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FINE STRUCTURE OF THE ABSORPTION AND EMISSION SPECTRA OF Ni^{2+}-IONS IN $BaLiF_3$

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The optical properties of Ni^{2+}-ion impurities in a new crystal, the inverted fluoroperovskite $BaLiF_3$, have been studied. In particular we have investigated the fine structure of the transition by means of absorption and emission spectra. By analogy to previous results we have assigned the structured absorption band around 1200 nm to the $^3A_2 \rightarrow {}^3T_1$ transition. Four zero-phonon lines are clearly visible in the absorption spectrum. The emission in the region 1250–1600 nm, due to the same $^3A_2 \rightarrow {}^3T_1$ transition, consists of two sharp lines with their vibrational sidebands.

Key words: Spectroscopy, Ni^{2+}, Perovskite.

1 INTRODUCTION

The development of tunable solid-state lasers has renewed the interest in the study of impurity ions in solids whose electronic transitions are broadened by strong electron-phonon coupling.

In order to have different laser systems available to cover the interesting near infrared spectral region it is important to study the spectroscopic properties of specific impurity ions in several materials.[1] In particular, host crystals doped with Ni^{2+} (d^8 configuration) show broad vibronically allowed absorption and emission bands.[2–5]

Although the laser emission of the Ni^{2+} ion has been investigated since 1963,[6] c.w. laser operation at room temperature has not yet been achieved.[7,8] However the chemical stability of the Ni^{2+} ion and the presence of several pump bands stimulated the interest in the search for new crystals as hosts for Ni^{2+}. In this work, the basic spectroscopic properties of Ni^{2+} in $BaLiF_3$ perovskite will be described.

The fluoroperovskite type materials, described by the general formula AMF_3 (A and M mono and divalent cation, respectively), crystallize in the cubic system; they belong to the space group O_h^1 or P_{m3m} [9]. The coordination number of the monovalent ion is 12 while that of the divalent ion is 6. $BaLiF_3$ is an *inverted* perovskite compared to the normal perovskite ($KMgF_3$) with the Ba and Li in exchanged position and therefore with the monovalent Li^+ surrounded by a octahedron of 6 F^- ions and the divalent Ba^{2+} surrounded by 12 F^- ions at the corner of a cube-octahedron (see Figure 1a and 1b). The symmetry of both metal sites is O_h and the Ni^{2+} ion could occupy either of them. However the crystal

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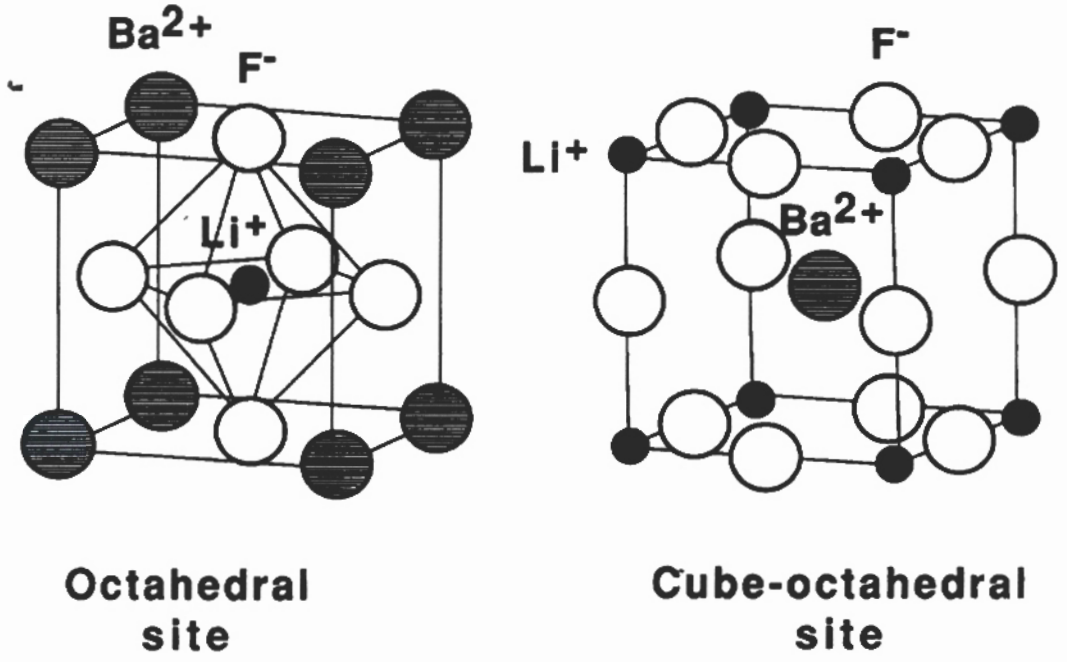

FIGURE 1 Crystal structure of $BaLiF_3$ fluoroperovskite showing the octahedral (Li^+) site (left) and cubo-octahedral (Ba^{2+}) site (right).

