



## DE-EXCITATION MECHANISMS OF THE $^3T_2$ EXCITED STATE IN $BaLiF_3 : Ni^{2+}$ CRYSTALS

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**Abstract**— $BaLiF_3$  crystals doped with transition metal ions are potential new laser active media. These crystals present an 'inverse' perovskite structure where the  $Ni^{2+}$  ions are located in octahedral sites. In this work, the temperature dependence of the fluorescence lifetime of nickel ions in the fluoperovskite  $BaLiF_3$  is reported. The lifetime at low temperatures is constant, dropping slowly above 240 K. From the experimental data, the radiative decay time ( $\tau = 4.8(1)$  ms), the temperature independent nonradiative decay time (0, 014(4) ms), and the thermal quenching activation energy ( $\Delta E = 1270(64)$   $cm^{-1}$ ) are determined. Excellent agreement with the Mott model is then demonstrated by using these parameters. © 1997 Elsevier Science Ltd. All rights reserved

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### 1. INTRODUCTION

In the last few years, a great interest in crystals doped with transition metal ions as laser active media has been regained. These ions, due to their vibronic characteristic of emission in the near infrared region, are potentially tunable laser media over a range of hundreds of nanometers. Particularly, the  $Ni^{2+}$  ion has been extensively studied in several host crystals [1-5], mostly because of the existence of an emission in the near infrared, due to the transition between the lower excited state level  $^3T_{2g}$  and the ground state  $^3A_{2g}$ .

In this work, the de-excitation mechanisms from the  $^3T_2$  state of  $Ni^{2+}$  ions in  $BaLiF_3$  crystals showing a luminescent emission band centered at 1500 nm are discussed. The  $BaLiF_3$  crystal is a new host that combines several interesting properties. For example, it exhibits a good chemical stability [6], allows an easy incorporation of nickel ions substitutionally on the crystal structure and presents a large band gap.  $BaLiF_3$  crystals are an 'inverse' perovskite with cubic structure (space group  $O_h^1$ -Pm3m) where the monovalent ion  $Li^+$  is at the center of six  $F^-$  octahedrons, whereas the  $Ba^{2+}$  divalent ions are in the 12-fold environment site, resulting in a different crystal field interaction from the classic perovskite structure

[7, 8]. The three main absorption bands of the  $BaLiF_3 : Ni^{2+}$  crystals are centered at 390 nm, 700 nm and 1180 nm at room temperature, which correspond to transitions between the ground state  $^3A_{2g}$  and the multiplets  $^3T_{1g}^b$ ,  $^3T_{1g}^a$ ,  $^3T_{2g}$ , respectively. Pumping the near infrared absorption band at 1180 nm with the 1064 nm laser line of a Nd:YAG laser, a broad and intense emission band is observed in the near infrared, centered at 1500 nm (300 nm of bandwidth). By pumping the 700 nm band ( $^3A_{2g} \Rightarrow ^3T_{1g}^a$ ) with the Krypton ion laser line (647 nm), the same emission band was observed [9].

Investigating the de-excitation mechanisms is crucial to understanding and establishing the spectroscopic conditions for the laser operation of the system. For this reason, the temperature dependence of the decay time and luminescent emission intensity were determined for several  $Ni^{2+}$  ion concentrations in the  $BaLiF_3$  host.

### 2. EXPERIMENTAL

The  $BaLiF_3 : Ni^{2+}$  samples were grown by the Czochralski technique [10] at our laboratories, with nickel concentrations determined by X-ray fluorescence; samples with 0.15, 0.30, 1.0 and 2.5 mol%, in the boule, were obtained. The accuracy in the determination of these concentrations is 2%. Conventional optical spectroscopy methods were used in this work and are briefly described here. For the decay time and luminescent intensity studies, the  $^3T_{1g}^a$  level of the

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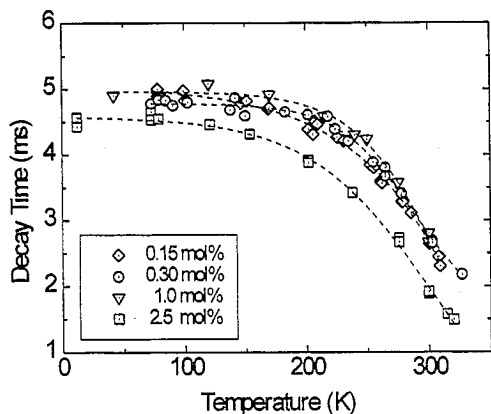


Fig. 1. Luminescent decay time dependence on the temperature for  $\text{Ni}^{2+}$  ions in  $\text{BaLiF}_3$ . Line: fitted by eqn (4) (see text).

