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## MATERIALS FOR IR TUNABLE LASER APPLICATIONS AND NON RADIATIVE DECAY PROCESSES

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**Abstract :** The optical spectroscopy of the new material for IR tunable laser applications  $\text{MgAl}_2\text{O}_4 : \text{Ni}^{2+}$  is presented. A comparison with well-known fluoride materials is made for IR fluorescent lifetimes and quantum efficiencies. For  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  doped fluorides, limitations of concentrations in doping ions are established. Multiphonon processes are studied with a single frequency model and a good agreement is found. It is shown that the "effective phonon frequency" is closer to mean frequency of the density of states curves than to their maximum and the electron-phonon coupling factors appears to vary with doping concentration.

**1. Introduction :** For several years  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  doped systems have been studied for IR tunable solid state laser applications. The greater part of the works concerns materials only with a well defined doping ion concentration, and the behaviour of radiative and non radiative transitions is rarely investigated in comparison with the I.R. laser emission, although lattice vibrations have opposite roles in the frequency tunability and emission intensity.

In this study we have examined a few well-known laser materials as  $\text{Mg F}_2 : \text{Ni}^{2+}$ ;  $\text{Mg F}_2 : \text{Co}^{2+}$ ;  $\text{K Zn F}_3 : \text{Ni}^{2+}$ ;  $\text{K Zn F}_3 : \text{Co}^{2+}$  and a new compound for IR tunable laser:  $\text{Mg Al}_2\text{O}_4 : \text{Ni}^{2+}$ . Informations are obtained concerning temperature and concentration limitations but also on non radiative transitions.

## 2. Results

### 2.1 Quantum efficiencies and ions concentration

Absorption and luminescence spectra of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  doped fluorides are consistent with preceding works [1] [2] [3] [4] [5] [6] [7]. For  $\text{Mg Al}_2\text{O}_4 : \text{Ni}^{2+}$  absorption and emission spectra are given in fig. 1. The absorption spectrum of  $\text{Mg Al}_2\text{O}_4 : \text{Ni}^{2+}$  is similar to the absorption spectra of  $\text{Ni}^{2+}$  ions in octahedral sites in other materials [8] [6] [7] and is not consistent with the spectrum of  $\text{Ni}^{2+}$  ions in tetrahedral sites [9]. As in the case of  $\text{Mg O} : \text{Ni}^{2+}$  [10] and  $\text{Li Ga}_5\text{O}_8 : \text{Ni}^{2+}$  [8], the absorption spectrum of  $\text{Mg Al}_2\text{O}_4 : \text{Ni}^{2+}$  is dominated by three spin-allowed broad band transitions. These are  ${}^3\text{A}_2(3\text{F}) \rightarrow {}^3\text{T}_1(3\text{P})$  in the deep blue,  ${}^3\text{A}_2(3\text{F}) \rightarrow {}^3\text{T}_1(3\text{F})$  in the red and  ${}^3\text{A}_2(3\text{F}) \rightarrow {}^3\text{T}_2(3\text{F})$  in the near infra-red. The relative positions of these three bands allow one to evaluate the crystal field parameter  $\text{Dq/B}$  by comparison with the Tanabe and Sugano's diagram for  $\text{Ni}^{2+}$  ion in octahedral site [11]. We find for  $\text{Mg Al}_2\text{O}_4 : \text{Ni}^{2+}$  a  $\text{Dq/B}$  ratio equal to 1.29, greater than in  $\text{Mg O} : \text{Ni}^{2+}$  ( $\text{Dq/B} = 1.11$  [10]) and  $\text{Li Ga}_5\text{O}_8 : \text{Ni}$  ( $\text{Dq/B} = 1.085$  [8]).

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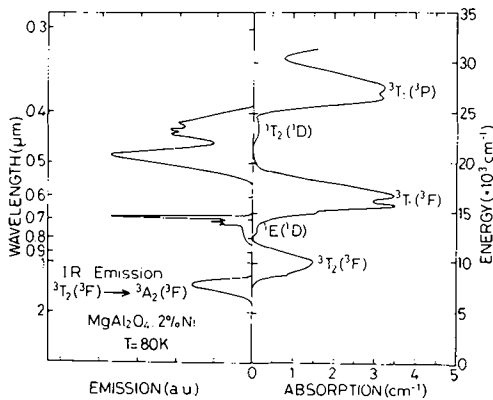


Fig. 1 : Absorption and emission spectra of  $\text{MgAl}_2\text{O}_4 : \text{Ni}^{2+}$  at 80 K.

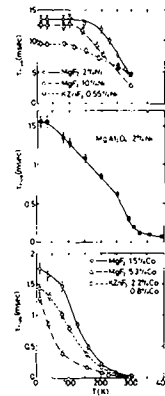


Fig. 2 : Temperature dependence of IR fluorescence lifetimes in  $\text{Ni}^{2+}$  and  $\text{Co}^{3+}$  doped matrices.

