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## Optical characterization of $\text{Ho}^{3+}$ ions in $\text{LiNbO}_3$ and in $\text{LiNbO}_3:\text{MgO}$ crystals

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**Abstract.** A detailed study of the optical absorption and emission spectra of  $\text{Ho}^{3+}$  ions in  $\text{LiNbO}_3$  crystals in the visible spectral region is presented. The positions of the crystal-field levels are given for the  $^5\text{F}_5$ ,  $^5\text{S}_2 + ^5\text{F}_4$ ,  $^5\text{F}_3$  and  $^5\text{G}_6$  multiplets of  $\text{Ho}^{3+}$  ions. The type and character of the Stark transitions have been determined by polarized absorption measurements. Optical absorption measurements and site-selective spectroscopy have shown the existence of two crystal-field sites for  $\text{Ho}^{3+}$  in the  $\text{LiNbO}_3$  matrix. The effect of co-doping with MgO on the optical spectra of  $\text{Ho}^{3+}$  ions has also been studied and a new  $\text{Ho}^{3+}$  site perturbed by the presence of a neighbouring  $\text{Mg}^{2+}$  ion is evidenced.

### 1. Introduction

Interest in the spectroscopy of rare-earth and transition-metal ions in  $\text{LiNbO}_3$  has been renewed after the appearance of  $\text{LiNbO}_3:\text{MgO}:\text{Nd}^{3+}$  minilasers [1]. This material combines the excellent electro-optic and non-linear properties of the  $\text{LiNbO}_3$  matrix together with the laser action from  $\text{Nd}^{3+}$  ions [2]. This permits the fabrication of devices such as the self- $Q$ -switch and self-frequency-doubled miniature lasers as well as waveguide lasers and optical amplifiers [3].

In this context, the study of other rare-earth ions as active centres in the  $\text{LiNbO}_3:\text{MgO}$  system appears as an interesting field as a previous step to evaluating the suitability of new systems for the actual requirements. Thus, a new field of research has been opened up for  $\text{LiNbO}_3$  doped with other possible active ions.

In this sense,  $\text{Ho}^{3+}$  appears as an interesting dopant ion. In fact, coherent emission for different wavelengths with a high-energy storage has been observed in a number of crystals and glasses doped with  $\text{Ho}^{3+}$  ions [4–6]. Indeed, laser action has been demonstrated for  $\text{Ho}^{3+}$ -doped  $\text{LiNbO}_3$  [7]. In particular, the laser emission at 2.1  $\mu\text{m}$  appears to be an interesting line because its long upper-state lifetime may allow high-energy storage and its eye-safe wavelength is useful for applications that require atmospheric propagation, such as a coherent laser radar. However, to date, the basic spectroscopic studies concerning  $\text{Ho}^{3+}$  ions in  $\text{LiNbO}_3$  are scarce.

On the one hand, in this work, an exhaustive study of the optical properties of  $\text{Ho}^{3+}$  ions in singly doped  $\text{LiNbO}_3$  crystals has been carried out in the visible spectral region. Characteristic bands of  $\text{Ho}^{3+}$  free ions are observed to be split according to  $\text{C}_3$  local symmetry. The positions of the crystal-field levels for some relevant multiplets in the visible spectral range are given. Polarized absorption measurements show the electric dipole character of the transitions and provide good information for labelling the corresponding Stark levels of the  $^5\text{F}_3$ ,  $^5\text{G}_6$ ,  $^5\text{F}_4 + ^5\text{S}_2$  and  $^5\text{F}_5$  multiplets.

Site-selective spectroscopy together with optical absorption measurements show the presence of non-equivalent sites for  $\text{Ho}^{3+}$  ions, presumably owing to the replacement of the  $\text{Li}^+$  and  $\text{Nb}^{5+}$  regular lattice sites.

As an interesting material, from the viewpoint of laser applications,  $\text{Ho}^{3+}$ -doped  $\text{LiNbO}_3:\text{MgO}$  has also been studied in order to determine the effect that co-doping with  $\text{Mg}^{2+}$  has on the spectroscopy of  $\text{Ho}^{3+}$ . As has been previously demonstrated, the addition of around 5 mol%  $\text{MgO}$  appears necessary to improve the quality of the  $\text{LiNbO}_3$  laser devices, reducing the optical damage produced by the photorefractive effect [8]. For the case of  $\text{Ho}^{3+}$  ions, new absorption lines associated with  $\text{Ho}^{3+}$  ions perturbed by  $\text{Mg}^{2+}$  ions are detected.

## 2. Experimental details

$\text{Ho}^{3+}$ -doped  $\text{LiNbO}_3$  and  $\text{LiNbO}_3:\text{MgO}$  have been grown by the Czochralski technique in our laboratory, from a congruent melt of grade I Johnson–Matthey powder. As a dopant,  $\text{Ho}_2\text{O}_3$ , in a concentration of 1 mol% relative to  $\text{Nb}^{5+}$  ions, has been added to the melt for both singly and doubly doped  $\text{LiNbO}_3$ . For the doubly doped system,  $\text{MgO}$  was added in a concentration of 5 mol%. Crystals were oriented using x-ray diffraction patterns. Then, plates 1 mm thick were cut and polished with their faces parallel or perpendicular to the ferroelectric  $C$  axis.

Polarized absorption spectra between 350 and 700 nm were obtained with a Cary 17 spectrophotometer using a Glan–Thompson calcite polarizer.

For measurements of the emission spectra a pulsed nitrogen-pumped dye laser was used as the excitation source. The width (FWHM) of the dye laser emission was 1 Å. The emitted light was focused on the entrance slit of a Spex 500M monochromator of 50 cm focal length. A cooled multialkali photomultiplier and a SR400 gated photon counter in continuous mode were used as the detection system. The monochromator control and the acquisition of data were made via a personal computer.

Both types of spectra (absorption and emission) were obtained at a low temperature (15 K) using a closed-cycle helium cryostat, provided with a temperature control.

## 3. Experimental results and discussion

In the  $\text{LiNbO}_3$  host, three similar sites are available for cationic impurities:  $\text{Li}^+$ ,  $\text{Nb}^{5+}$  and structural vacancy sites. In these sites, the local environment of the ion consists of oxygen octahedra distorted along one of the (111) axes which, in turn, lies in the trigonal ferroelectric axis of the crystal. However, since the sites of the octahedra are equivalent in size and local symmetry [9], the charge of the impurity is expected to play a major role in determining the preference among these sites.

