$BaLiF_3$:Ni^{2+}
SPECTROSCOPIC ANALYSIS OF LASER CAPABILITIES

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$BaLiF_3$:Ni^{2+} is an inverted perovskite, where the atoms A and M are in exchanged positions and, therefore, different spectroscopic properties are expected. This crystal shows a vibronically emission band in near infrared around 1.5 μm and is very promising for a suitable laser material. We have investigated the basic spectroscopy of $BaLiF_3$:Ni^{2+} concerning absorption and emission bands and transition probabilities.

INTRODUCTION

The optical properties of fluoperovskites with the general formula ABF_3 (A and B mono- and divalent cations, respectively) doped with divalent transition metal ions have been of great interest to solid state spectroscopists. The lattice belongs to the P_{m3m} space group where the divalent B ions are placed in the center of inversion of the fluorine octahedra. This situation allows a "perfect" O_h symmetry for divalent 3d ion substitutional impurities. Fluoperovskites are of some significance in the field of laser materials. Since the pioneering paper of Johnson et al.[1] who found laser activity in $KMgF_3$:Ni $^{2+}$, much work has been done in order to investigate the spectroscopic properties of fluoperovskites crystals doped with transition metal ions such as Ni^{2+} [1-5], Co^{2+} [6,7], V^{2+}[5-8], Fe^{2+} [9] and Mn^{2+} [7, 10-15].

Host materials doped with Ni^{2+} in octahedral sites show a vibronically broadened emission band in the near infrared around 1.5 μm, wich is useful for tunable solid state lasers. Although Ni^{2+} in this symmetry is being investigated since 1963 [16], CW- operation at room temperature has not yet been achieved. The highest temperature reported so far is for MgO:Ni^{2+} which has been CW-opereted at 30°C [8]. We have investigated the spectroscopic properties of new Ni^{2+} -doped perovskites, $BaLiF_3$:Ni^{2+}, as potential new laser materials.

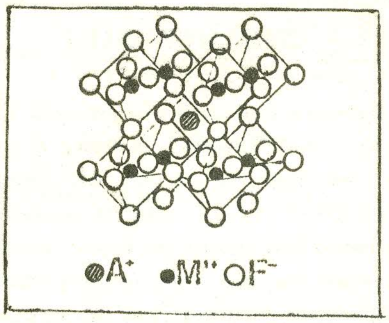

FIGURE 01: *Tridimentional octahedral piling MF_6 limiting sites with 12 fluorine neighbors occuped by A^+ ion.*

CRYSTALS

The perovskite-type materials crystallize in a single cubic system, belongs to the space group $O_h{}^1$ or P_{m3m} As shown in FIGURE 01, the structure can be described as tridimentional octahedral piling MF_6 limiting sites with 12 fluorine neighbors occupied by A^+ ion. $BaLiF_3$ is an inverted perovskite compared to the classical perovskite (FIGURE 02), where Barium and Lithium are in exchanged positions [Ba (1/2,1/2,1/2) and Li (0,0,0)]. In spite of this fact the local symmetry is the same (O_h).

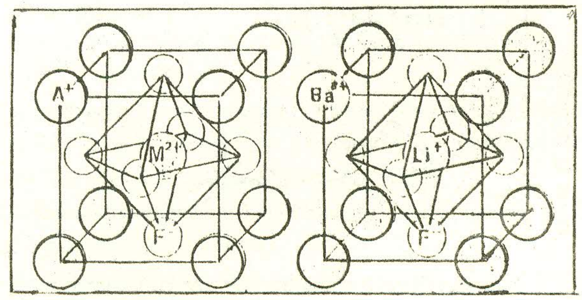

FIGURE 02: *Fluoperovskite structures AMF_3 and $BaLiF_3$.*

As pure material, $BaLiF_3$ is a colorless crystal transparent from UV to IR, possessing a refraction index of 1.544 at 589 nm. The lattice parameter is 3,996 Å and the density is 5.237g/cm [17]. The crystal is non hygroscopical, presenting a high chemical stability and does not show phase transition . $BaLiF_3$ allows the substitution of the Li^+ ion (ionic radius 0.60 A) by the Ni $^{2+}$ ion (0,69Å).