$\text{Ni}^{2+}$  ion was excited, with the 647 nm Krypton ion laser line (Coherent—model Innova 400). The laser beam was focused into the chopper blade in such way that the beam rise time was shorter than  $10 \mu\text{s}$ , with a duration of approximately 1 ms and a period of 12 ms. The samples were placed in a cryostat (Displex Cs-200—Air Products) that allows operation in the range from 10 to 300 K. The excitation and detection directions were taken in a perpendicular geometry in order to reduce the influence of the scattered light from the incident beam. For the decay time and emission intensity measurements in the infrared region, a Germanium detector ( $50 \mu\text{s}$  response time) was used; the signal was stored in a Boxcar PAR 4420 integrator and analysed by a signal processor PAR 4402.

### 3. RESULTS AND DISCUSSION

For a simple process of nonradiative decay, the temperature dependence of the luminescent decay time  $\tau$  of an ion in a crystal is given by [11]:

$$\frac{1}{\tau(T)} = \frac{1}{\tau_R(T)} + \frac{1}{\tau_{NR}(T)} \quad (1)$$

where  $\tau_R(T)$  is the radiative decay time and  $\tau_{NR}(T)$  is the nonradiative decay time of the luminescent ion. Generally, for the transition metal ion  $\text{Ni}^{2+}$ , the nonradiative processes result in multiphonon emission from the excited vibrational states of the  ${}^3\text{T}_2$  level to the highly excited vibrational states of the ground state level  ${}^3\text{A}_2$  [12]. The temperature dependence of the nonradiative decay time, in the Mott model [11], can be described by a single Arrhenius factor related to the occupation probability of the electrons in the vibrational excited state, given by:

$$\frac{1}{\tau_{NR}(T)} = \frac{1}{\tau_{NR}^0} \exp(-\Delta E/KT) \quad (2)$$

where  $K$  is the Boltzmann constant and  $\Delta E$  is the

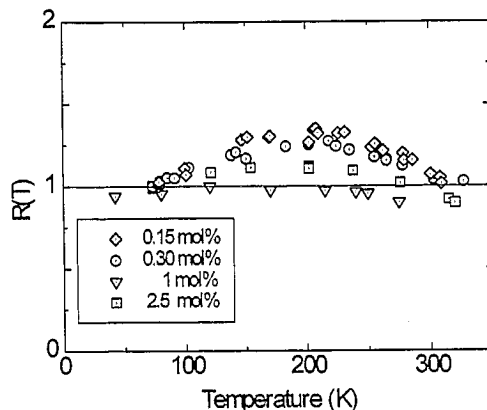


Fig. 2. Measured temperature dependence of  $R(T)$ , the ratio of the relative fluorescence lifetime, to the relative total fluorescence intensity (eqn (3)) (see text).

activation energy, that is, the energy difference between the ground state of the  ${}^3\text{T}_2$  level and the crossover of the potential energy surfaces of the levels  ${}^3\text{A}_2$  and  ${}^3\text{T}_2$ . Assuming that the decay is exponential and the optical absorption intensity is independent of temperature (considering pumping at 647 nm and a temperature change from RT to 10 K, the decrease in the optical absorption was only 5%), the integrated luminescent intensity  $I(T)$  is given by [13]:

$$I(T) = I_0 \frac{\tau(T)}{\tau_R(T)} \quad (3)$$

where  $I_0$  is the beam intensity incident on the sample.

Thus, the ratio  $R(T)$  of the relative decay time,  $\tau(T)/\tau(0)$ , to the relative intensity,  $I(T)/I(0)$ , is given by:

$$R(T) = \frac{\tau(T)/\tau(0)}{I(T)/I(0)} = \frac{\tau_R(T)}{\tau_R(0)} \quad (4)$$

The ratio  $R(T)$  allows one to determine the influence of the temperature on the radiative decay. Experimentally, if the ratio  $R(T)$  is temperature independent (and thereafter  $\tau_R(T)$  is also independent) then the decrease of decay time with the temperature can be attributed to nonradiative processes. Experimentally, the ratio  $R(T)$  can be determined and the temperature dependence of the decay time curves can be fitted as a convenient Arrhenius function. In  $\text{BaLiF}_3 : \text{Ni}^{2+}$ , the ratio  $R(T)$  obtained is temperature independent (within a range of 20% of variation that can be explained as an experimental error). Thus, with the eqns (1) and (2), the decay time can be given by [11]:

$$\tau(T) = \frac{\tau_R}{1 + \frac{\tau_R}{\tau_{NR}^0} \exp(-\Delta E/KT)} \quad (5)$$