A number of studies using optical techniques and electron paramagnetic resonance have been devoted to determining the site symmetry for different impurities in the  $\text{LiNbO}_3$  matrix [10, 11]. In all cases the symmetry proposed for the impurity site was  $C_3$  symmetry.

For the case of rare-earth-ion-doped  $\text{LiNbO}_3$ , previous results have shown that these impurities substitute for  $\text{Li}^+$  and  $\text{Nb}^{5+}$  in the matrix, rejecting the structural vacancy sites [12, 13].

Figure 1 shows a simplified scheme of levels of  $\text{Ho}^{3+}$  in  $\text{LiNbO}_3$ . It consists of several multiplets inside the  $4f^{10}$  configuration, where  $^5I_8$  is the ground-state multiplet. Data were

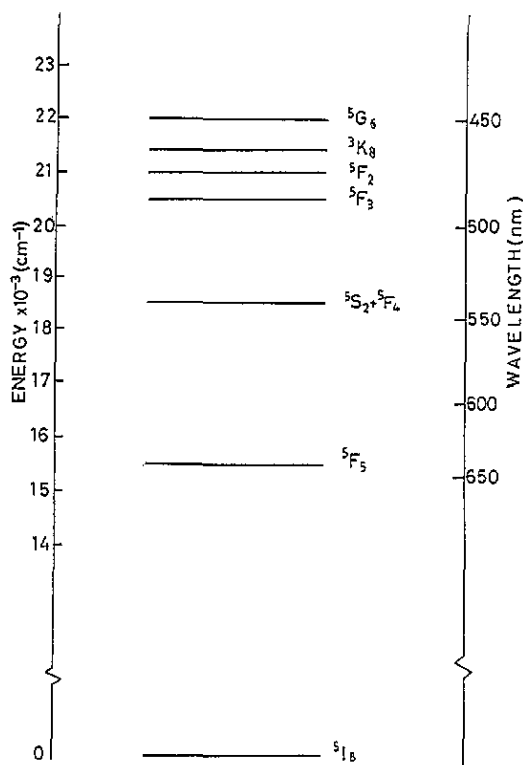


Figure 1. Simplified scheme of levels for  $\text{Ho}^{3+}$  in  $\text{LiNbO}_3$  from absorption spectra.

obtained from the absorption spectra taken at a low temperature (15 K). The positions of the energy levels were obtained from the centre of gravity of the different group of lines.

The experimental results obtained in this work for  $\text{Ho}^{3+}$  in  $\text{LiNbO}_3$  and  $\text{Ho}^{3+}$  in  $\text{LiNbO}_3:\text{MgO}$  can be divided into two groups: (a) absorption spectra in the visible region from the fundamental  $^5\text{I}_8$  multiplet to the  $^5\text{F}_5$ ,  $^5\text{S}_2 + ^5\text{F}_4$ ,  $^5\text{F}_3$  and  $^5\text{G}_6$  multiplets and (b) emission spectra in the region around 550 nm corresponding to the transition between the Stark levels of  $^5\text{S}_2 + ^5\text{F}_4$  multiplets and the  $^5\text{I}_8$  fundamental multiplet.  $^3\text{K}_8$  and  $^5\text{F}_2$  multiplets are not studied in this work as they appear very close in energy and with very low intensity.

### 3.1. Absorption spectra of $\text{Ho}^{3+}:\text{LiNbO}_3$

According to the  $\text{C}_3$  symmetry assumed for  $\text{Ho}^{3+}$  in  $\text{LiNbO}_3$ , any  $J$  level of the free ion will split into a number of A and E crystal-field levels depending on the  $J$ -value. The type of the split level (E or A), as well as the character (electric or magnetic dipole), can be determined by studying the polarization character of the transitions involved [14]. This can be performed experimentally from optical absorption measurements, by taking the so-called  $\sigma$ -,  $\pi$ - and  $\alpha$ -polarized spectra.

The  $\pi$  and  $\sigma$  spectra are taken from samples with the ferroelectric  $C$  axis lying along their faces and the electric field of the light beam parallel (for  $\pi$ ) and perpendicular (for  $\sigma$ ) to the  $C$  axis. The  $\alpha$  spectrum is taken from samples with the  $C$  axis perpendicular to their faces, so that the electric field of the light beam is perpendicular to the  $C$  axis. Thus, from the experimental data, the character of each transition can be inferred by taking into account the selection rules given by group theory.

Figures 2, 3, 4 and 5 show the  $\sigma$ - and  $\pi$ -polarized absorption spectra associated with the transitions between the fundamental  $^5I_8$  multiplet and the upper sublevels of  $^5F_5$ ,  $^5S_2 + ^5F_4$ ,  $^5F_3$  and  $^5G_6$  multiplets, respectively, of  $\text{Ho}^{3+}$  in  $\text{LiNbO}_3$ .

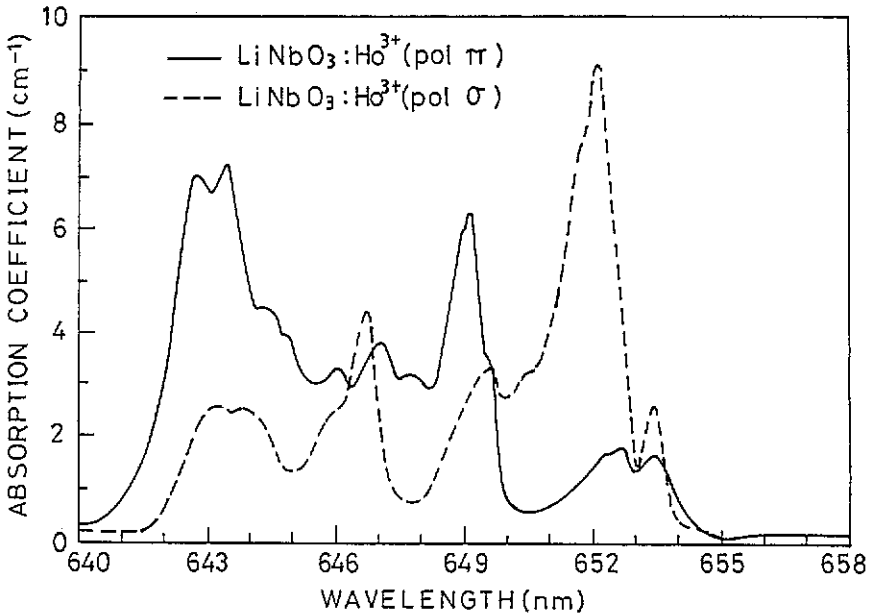


Figure 2. Absorption spectra corresponding to the  $^5I_8 \rightarrow ^5F_5$  transition of  $\text{Ho}^{3+}$  ions in  $\text{LiNbO}_3$  at 15 K.