field that Ni^{2+} ion would experience in the two lattic sites should be very different: the field splitting between the e_g and t_{2g} d-orbitals in the two cases would be

$$\Delta_{cube-oct} = -\frac{1}{2}\Delta_{oct}.$$

2 RESULTS AND DISCUSSION

The absorption spectrum of $BaLiF_3:Ni^{2+}$ for the sample 0.3 mol% Ni concentration and 5.3 mm thick is shown in Figure 2. The general structure of the spectrum is quite similar to those of $KMgF_3:Ni^{2+}$ and $KNiF_3$, and three main, broad, absorption bands peaking at 1180 nm, 700 nm and 390 nm are displayed. Moreover there is a narrow structure at about 650 nm, that overlaps the 700 nm band and a weaker absorption band peaking at 500 nm.

The similarity of this spectrum of $BaLiF_3:Ni^{2+}$ with that of $KMgF_3:Ni^{2+}$ where the Ni^{2+} is known to replace the Mg^{2+} in octahedral site [3], suggests the same Ni^{2+} coordination in both systems. At first sight one could suppose that Ni^{2+} should replace the equally charged Ba^{2+}. However the preference of Ni^{2+} for the Li^+ rather than the Ba^{2+} site could be attributed to the similar ionic radii of Ni^{2+} (0.69 Å) and Li^+ (0.68 Å) while that of Ba^{2+} is very different (1.34 Å). The Ni^{2+} ion in the Li^+ site requires charge compensation which may be provided by either a Li^+ vacancy or by a Ba^{2+} vacancy, charge compensating for two Ni^{2+} ions.

The main absorption bands were thus attributed to transitions to levels originating from crystal field splitting of the d orbitals and from the electron-electron interaction of Ni^{2+} ion in an octahedral environment, according to the classical Tanabe—Sugano diagram. These

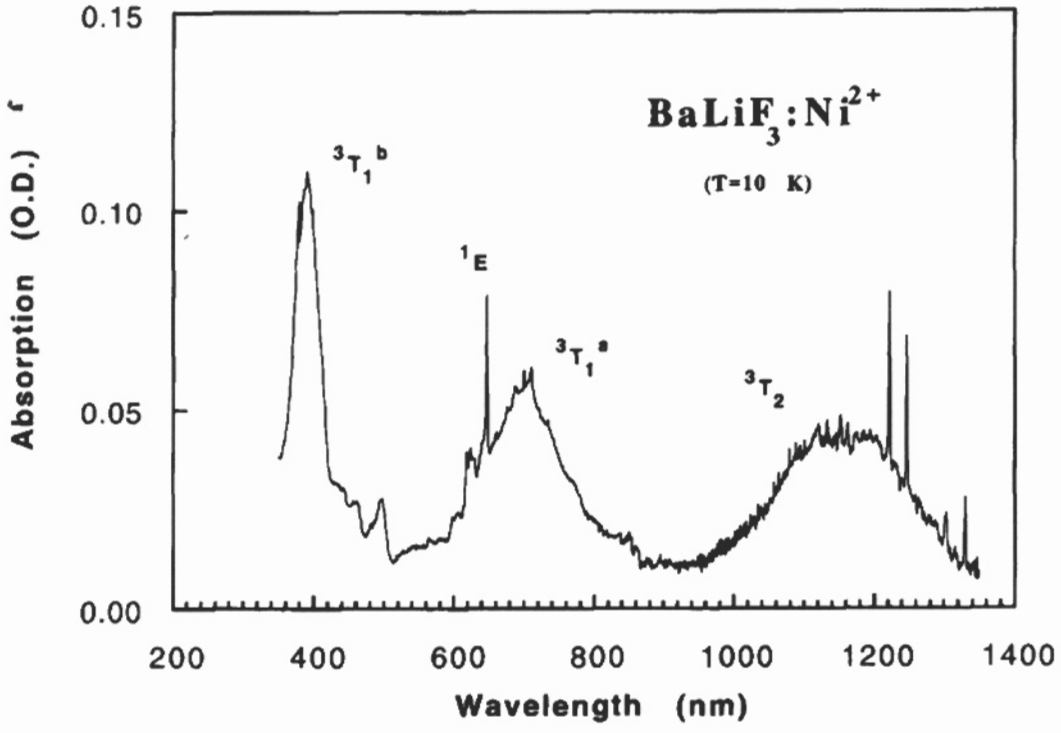

FIGURE 2 Absorption spectrum at 10 K of $BaLiF_3:Ni^{2+}$ 0.3 mol%.

bands correspond to electronic transitions between the ground state, $^3A_{2g}$, and four excited states of symmetries $^3T_{2g}$, $^3T^a_{1g}$, ^1E_g and $^3T^b_{1g}$ respectively.