The BaLiF doped with Ni was synthesised by the CZOCHRALSKI technique [18]. The crystal presented optical transparency, free of visible inhomogeneities and none of them cracked even without an annealing process. The Ni-concentration, which was determined by spectrografic methods, was 7.8 x 10^{18} Ni/cm^{-3} in $BaLiF_3$. The crystal had to be cooped with Pb. Cubic

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samples of 50 mm diameter are sawed with a diamond saw and finely polished for the spectroscopic study.

RESULTS

ABSORPTION SPECTRA

The absorption spectra were all recorded using a CARY model 17D spectrophotometer. For the 10 K mesurements the sample was placed in a Helium closed-cycle cryostat. The absorption spectrum of $BaLiF_3:Ni^{2+}$ is shown in FIGURE 03. The major features of this spectrum include a broad band with a peak near 1100nm. Another two bands appear peaking at 700nm and 390nm. At 10K we observed two zero-phonon lines at 1222nm (8183.3 cm^{-1}) and 1247nm (8019.3 cm^{-1}). The absorption cross section was calculeted from the absorption coefficient and the Ni concentration. Table 01 shows the absorption cross sections as function of temperature. The $BaLiF_3:Ni^{2+}$, $KZnF_3:Ni^{2+}$ and $KMgF_3:Ni^{2+}$ optical absorption spectra are very alike [19], showing only minor displacement in energy due to different lattice parameters.

TABLE 01

ABSORPTION CROSS SECTION ($x10^{-20}$ CM^2)

BAND (NM)	ROOM TEMP.	BAND (NM)	10K
390	4.37	380	4.80
700	3.41	690	3.15
1150	2.87	1140	2.96

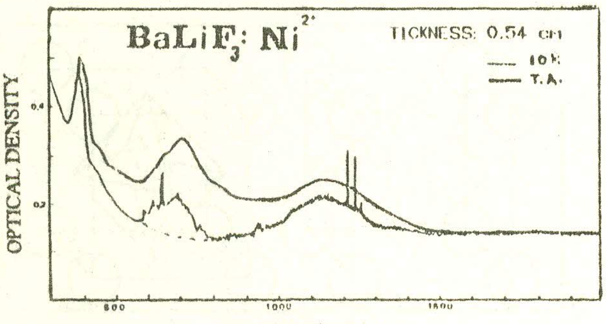

FIGURE 03: *Optical absorption spectrum of $BaLiF_3:Ni^{2+}$.*

EXCITATION SPECTRUM

The excitation spectra were obtained using a arrangement of two monochromators. One Spex model 1670 monochromator to scan the excitation radiation and one Bausch & Lomb monochromator to select the emission. The light source used was a 150 Watts Xenon lamp with the intensity modulated by a chopper. The detector used for these measurements was a cooled InSb connected to a lock-in amplifier.

The Ni^{2+} bands, which are due to octahedral sites, are also identified by the excitation spectrum, as shown in FIGURE 04, for the broad band fluorescence centered at 1500 nm.

The simplefied energy level diagram according to the classical Tanabe-Sugano Diagram [20] relates the normalized energy of the low lying states to the normalized strength of the eletrostatic crystal field splitting. This is shown in FIGURE 05, where the normalization constat B is the so-called Racah parameter. The crystal field parameter Dq = 810cm^{-1} and the Racah parameter B=760 cm^{-1} are obtained for $BaLiF_3$:Ni^{2+} crystal (Dq/B=0.83).