At this point, it is interesting to mention that, for all the transitions studied in this work, the  $\alpha$  and  $\sigma$  absorption spectra showed the same bands, while the  $\pi$ -polarized absorption spectra were, in each case, significantly different. New absorption lines that were not observed in the  $\alpha$  or  $\sigma$  spectra appear in the  $\pi$  configuration. Thus, the transitions observed between the Stark sublevels are either  $\alpha$  and  $\sigma$  polarized or  $\pi$  polarized, and this behaviour reveals the electric dipole character of the transitions.

From the selection rules for electric dipole transitions with linearly polarized radiation for an ion in  $C_3$  symmetry, it is possible to conclude that transitions between an E level and an A level are allowed in a  $\sigma$ -polarized configuration, transitions between two A levels will be  $\pi$  polarized, and transitions between two E levels will have both  $\sigma$  and  $\pi$  characters. According to this, it can be inferred that the ground state of  $^5I_8$  is A, because most of the bands observed in the  $\pi$ -polarized spectra disappear or drastically decrease their intensity in the  $\sigma$ -polarized spectra.

However, it is important to mention here the difficulties in determining the polarization character of each particular transition, i.e. the levels involved (A or E). These difficulties arise from three main effects:

- (i) mixing and high multiplicity for most of the multiplets;
- (ii) thermal population of Stark levels other than the lowest  $^5I_8$  Stark level;
- (iii) the presence of non-equivalent crystal-field sites for  $\text{Ho}^{3+}$  ions.

Let us now discuss these three effects separately.

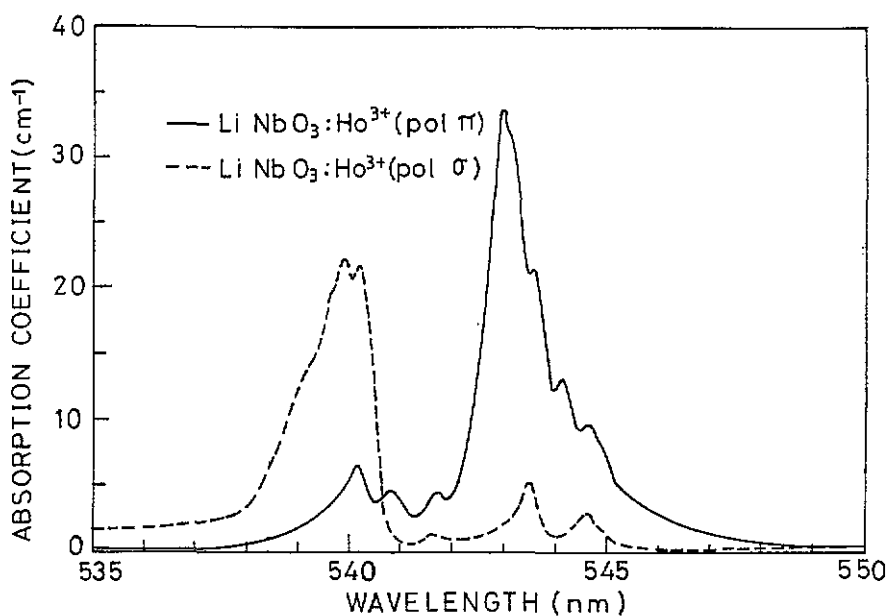


Figure 3. Absorption spectra corresponding to the  $^5I_8 \rightarrow ^5F_4 + ^5S_2$  transition of  $\text{Ho}^{3+}$  in  $\text{LiNbO}_3$  at 15 K.

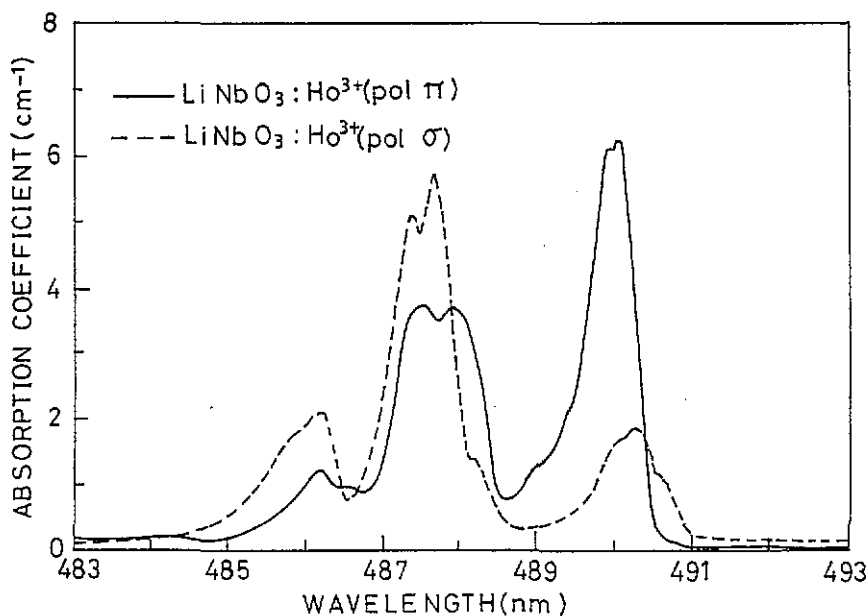


Figure 4. Absorption spectra corresponding to the  $^5I_8 \rightarrow ^5F_3$  transition of  $\text{Ho}^{3+}$  in  $\text{LiNbO}_3$  at 15 K.

