energy if this one is close to the threshold level, and it remains roughly constant for greater pump energies as it is shown in Figure 6. The structure of these spectra can be related to the existence of several different broad site distributions for Nd^{3+} in this matrix.

In order to explain this spectral behaviour qualitatively, a simple four level spectral rate-equation laser model has been developed. The existence of two kinds of populations with a different emission spectrum, each of them with a homogeneous spectral broadening was assumed; so the rate equations are:

$$\frac{dn_1}{dt} = W_1 - n_1 \left[A_1(\lambda) d\lambda - n_1 \int B_1(\lambda) \Phi(\lambda) d\lambda \right]; \quad \frac{dn_2}{dt} = W_2 - n_2 \left[A_2(\lambda) d\lambda - n_2 \int B_2(\lambda) \Phi(\lambda) d\lambda \right]$$

$$\frac{d\Phi(\lambda)}{dt} = \gamma [n_1 A_1(\lambda) + n_2 A_2(\lambda)] + \Phi(\lambda) [n_1 B_1(\lambda) + n_2 B_2(\lambda)] - K \Phi(\lambda)$$

where t is the time, n_1 and n_2 are the population inversion for populations 1 and 2, W_1 and W_2 are the respective pumping rates, assumed to be proportional to the respective concentrations, $\Phi(\lambda)$ is the spectral photon density being λ the optical wavelength, K is cavity losses rate, γ a factor that encloses the quantum yield and the axial emission ratio of the spontaneous emission, whose coefficients are $A_1(\lambda)$ and $A_2(\lambda)$ for both populations, $B_1(\lambda)$ and $B_2(\lambda)$ are the stimulated emission coefficients, proportional to $A_1(\lambda)$ and $A_2(\lambda)$ respectively.

For the calculations we have used a rectangular pump function of a duration similar to the experimental flash-lamp pulses (about 100 μs). The functions $A(\lambda)$, $B(\lambda)$ are assumed to be gaussians with the same halfwidth $\delta\lambda$, but centered at different wavelengths λ_1 and λ_2 , being the spectral separation between centers of the spectra $\Delta\lambda = \lambda_1 - \lambda_2$.

In some conditions it is possible to obtain from this simple model and for different input energies, a spectral behaviour which is similar to the experimental results of Fig. 6. as is shown in Fig. 7. For low pump energies only the more efficient (and/or concentrated) of the populations is able to lase and as the pump rate becomes greater, the effect of overlapping between both emission spectra enlarges the output laser spectrum towards the emission spectrum of the other population.

This fit is only possible in some conditions; first, both populations must have different concentrations and/or spontaneous emission decay rates; on the other hand the spectral separation $\Delta\lambda$ between both spectra centers must be about 1.5 times the halfwidth $\delta\lambda$ of each spectrum. For less separated spectra centers, this enlargement is too weak or does not exist at these levels of pump energy; with a larger separation the output laser spectrum tends to have two peaks.

The ratio between experimental halfwidths of the emission spectrum around 1.06 μm (Fig. 2) and laser spectrum (Fig.6) is about 20:1, which is close to the ratio obtained from the theoretical model (Fig. 7).

Fig. 5.-Laser output energy as a function of the input energy.

Fig. 6.- Experimental laser output spectra for energy inputs: a) 1.1 times the threshold input energy. b) 1.5 times. c) 2.2 times.

Fig. 7: Laser output spectra obtained from the laser model spectral rate equations. Population 1 has a concentration and a spontaneous emission decay rate twice and 1.3 times respectively than population 2. $\Delta\lambda = 1.5 \delta\lambda$, $K = 1.5 \times 10^8 \text{ s}^{-1}$. a) Input energy 1.6 times the threshold level. b) 2.3 times.

IV. CONCLUSIONS

Nonradiative energy transfer has been demonstrated from the steady-state and time resolved emission spectra and the donor fluorescence decays. Transfer efficiencies were calculated as a function of temperature by using the Cr^{3+} lifetimes of the single doped and codoped samples. The Cr^{3+} decay intensity of the codoped sample is consistent with a dipole-dipole transfer process.

Laser experiments have been carried out in a diffusive cavity pumped by Xenon flash-lamps. Laser output spectra were measured for three different pump energy inputs, showing a behaviour related to the existence of several different broad site distributions for Nd^{3+} in this matrix. A simple four level spectral rate-equation laser model can give a qualitative explanation of this behaviour.

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