The IR emission of interest for possible laser operation and which is attributed to the vibronic transition  $3T_2(3F) \rightarrow 3A_2(3F)$ , extends from 1.1 to 1.5  $\mu\text{m}$  with a peak at about 1.26  $\mu\text{m}$ . No clear structure is observed in the IR emission shape. This is opposite to  $\text{MgO} : \text{Ni}^{2+}$  [12] [10] and  $\text{MgF}_2 : \text{Ni}^{2+}$  [2] for which sharp zero-phonon lines are observed at low temperature as well as structure in the vibrational sidebands. This confirms that the electron-phonon coupling is very strong in  $\text{MgAl}_2\text{O}_4 : \text{Ni}^{2+}$ .

The decrease in IR lifetimes with temperature found in  $\text{MgAl}_2\text{O}_4 : \text{Ni}^{2+}$ ,  $\text{MgF}_2 : \text{Co}^{2+}$  and  $\text{KZnF}_3 : \text{Co}^{2+}$  indicates that non radiative deexcitation processes are important even at low temperatures in these materials (Fig. 2). This hypothesis is strengthened by measuring the quantum efficiencies of the IR transitions at room temperature with an integrating sphere and by comparing the materials to each other as given in table I. Now if one looks at fig. 2 when nickel concentration is increased from 2 % to 10 % in  $\text{MgF}_2$  then the IR lifetime, at 80 K for instance, is reduced by 7.5 %. In  $\text{MgF}_2 : \text{Co}^{2+}$ , a cobalt concentration increase from 1.5 % to 5.3 % induces an IR lifetime variation of 72 % at 80 K. In contrast when cobalt concentration in  $\text{KZnF}_3$  increases from .8 to 2.2 %, the IR lifetime remains unchanged at any temperature. As for  $\text{MgAl}_2\text{O}_4 : \text{Ni}^{2+}$ , only one sample was studied. From these experimental facts, it is concluded that  $\text{MgF}_2 : \text{Ni}^{2+}$  laser crystal may be used with higher nickel concentration ( $\approx 5\%$ ), at 80 K, than usually considered [12] without having an important self-quenching. However in  $\text{KZnF}_3 : \text{Co}^{2+}$  and in  $\text{MgF}_2 : \text{Co}^{2+}$ , cobalt concentration has to be weaker than 2 % otherwise non radiative effects are dominating.

## 2.2 Multiphonon processes

For each compounds, the non radiative decay rate ( $W_{nr}$ ) has been determined as a function of temperature by  $W_{nr} = 1/\tau_F(T) - 1/\tau_0$  where  $\tau_F(T)$  is the total IR fluorescence lifetime at temperature T and  $\tau_0$  is the radiative lifetime.  $\tau_0$  is obtained by measuring the IR quantum efficiency at room temperature as above mentioned.  $\tau_0$  has been verified to be temperature independent since integrated absorption of the vibronic absorption is about constant with temperature : vibronic bands do not contain vibration forced electric-dipole transitions. On the

Compound	T(ms) 80 K	$\tau$ (ms)	$\eta$	$n$ 300 K	$W_{nr}(0)$ sec <sup>-1</sup>	$M_{nr}$ (cm <sup>-1</sup> )	N	S
MgF <sub>2</sub> : Ni <sup>2+</sup>	2%	13.5	14	0.965	0.5	2.7	325	20
	10%	12.5	14	0.895	0.35	8.8	325	20
KZnF <sub>3</sub> : Ni <sup>2+</sup>	0.55%	9.5	10	0.95	0.45	5.3	229	28
MgAl <sub>2</sub> O <sub>4</sub> : Ni <sup>2+</sup>	2%	1.35	13.5	0.1	0.02	571.4	409	21
MgF <sub>2</sub> : Co <sup>2+</sup>	1.5%	1.45	5	0.29	8x10 <sup>-3</sup>	320	270	20
	5.3%	0.4	5	0.08	4x10 <sup>-3</sup>	530	200	27
KZnF <sub>3</sub> : Co <sup>2+</sup>	0.82%	1	3.25	0.31	9x10 <sup>-3</sup>	400	230	23
	7.2%	1	3.25	0.31	9x10 <sup>-3</sup>	400	230	23

Table I : Infrared lifetimes, quantum efficiencies and parameters of the non radiative multiphonon processes for the various studied materials.