(i) The high multiplicity  $2J + 1$  of the multiplets involved gives rise to a high number of Stark levels, which overlap and produce a large number of absorption bands.

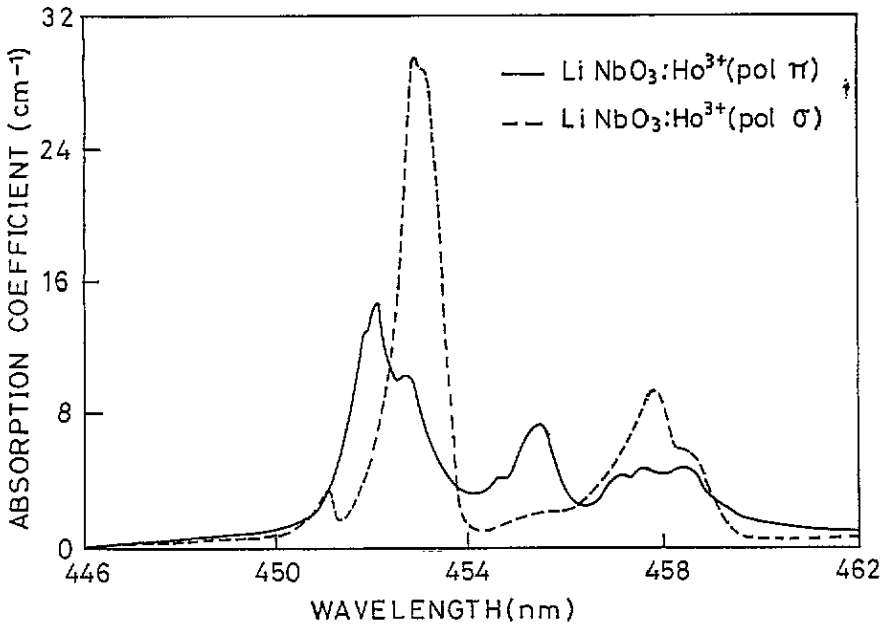


Figure 5. Absorption spectra corresponding to the  ${}^5I_8 \rightarrow {}^5G_6$  transition of  $\text{LiNbO}_3:\text{Ho}^{3+}$  at 15 K.

(ii) Some absorption lines in the spectra can be associated with transitions from thermally excited Stark levels of the  ${}^5I_8$  fundamental multiplet. In fact, the thermal population of Stark sublevels at 8 and 18  $\text{cm}^{-1}$  can be expected for the temperature at which the spectra were obtained [7].

(iii) For all the bands studied here the number of lines detected is greater than predicted by group theory for  $C_3$  symmetry. Some of the lines seem to be split slightly into two lines, and this small splitting, as will be discussed later, cannot be explained in terms of thermalized transitions. As in other doped  $\text{LiNbO}_3$  systems this could be explained in terms of the occurrence of two different lattice sites for  $\text{Ho}^{3+}$  ions, one possibly substituting for  $\text{Nb}^{5+}$  ions and the other substituting for  $\text{Li}^+$  ions [15, 16].

As an example of these features, figure 6 shows the  $\sigma$  and  $\pi$  absorption spectra in the 640–645 nm region where a relevant portion of the  ${}^5I_8 \rightarrow {}^5F_5$  free-ion transition takes place (the portion associated with the higher-energy sublevel of the  ${}^5F_5$  multiplet). First, in these spectra a strong  $\pi$  contribution is observed, although an important  $\sigma$  contribution is also detected. However, this  $\sigma$  contribution has been associated with thermalized transitions. A detailed analysis of this spectrum revealed that the first two peaks which appear in the  $\pi$  spectrum (peaks a and d in figure 6), correspond to an  $A \rightarrow A$  transition for two different spectroscopic sites (see section 3.2 below). In the  $\sigma$  spectrum, two peaks (b and e) shifted 8  $\text{cm}^{-1}$  towards lower energies relative to peaks d and a are observed. These peaks have been associated with thermalization of the first excited level of the fundamental  ${}^5I_8$  multiplet for each spectroscopic site for  $\text{Ho}^{3+}$  ions. Thus, by a simultaneous analysis of the  $\sigma$  and  $\pi$  spectra, together with their temperature dependence, it was possible to label the first two levels of the ground-state multiplet as A (0  $\text{cm}^{-1}$ ) and E (8  $\text{cm}^{-1}$ ). The third sublevel of the  ${}^5I_8$  multiplet is at about 18  $\text{cm}^{-1}$  and produces the doublet structure in the low-energy tail of the  $\pi$  spectrum (peak c). These two excited sublevels produce a ‘thermal structure’

in the absorption spectra and can mask the polarization character of the transitions from the lowest energy level, an A level.

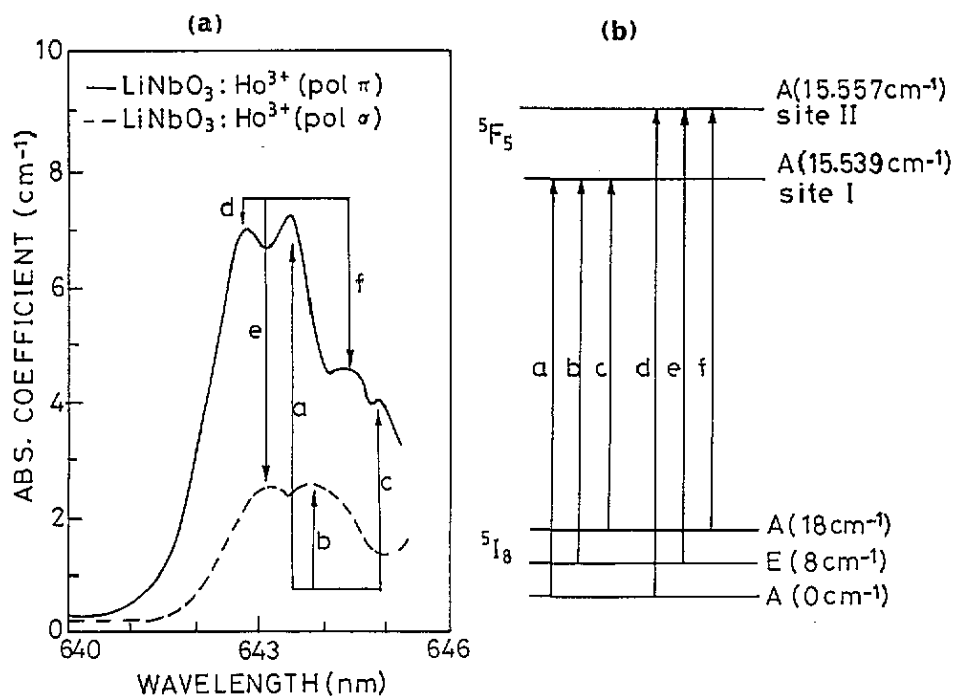


Figure 6. (a) Absorption spectra corresponding to the high-energy side of the  ${}^5I_8 \rightarrow {}^5F_5$  transition of  $\text{Ho}^{3+}$  ions in  $\text{LiNbO}_3$  at 15 K. (b) Assignment of the observed transitions.