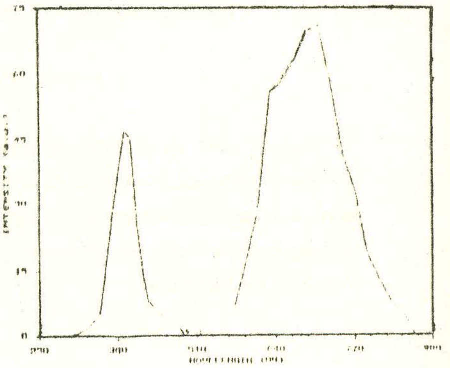

FIGURE 04: *Excitation spectrum of the infrared luminescent band.*

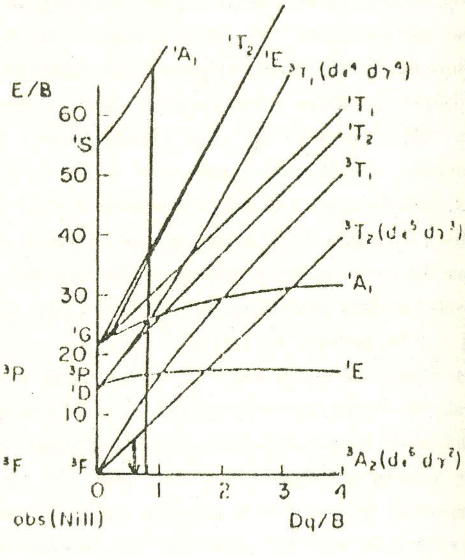

FIGURA 05: *Simplified Tanabe-Sugano diagram to Ni^{2+}.*

EMISSION DATA

The emission measurements were done with a Nd:YAG laser (MODEL 116 - QUANTRONIX) oscillating at 1,064 µm. The luminescence was collected at 90^0 and dispersed with a monochromator (SPEX - 0,5m - grating 300 gr/mm). Detection was done with a cooled InSb detector and lock-in amplifier. A closed-cycle cryogenerator was used for the low temperatures. A Kr^+ ion laser (MODEL 400-k3 - Coherent) was also used as an excitation source. Two bands belonging to the Ni^{2+} ion in an octahedron are observed in the luminescence spectra of the $BaLiF_3$:Ni^{2+} , in the near-IR and in the green region.

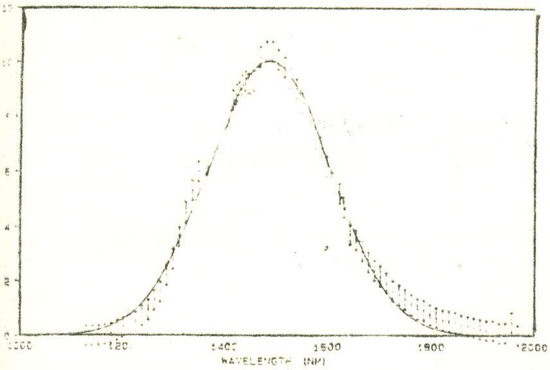

FIGURE 06: BaLiF$_3$:Ni^{2+} infrared emission.

The emission produced by pumping in the 1100nm absorption band, at room temperature, is shown in FIGURE 06. It appears as a intense broadband peaking near 1500nm, corresponding a transition $^3A_{2g} \mapsto {}^3T_{2g}$. This band has been qualitatively interpreted as a mixture of magnetic dipole and phonon assisted eletric transitions, whereas the forbidden eletronic transition gives rise to a vibronic band due to phono creation.

As others Ni^{2+} doped fluoperovskites (KZnF$_3$ and KMgF$_3$), BaLiF$_3$ shows two emission bands, one in the visible (500 nm) and other in the infrared. This visible emission was observed using a Xe arc lamp as a pumping source at 390 nm or exciting the crystal with an Argon laser operated at UV multi-line [351.1 - 363.8 nm]. FIGURE 07 portrays the room temperature luminescence spectra centered at 500 nm.

The decay time (τ), at room temperature, of aproximately 3 ms was measured with a boxcar averager. The calculeted emission cross section is 3×10^{-21} cm^2.