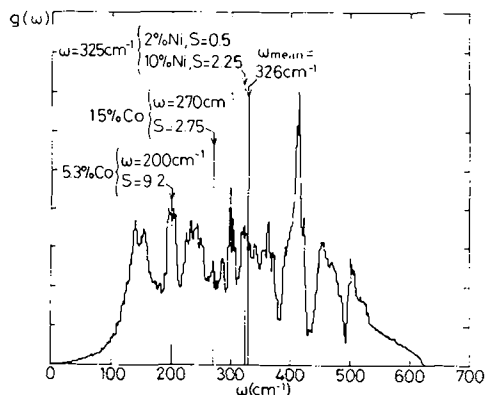


Fig. 3 : Phonon density of states  $g(\omega)$  for Mg F<sub>2</sub>, from [15]. Energies and coupling factors of the phonon modes for multiphonon non-radiative desexcitation of Ni<sup>2+</sup> and Co<sup>2+</sup>.

basis of a single frequency ( $\omega$ ) model, the transition probability thermal behaviour for multiphonon non radiative desexcitation can be written [13] :

$$W_{nr}(t) = W_{nr}(0) \exp[-2 n S_0] N! S_0^{-N} \left\{ \frac{(n+1)}{n} \right\}^{N/2} \times I_N[2S_0 \sqrt{n(n+1)}] \quad (1)$$

where  $S_0$  is Huang-Rhys parameter,  $W_{nr}(0)$  the probability at 0K.  $I_N$  is the modified Bessel function and  $n = \left[ \exp\left(\frac{h\nu}{kT}\right) - 1 \right]^{-1}$ . The number of phonons involved is  $N$  where  $N h \omega = \Delta E$ ,  $\Delta E$  is the energy gap, namely the energy difference between the lowest spin-orbit level in the first excited state and the highest spin-orbit level in the fundamental state. There is always a good agreement between the theoretical curves and the measured values of decay rates. Phonon energies determined in this way, correspond to maxima of the phonon states density curves for Mg F<sub>2</sub> matrices. For all materials studied here, the number of phonons involved in the non radiative processes is between 20 and 30 with energies varying from 200 to 400 cm<sup>-1</sup> with very various coupling factors (Table I). In spite of these fluctuations these parameters are similar to ones given in other works (Mg O : Ni<sup>2+</sup>,  $h\nu = 308$  cm<sup>-1</sup>,  $N = 26$  [10] ; LiGa<sub>5</sub>O<sub>8</sub> : Ni<sup>2+</sup>,  $h\nu = 250$  cm<sup>-1</sup>,  $N = 25$  [8]).

It must be noted in fig. 3 that phonon energies for non radiative multiphonon processes remain near average lattice energy.

In Mg Al<sub>2</sub>O<sub>4</sub> : Ni<sup>2+</sup> we have not at hand any states density curves but the value (409 cm<sup>-1</sup>)<sup>4</sup> is no doubt much lower than the cut-off frequency in an oxyde (usually 600 cm<sup>-1</sup>).

Another important fact has to be noticed ; it is the apparent variation of the coupling factor  $S$ , as a function of concentration. This effect of concentration sensitive electron-phonon coupling was already noticed for radiative transitions [14]. However, for radiative transitions, it is difficult to avoid completely any reabsorption on the o-phonon line at higher concentration and coupling parameter determined from side bands to o-phonon intensity may contain some errors. Here for the first time an analogous phenomena is observed in a inorganic material directly for non-radiative transitions so without such uncertainty.

### 3. Conclusion

Luminescent and absorption experiments have been carried out on many  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  doped systems. Among these materials,  $\text{Mg Al}_2\text{O}_4 : \text{Ni}^{2+}$  is a new compound for tunable laser applications. Unfortunately non radiative desexcitation processes in  $\text{Mg Al}_2\text{O}_4 : \text{Ni}^{2+}$  are dominating even at low temperature ( $\eta = 10\%$ ,  $W_{nr}(0) = 570 \text{ sec}^{-1}$  at 80 K) which will reduce considerably the laser capabilities of this material. So, though being of interest for the wavelength domain covered by its infrared emission ( $1.1 \mu\text{m} < \lambda < 1.5 \mu\text{m}$ ),  $\text{Mg Al}_2\text{O}_4 : \text{Ni}^{2+}$  does not seem in the long run to be a very good laser candidate.

The IR fluorescence lifetime self-quenching allowed us to define concentration limits for nickel ( $\approx 5\%$ ) and cobalt ( $\approx 1\%$  to  $2\%$ ) in  $\text{Mg F}_2$  and  $\text{K Zn F}_3$ . Beyond these limits the quality of the laser emission will be certainly compromised.

The dependence of the electron-phonon coupling as function of the concentration is not quite understood, actually this effect and its origins and consequences are under investigation. As in [14] this phenomena should be considered as a new self-quenching process to be taken into account when direct resonant or phonon assisted energy transfers cross relaxation do not exist. However from [14] the absolute value of  $W_{nr}(T)$  should increase much more than it is observed when the S coupling factor increases even slightly because a factor  $S_0^N$  is hidden in  $W_{nr}(0)$ .

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