Owing to both thermalization of ground-state levels and site splitting unequivocal identification of all the features appearing in the absorption spectra becomes a very difficult task. However, the analysis of the polarization spectra as well as the changes observed in the absorption spectra after co-doping with MgO allow identification of a large part of the spectra.

Let us now discuss in more detail the absorption spectra related to each excited multiplet separately.

**3.1.1. Transition  ${}^5I_8 \rightarrow {}^5F_5$ .** For the group of absorption lines associated with the transition  ${}^5I_8 \rightarrow {}^5F_5$ , several overlapping peaks are clearly detected. The polarized spectra corresponding to this transition are shown in figure 2 for the whole multiplet. In  $C_3$  symmetry, the  ${}^5F_5$  splits into seven Stark sublevels: three A and four E levels. In the  $\sigma$ -polarized spectrum, five energy levels have been identified, which correspond to the four expected E levels and one extra level, probably due to the splitting produced by the different lattice sites of  $\text{Ho}^{3+}$  in  $\text{LiNbO}_3$ . Something similar is observed in the  $\pi$ -polarized spectrum where six bands appear: in this case, three pairs of lines from transitions to the three excited Stark levels with an A character. In addition, thermal population of  ${}^5I_8$  Stark levels other than the lowest energy level is taking place. This has been proved by means of their temperature dependence.



Table 1 shows the energy positions and symmetry character of the different Stark levels for this multiplet together with an assignment of the different crystal-field sites for  $\text{Ho}^{3+}$  in  $\text{LiNbO}_3$  (when possible). This has been carried out by means of a comparison of the absorption spectra of the  $\text{Ho}^{3+}$  singly doped  $\text{LiNbO}_3$  samples and the  $\text{Ho}^{3+}$  MgO co-doped  $\text{LiNbO}_3$  samples, as will be discussed later. Decreasing peaks with increasing MgO content have been associated with one type of site, labelled I in the tables, while increasing peaks have been associated with sites labelled II.

Table 1. Absorption lines of  $\text{Ho}^{3+}$  in  $\text{LiNbO}_3$  in the region of the  ${}^5I_8 \rightarrow {}^5F_5$  transition.

$\lambda$ (nm)	Energy ( $\text{cm}^{-1}$ )	Stark level identification
642.80	15 557	A $\rightarrow$ A (II) } A $\rightarrow$ A (I) }
643.54	15 539	
645.90	15 482	
646.70	15 463	A $\rightarrow$ E
647.19	15 451	A $\rightarrow$ A
647.70	15 439	A $\rightarrow$ A
649.00	15 408	A $\rightarrow$ A (II) } A $\rightarrow$ A (I) }
649.20	15 403	
649.50	15 396	A $\rightarrow$ E
650.40	15 375	A $\rightarrow$ E
651.70	15 344	A $\rightarrow$ E (II) } A $\rightarrow$ E (I) }
652.18	15 333	
652.70	15 321	Thermal
653.42	15 304	A $\rightarrow$ E

For some of the transitions, contributions in the  $\sigma$  and  $\pi$  spectra have been observed simultaneously. This is due to the overlapping with thermalized transitions from the first excited states of the fundamental level as revealed by the temperature dependence of the spectra. Single thermalized transitions have also been detected.

3.1.2. Transition  ${}^5I_8 \rightarrow {}^5F_4 + {}^5S_2$ . Figure 3 shows the absorption spectra from the  ${}^5I_8$  to the  ${}^5F_4 + {}^5S_2$  multiplets which are very close in energy. As previous calculations have shown, the most intense absorption in this region must be related to the  ${}^5F_4$  multiplet [16]. According to the  $J$ -values and the  $C_3$  symmetry, one expects 2E+1A levels for the  ${}^5S_2$  multiplet, and 3E+3A levels for the  ${}^5F_4$  multiplet. However it was not possible to resolve the Stark transitions for each multiplet. The spectra show six absorption peaks with a clear  $\sigma$  character and five levels with a clear  $\pi$  character. Within the more intense peaks detected in both  $\sigma$  and  $\pi$  spectra, a splitting is observed which is due to different lattice sites for  $\text{Ho}^{3+}$  in  $\text{LiNbO}_3$ , as it shows the change in their relative intensities on comparison with the MgO co-doped sample. Table 2 shows the energy of the peaks and their symmetry character. The association of some of the absorption peaks with  $\text{Ho}^{3+}$  type I or type II sites has only been possible for two of the bands observed. In other cases, although it is impossible to distinguish between sites, we can relate some pairs of peaks to one Stark level split by the effect of two different sites. These are indicated by braces in tables 1–4.

3.1.3. Transition  ${}^5I_8 \rightarrow {}^5F_3$ . The polarized absorption spectra in the region of the  ${}^5I_8 \rightarrow {}^5F_3$  transition are shown in figure 4. The energies and symmetry character of the Stark levels are listed in table 3. 13 lines can be observed, although just five (3A+2E) are expected in  $C_3$  symmetry. Some of the extra lines are due to thermal population of

**Table 2.** Absorption lines of  $\text{Ho}^{3+}$  in  $\text{LiNbO}_3$  in the region of the  ${}^5\text{I}_8 \rightarrow {}^5\text{F}_4 + {}^5\text{S}_2$  transition.