Figure 1 presents the decay time curves, fitted by

Table 1. Parameters giving the temperature dependence of the fluorescence lifetime of Ni<sup>2+</sup> in BaLiF<sub>3</sub>, shown in Fig. 3

C(mol%)	$\tau[RT](\text{ms})$	$\tau_R(\text{ms})$	$\tau_{NR}^0(\text{ms})$	$\Delta E(\text{cm}^{-1})$
0.15	2.76 (5)	5.0 (1)	0.025 (5)	1150 (50)
0.30	2.88 (5)	4.8 (1)	0.010 (3)	1370 (60)
1.0	2.68 (5)	5.0 (1)	0.008 (3)	1390 (80)
2.5	2.09 (5)	4.5 (1)	0.013 (3)	1170 (40)

eqn (5) and the ratio  $R(T)$  (eqn (4)) is shown in Fig. 2, both for several concentrations of Ni<sup>2+</sup> in BaLiF<sub>3</sub>. Table 1 shows the parameters obtained by theoretical fit (Mott model) for crystals with different concentrations.

As described in the experimental section, indirect excitation of the <sup>3</sup>T<sub>2</sub> level was used for the decay time studies by exciting the <sup>3</sup>T<sub>1g</sub> level with the 647 nm Krypton ion laser line. The temporal behavior of the luminescence intensity observed when excited by the modulated krypton laser presents a single exponential decay, indicating only one decay process (Fig. 3), with a decay time  $2.8 \pm 0.2$  ms. By pumping the crystal with the 1064 nm line of a Nd:YAG laser, the same decay time was observed ( $\tau = 3.0 \pm 0.2$  ms) [9].

This long radiative decay time is expected, assuming that the transition from the <sup>3</sup>T<sub>2</sub> is not allowed by electric dipole mechanisms. In Fig. 1, one can observe that the luminescent decay time begins to decrease at the same temperature (240 K) for several concentrations, except for the sample with 2.5 mol%. This shows that the nonradiative de-excitation mechanism has an activation temperature independent of the nickel ions concentration up to 1 mol%, which is confirmed by the activation energies ( $\Delta E$ ) presented in Table 1. The average activation energy is  $1270 \text{ cm}^{-1}$ ,

with an uncertainty of  $120 \text{ cm}^{-1}$ . This is the potential barrier energy for one electron to change from the excited <sup>3</sup>T<sub>2g</sub> to the ground electronic (highly excited vibronic) <sup>3</sup>A<sub>2g</sub> state, and it is essentially the energy difference between the relaxed excited state (<sup>3</sup>T<sub>2g</sub>) in the first vibronic level, to the highly vibronic level of the ground state (<sup>3</sup>A<sub>2g</sub>) at the crossing point of the two levels. As the phonon density of states energy peaks at  $509 \text{ cm}^{-1}$  [14], at least three phonon modes are necessary to overcome the potential barrier and allow for nonradiative decay. In this simple model, one would expect a fast onset of the nonradiative transitions with the temperature. This apparent contradiction can be explained by group theory. The crystal phonon symmetry is a subgroup of the lattice vibrational modes. For the BaLiF<sub>3</sub> crystal (cubic symmetry), the allowed even vibrational modes are  $A_{1g}$ ,  $E_g$  and  $T_{2g}$ , and the allowed odd modes are  $T_{1u}$ ,  $T_{1u}$  and  $T_{2u}$  [15]. Since the symmetry of both states involved in the transition is even (<sup>3</sup>T<sub>2g</sub> and <sup>3</sup>A<sub>2g</sub>), the odd modes are disregarded as promoting modes for the nonradiative transitions. Multiplying the irreducible representation of the <sup>3</sup>T<sub>2g</sub> by the vibrational modes representation  $A_{1g}$ ,  $E_g$  and  $T_{2g}$ , one can determine that none of these vibrational modes may act as a promoting mode for the <sup>3</sup>T<sub>2g</sub> → <sup>3</sup>A<sub>2g</sub> transition.