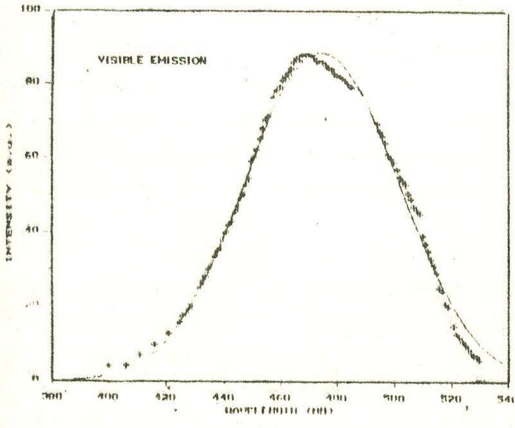

FIGURE 07: Visible emission of BaLiF$_3$:Ni^{2+}.

CONCLUSION

A crystal field parameter Dq of 810 cm^{-1} and a Racah parameter B of 760 cm^{-1} were calculated. the results agree with the expected figures once BaLiF$_3$'s lattice is tighter than KZnF$_3$'s lattice wich possesses Dq = 698 cm^{-1} e B = 950 cm^{-1}.

The magnetic dipole character of the T band in the infra-red region can be confirmed by the MCD results.

Some of the limitations encountered in trying to optimize laser parameters include scattering centers and parasitic absorption bands in the laser spectral region. We are working in investigating upper excited-states of the system which may be detrimental to the system through excited state absorption of pumping light, or may be useful for alternate pumping mechanisms.

REFERENCES

[1] Johnson, L. F., Guggenheim, H. J. and Thomas, R. A., Phys. Rev. 149, 179 (1966).

[2] Vehse, W. E., Lee, K. H., Yun, S. I. and Sibley, W. A., J. Lumin. 10, 149 (1975).

[3] Johnson, L. F., Guggenheim, H. J., Bahnck, D. and Johnson, A M., Opt. Lett. 8, 371 (1983).

[4] Russi, R., Barbosa, G.A., Rousseau, M. and Gesland, J. Y., J. e Phys. 45, 1773 (1984).

[5] Sturge, M. D., Solid State Commun. 9, 889 (1971).

[6] Sturge, M. D., Phys. Rev. 8 , 6 (1973).

[7] Lee, K. H.and Sibley, W. A., Phys. Rev. B 12, 3392 (1975).

[8] Moncorgé, R. and Benyattou, T., Phys. Rev. B 37, 9186 (1988).

[9] Walsh, D. and Lange, J., Phys. Rev. B 23, 8 (1981).

[10] Ferrguson, J., Guedel, H. U., Krausz, E. R. and Guggenheim, H. J.,Molecul. Phys. 28, 879 (1974).

[11] Sibley, W. A., Yun, S. Y. and Vehse, W. E., J. Phys. Chem. 6, 1105 (1973).

[12] Yun, S. Y., Lee, K. H., Sibley, W. A. and Vehse, W. E., Phys. Rev. B 10, 1665 (1974).

[13] Rodriguez, F. and Moreno, M.,J. Chem. Phys. 84, 692 (1986).

[14] Rodriguez, F., Moreno, M., Tressaud, A. and Chaminade, J. P., Cryst. Latt. Def. and Amorph. Mat. 16, 221 (1987).

[15] Dubicki, L., Ferguson, J., Osborne, G. A. and Trabjerg, I., Coll. Intern. CNRS n.255, 217 (1976).

[16] Johnson, L. F. et al., Phys. Rev. Lett. 11, 318 (1963).

[17] Galasso, F. S., "Structure and Properties of Inorganic Solids" (Pergamon Press) (1976).

[18] Baldochi, S. L. and Gesland, J. Y., . 27(3), 577 (1992).

[19] Knox, K., Shulman, R. G. and Sugano, S., Phys. Rev. 130 (2),512 (1963).

[20] Sugano, S., Tanabe, Y. and Kamimura, H., "Multiplets of transition metal ions in crystals" (Academic Press) (1970).