$\lambda$ (nm)	Energy ( $\text{cm}^{-1}$ )	Stark level identification
538.87	18 557	A $\rightarrow$ E
539.52	18 535	A $\rightarrow$ E
539.82	18 524	A $\rightarrow$ E (II)
540.17	18 512	A $\rightarrow$ E (I)
540.82	18 490	A $\rightarrow$ A
541.77	18 458	A $\rightarrow$ A
542.89	18 420	A $\rightarrow$ A
543.10	18 413	A $\rightarrow$ A
543.48	18 400	A $\rightarrow$ E
544.13	18 378	A $\rightarrow$ A
544.66	18 360	A $\rightarrow$ E

levels in the  ${}^5\text{I}_8$  multiplet, as in the former cases. The other lines have been identified as site splitting of the Stark levels by comparing the results with those for the  $\text{LiNbO}_3:\text{MgO}:\text{Ho}^{3+}$  samples and because they always appear in pairs with very similar intensities. For this multiplet the major part of the absorption spectrum has been identified.

**Table 3.** Absorption lines of  $\text{Ho}^{3+}$  in  $\text{LiNbO}_3$  corresponding to the  ${}^5\text{I}_8 \rightarrow {}^5\text{F}_3$  transition.

$\lambda$ (nm)	Energy ( $\text{cm}^{-1}$ )	Stark level identification
485.90	20 580	A $\rightarrow$ E (II)
486.15	20 569	A $\rightarrow$ E (I)
486.57	20 552	Thermal
487.38	20 517	A $\rightarrow$ E (II)
487.55	20 510	A $\rightarrow$ A (II)
487.70	20 504	A $\rightarrow$ E (I)
487.95	20 494	A $\rightarrow$ A (I)
488.20	20 483	Thermal
488.93	20 452	A $\rightarrow$ A
489.91	20 420	A $\rightarrow$ A (II)
490.06	20 405	A $\rightarrow$ A (I)
490.22	20 359	Thermal
490.56	20 384	Thermal

**3.1.4. Transition  ${}^5\text{I}_8 \rightarrow {}^5\text{G}_6$ .** In figure 5, the spectra of  $\text{Ho}^{3+}:\text{LiNbO}_3$  corresponding to the transition  ${}^5\text{I}_8 \rightarrow {}^5\text{G}_6$  are shown. This band is the most intense in the visible region of the spectrum. The large number of lines predicted by crystal-field theory ( $5A+4E$ ) makes it difficult to identify the whole spectra. However, an attempt has been made to assign the ten lines found to transitions between the ground level and the  ${}^5\text{G}_6$  multiplet. Not all the Stark levels of  ${}^5\text{G}_6$  have been detected. For three of the observed bands, two different lattice sites can be detected (table 4), although, in this case, a complete assignment (site I or II) cannot be made. At 458.34 nm, two peaks cannot be resolved.

### 3.2. Effect of co-doping with Mg

Figures 7 and 8 show the absorption spectra in the region corresponding to the transitions  ${}^5\text{I}_8 \rightarrow {}^5\text{G}_6$  and  ${}^5\text{I}_8 \rightarrow {}^5\text{F}_3$ , respectively, for  $\text{LiNbO}_3:\text{Ho}^{3+}$  compared with

Table 4. Absorption lines of  $\text{Ho}^{3+}$  in  $\text{LiNbO}_3$  in the region of the  $^5I_8 \rightarrow ^5G_6$  transition.

$\lambda$ (nm)	Energy ( $\text{cm}^{-1}$ )	Stark level identification
450.54	22 195	A $\rightarrow$ E
451.03	22 171	A $\rightarrow$ E
451.71	22 138	A $\rightarrow$ A
452.03	22 122	A $\rightarrow$ A
452.86	22 082	A $\rightarrow$ E
453.15	22 067	A $\rightarrow$ E
454.98	21 979	A $\rightarrow$ A
455.22	21 977	A $\rightarrow$ A
457.75	21 846	A $\rightarrow$ E
458.34	21 818	A $\rightarrow$ A + E

$\text{LiNbO}_3:\text{MgO}:\text{Ho}^{3+}$ . A diminution in the optical absorption of the  $\text{Ho}^{3+}$  ions by a factor of around 3 is observed after co-doping with  $\text{MgO}$ . The same behaviour is observed in the rest of the transitions. This effect has been reported to occur in  $\text{LiNbO}_3$  doped with other rare-earth ions when  $\text{MgO}$  is added [17]. As is known,  $\text{Mg}^{2+}$  ions occupy  $\text{Li}^+$  sites in the  $\text{LiNbO}_3$  matrix and it changes the segregation of the other impurity in the  $\text{LiNbO}_3$  matrix.

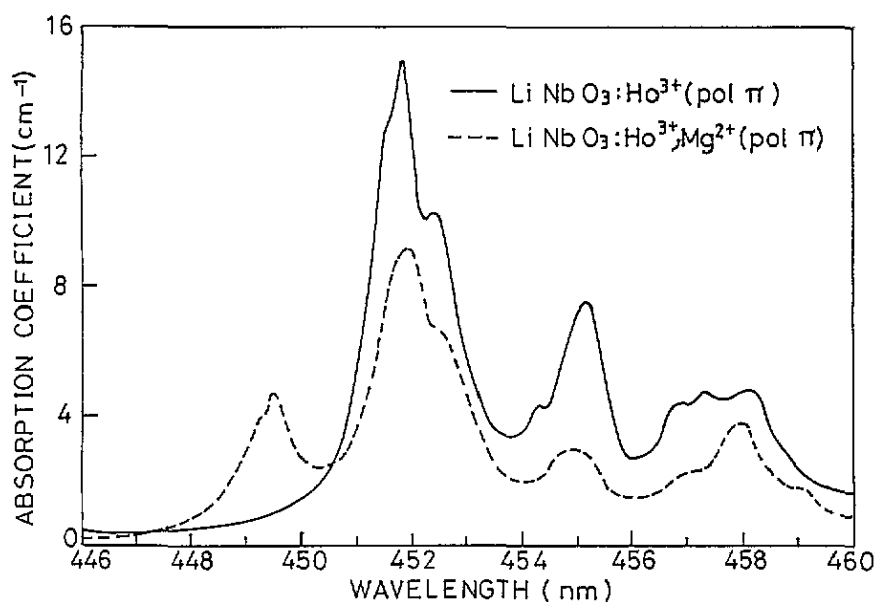


Figure 7. Comparison between the  $\pi$ -polarized  $^5I_8 \rightarrow ^5G_6$  transition of  $\text{LiNbO}_3:\text{Ho}^{3+}$  and  $\text{LiNbO}_3:\text{MgO}:\text{Ho}^{3+}$ . Spectra were taken at 15 K.