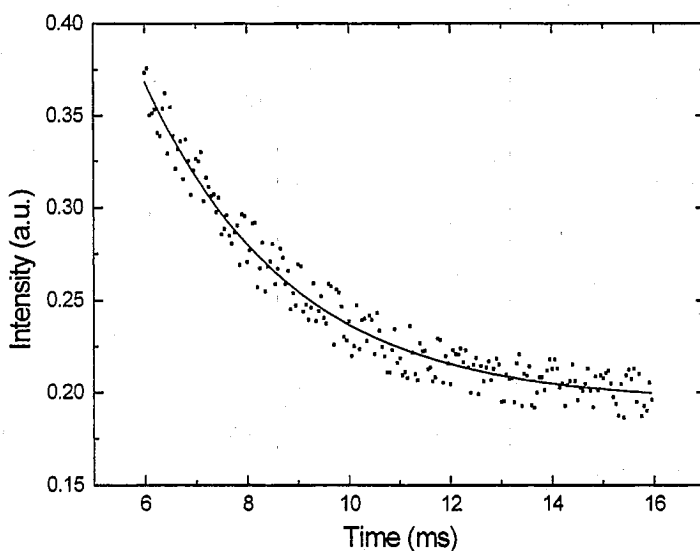


Fig. 3. Temporal behavior of the luminescence intensity when excited by a modulated Kr<sup>+</sup> ion laser operating at 647 nm. The solid line is the fit of an exponential decay with a constant of 2.8 ms (0.2 ms).

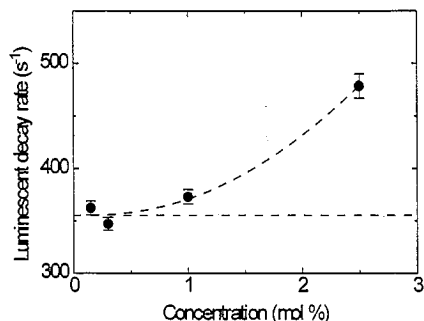


Fig. 4. Luminescent decay rate vs concentration of  $\text{Ni}^{2+}$  in  $\text{BaLiF}_3$  at room temperature.

Therefore, a nonradiative multiphonon process transition is very unlikely, according to the experimental observations of a very gradual onset of nonradiative transitions.

It should be noted that there is a slight dependence of the decay time on the temperature. At room temperature, the decay time is about two times shorter than at low temperature, showing that the temperature dependence of this deexcitation mechanism is very weak. Therefore, the room temperature luminescence quantum efficiency is reduced by approximately a factor two and this is not a determining factor in the laser optical cycle.

#### 4. CONCENTRATION QUENCHING

As can be seen by Fig. 1, the decay time behaviour of the 2.5 mol%  $\text{Ni}^{2+} : \text{BaLiF}_3$  is quite different from the other ones. Even at low temperatures, there is a temperature independent reduction of the decay time, showing that nonradiative processes due to concentration effects are already present. In order to determine the effects of the concentration on the decay time, the transition probabilities  $\tau^{-1}[RT]$  are plotted as a function of concentration (Fig. 4). We can see that the 1 mol% is within the limit of the initiation of transfer processes. In general, the decay time of the metastable level does not depend on the Ni concentration. The concentration quenching mechanism can be related to energy transfer and cross relaxation processes between ion pairs, most probably involving the intermediary fluorine ions [2].

#### 5. CONCLUSION

The decrease of the luminescent decay time of  $\text{Ni}^{2+}$  ions in the  $^3\text{T}_2$  state in  $\text{BaLiF}_3$ , as a function of the temperature, for all concentrations, is due to a non-

radiative deexcitation mechanism that can be fitted by the Mott model. Therefore, based on this model, we conclude that there is an activation energy of about  $1270(64)\text{cm}^{-1}$ . This nonradiative mechanism is a result of the multiphonon process from the excited vibrational state of the  $^3\text{T}_{2g}$  level to the highly excited vibrational state of the ground state  $^3\text{A}_2$ . In spite of the low activation energy (amounting to less than three phonons) involved in the non radioactive process, none of the active modes of the  $\text{BaLiF}_3$  are promoting modes for this process, as shown by the slowly varying temperature dependence of the decay time.

The decrease in the luminescence quantum efficiency to 50% at room temperature is not a determinant factor for laser action in this material. We have also observed a reduction of this radiative decay time with the nickel concentration, probably due to intercentre energy transfer, which is clearly seen in the highest concentration sample. Therefore, there is an indication that the best concentration for laser purpose samples should be up to 1 mol%.

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