Figure 3 shows part of the absorption spectrum on an expanded scale. Following the same arguments given in reference[3] we attribute the 1150 nm band ($^3A_{2g} \rightarrow {}^3T_{2g}$) to a magnetic dipole transition containing superposition of zero-phonon lines and broader phonon side bands. In the octahedral symmetry, the first excited level ($^3T_{2g}$) splits in four spin-orbit components while the ground state remains degenerate. The lines at 1222 nm (8183.3 cm^{-1}), 1247 nm (8019.3 cm^{-1}), 1302 nm (7680.5 cm^{-1}) and 1330 nm (7518.8 cm^{-1}) can be interpreted as the no-phonon transitions to the Γ_2, Γ_5, Γ_4, Γ_3 spin-orbit components of the state $^3T_{2g}$, respectively.

The spin-orbit splitting between the 1222 nm and the 1247 lines is 164cm^{-1} and between the 1302 nm and the 1330 lines is 161.7cm^{-1}. The related lines in $KMgF_3:Ni^{2+}$ and $KZnF_3:Ni^{2+}$ systems have a spin-orbit splitting very close to the above values.[3]

The above interpretation for the four zero-phonon lines is also supported to some extent by the calculated magnetic dipole oscillator strengths of the four spin-orbit lines.[10] However experimental assignment of the observed $^3A_{2g} \rightarrow {}^3T_{2g}$ transition of Ni^{2+} in octahedral sites[3,4,10] point to much larger intensities for transitions into the Γ_3 and Γ_4 states, while those into the Γ_5 and Γ_2 states are almost completely obscured by the overlapping phonon sidebands.

A different interpretation can thus be the assignments of the more intense 1222 nm and 1247 nm lines to the Γ_4 and Γ_3 no-phonon lines of the Ni^{2+} in octahedral site while the two less intense lines (with the same energy separation) could be due to Ni^{2+} in a different lattice site or with different neighbours producing a lower crystal field.

Figure 3 shows also the infrared emission spectra at 10 K. It is evident the coincidence of the zero-phonon emission lines at 1247 nm and 1330 nm, with two of the

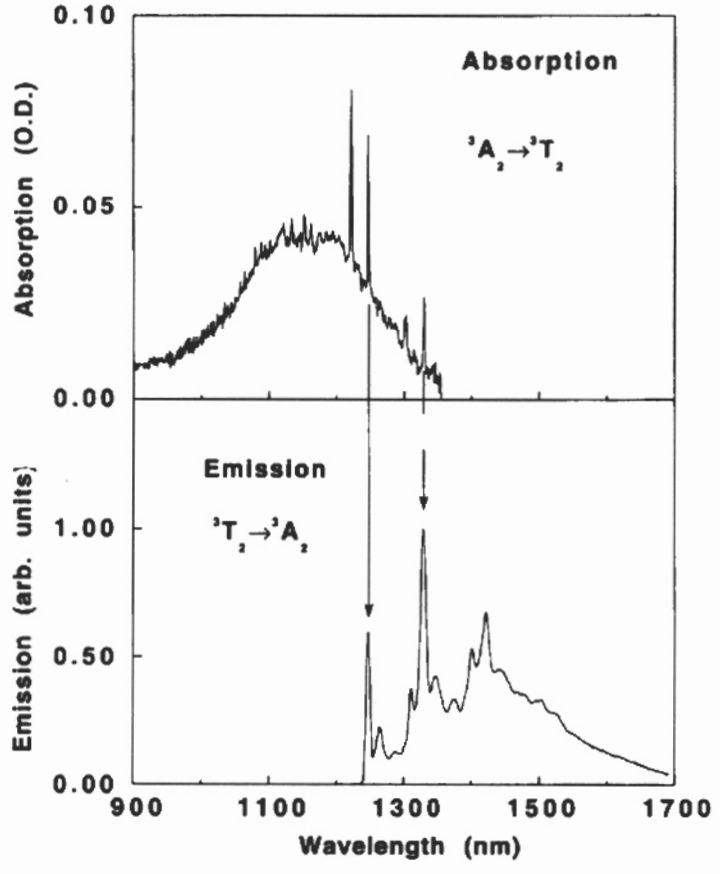

FIGURE 3 Infrared absorption and emission spectra of $BaLiF_3:Ni^{2+}$ at 10 K.

absorption lines. This observation could be explained by assuming the presence of two emitting sites, with transitions from the lowest level of the $^3T_{2g}$ multiplet at 1247 nm and 1330 nm respectively.

The same emission bands are excited by pumping either in the $^3A_{2g} \rightarrow {}^3T_2$ absorption (Nd-YAG laser) or in the $^3A_{2g} \rightarrow {}^3T_1$ absorption (He-Ne laser): we could not determine if the relaxation $^3T_1 \rightarrow {}^3T_2$ is radiative or nonradiative.

Magnetic circular dichroism and excited state absorption experiments are presently in progress to obtain a more complete description of Ni^{2+} in this system.

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