A more detailed inspection of these figures reveals an important effect observed when co-doping with  $\text{MgO}$ : a change in the relative intensity of the pairs of lines in the absorption bands associated with  $\text{Ho}^{3+}$  ions (see the peaks indicated by arrows in figure 8). This effect has also been observed in  $\text{LiNbO}_3$  crystals doped with other rare-earth ions [17, 18] and supports the existence of two optically non-equivalent sites for  $\text{Ho}^{3+}$  in  $\text{LiNbO}_3$ . As has

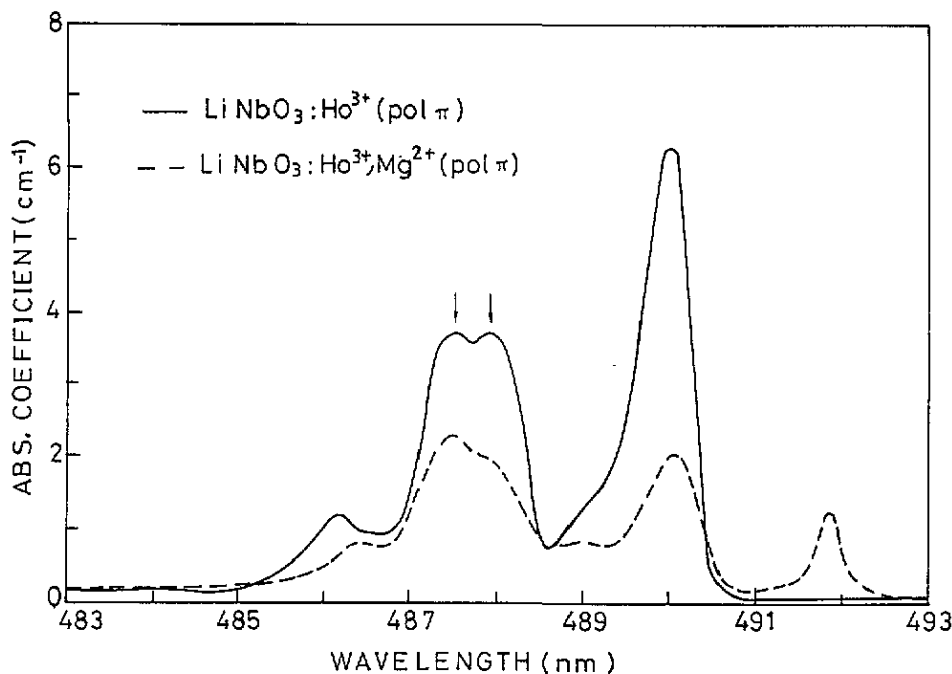


Figure 8. Comparison between the  $\pi$ -polarized  $^5I_8 \rightarrow ^5F_3$  transition of  $\text{LiNbO}_3:\text{Ho}^{3+}$  and  $\text{LiNbO}_3:\text{MgO}:\text{Ho}^{3+}$ . Spectra were taken at 15 K.

already been reported,  $\text{Mg}^{2+}$  ions occupy  $\text{Li}^+$  sites [9, 19, 20]. Thus, a relative reduction in the number of  $\text{Ho}^{3+}$  ions in  $\text{Li}^+$  sites with respect to  $\text{Ho}^{3+}$  ions in  $\text{Nb}^{5+}$  sites takes place when  $\text{MgO}$  is added. As a consequence, absorption peaks due to  $\text{Ho}^{3+}$  ions in  $\text{Li}^+$  sites will decrease with respect to  $\text{Ho}^{3+}$  ions in  $\text{Nb}^{5+}$  sites. This was indeed detected in our absorption spectra and was used to make an identification of some of the doublets in terms of lattice sites I and II (see tables 1–4) which could be associated with  $\text{Li}^+$  or  $\text{Nb}^{5+}$  sites, respectively. Further work is now under way to confirm this point.

In addition, it is clearly appreciated that, when  $\text{MgO}$  is added, new absorption lines, which did not appear in the singly doped crystal, are detected. These lines are always clearly observed on the higher- or lower-energy sides of peaks in the absorption spectra associated with some multiplets (figures 7 and 8, respectively). Another peculiarity is that these new lines appear only in the  $\pi$  spectra. As reported for other systems, these bands should be associated with  $\text{Ho}^{3+}$  ions perturbed by the proximity of  $\text{Mg}^{2+}$  ions, giving place to new crystalline-field sites and therefore new bands. The fact that the new bands appear only in the  $\pi$  spectra suggests that all these new transitions of the perturbed  $\text{Ho-Mg}$  centres are  $A \rightarrow A$  type. A possible explanation for the  $A$  character of these bands is that the perturbation from  $\text{Mg}^{2+}$  ions is strong enough to reduce the  $C_3$  local symmetry of some  $\text{Ho}^{3+}$  ions, splitting all the  $E$  levels into two  $A$  levels. This could also explain why the new bands are only seen on the sides of the absorption peaks of the multiplets.

On the other hand, an increase in the half-width of the  $\text{Ho}^{3+}$  absorption lines is also found. This could be interpreted in terms of a perturbation of the crystal-field sites of  $\text{Ho}^{3+}$  by the presence of  $\text{Mg}^{2+}$  ions, giving rise to an inhomogeneous broadening which is greater than in the case of the singly doped system.

#### 4. Fluorescence spectra

Site-selective spectroscopy measurements have been performed for the LiNbO<sub>3</sub> system. The complexity in the spectra of Ho<sup>3+</sup> in LiNbO<sub>3</sub>, mainly due to overlap between absorption lines of different sites, makes it difficult to resolve the emissions associated with only one site. Indeed, owing to the large number of sublevels involved in the transition and the small energy separation between them, it is not possible to make an assignment of the peaks observed. However, the fluorescence measurements should confirm the presence of different Ho<sup>3+</sup> sites in the matrix.

Fluorescence measurements have been carried out in the region of 550 nm ( $^5S_2 + ^5F_4 \rightarrow ^5I_8$ ) where the most intense emission of Ho<sup>3+</sup> ions takes place in the visible region. Excitation has been performed in the  $^5G_6$  and in the  $^5F_3$  multiplets. The emission spectra were taken at a low temperature (15 K) in order to simplify the spectra, avoiding emissions from thermally populated Stark levels of the  $^5F_4 + ^5S_2$  excited multiplets. The excitation was carried out in the  $\pi$  configuration.

As an example, figure 9 shows the emission spectra associated with the  $^5S_2 + ^5F_4 \rightarrow ^5I_8$  transition of Ho<sup>3+</sup> in a LiNbO<sub>3</sub> crystal under three different excitation wavelengths lying in the  $^5F_3$  multiplet at 490.9, 490.0 and 489.6 nm. These excitation wavelengths lie within a Stark level in which different sites had been detected by optical absorption measurements. Excitation wavelengths are indicated by arrows in the corresponding absorption spectrum in the inset.

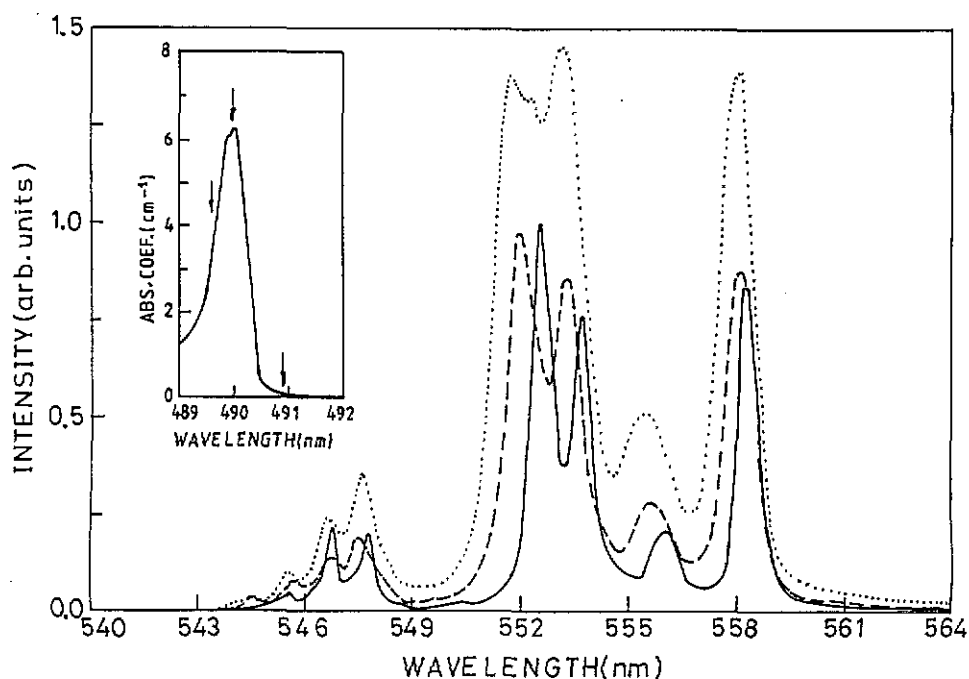


Figure 9. Emission bands associated with the  $^5F_4 + ^5S_2 \rightarrow ^5I_8$  transition of LiNbO<sub>3</sub>:Ho<sup>3+</sup>, taken at 15 K for different excitation wavelengths: —,  $\lambda_{exc} = 490.90$  nm; ---,  $\lambda_{exc} = 490.00$  nm; ·····,  $\lambda_{exc} = 489.60$  nm. In the inset, the absorption band corresponding to the  $^5I_8 \rightarrow ^5F_3$  transition is shown. Excitation wavelengths are indicated by arrows.

As can be seen in figure 9, the emissions obtained for each excitation wavelength are quite different; the associated emission lines are shifted and their relative intensities are also different. This confirms the existence of at least two sites for  $\text{Ho}^{3+}$  ions in our system. Figures 9(a) and 9(b) correspond to the emission spectra under excitation mainly into two different sites, while the spectrum in figure 9(c) shows the contribution of both sites, because at 489.6 nm both sites are simultaneously excited.

Similar results are also obtained for other excitation wavelengths in the  ${}^5\text{F}_3$  multiplet and inside the  ${}^5\text{G}_6$  multiplet. In most cases, the emission obtained was the envelope curve of the two emissions represented in figures 9(a) and 9(b). This is because the two  $\text{Ho}^{3+}$  sites were simultaneously excited because of the overlap of their optical absorption bands.

Emission spectra have also been studied in the region of the  ${}^5\text{S}_2 + {}^5\text{F}_4 \rightarrow {}^5\text{I}_8$  transition for samples co-doped with  $\text{Mg}^{2+}$  ions. Excitation in the  ${}^5\text{F}_3$  and  ${}^5\text{G}_6$  bands has been performed and, as it occurs for the case of the absorption spectra, a change in the relative intensities and in the width of the emission lines is observed as a consequence of the change in the distribution of sites for  $\text{Ho}^{3+}$  in the  $\text{LiNbO}_3$  crystal when  $\text{Mg}^{2+}$  ions are added.

Excitation has also been performed in the new absorption bands which appear when MgO is incorporated. In these cases, the spectra obtained were similar to the previous spectra, and no new emission lines were detected. This confirms that the new absorption lines appearing in the  $\text{LiNbO}_3:\text{MgO}$  samples are associated with  $\text{Ho}^{3+}$  ions.

## 5. Conclusion

The optical spectroscopy of  $\text{Ho}^{3+}$  in  $\text{LiNbO}_3$  has been investigated in the visible range of the spectrum. It appears as a complicated system from the viewpoint of a complete characterization due to several features such as high  $J$ -value and the presence of thermalized transitions. In spite of this, the determination of the energy position and the polarization character for most of the crystal-field levels has been determined.

As occurs in most of the previously studied doped  $\text{LiNbO}_3$ , the coexistence of different lattice sites for  $\text{Ho}^{3+}$  ions has been observed. In this sense, the use of the absorption spectra of doubly doped  $\text{LiNbO}_3:\text{MgO}:\text{Ho}^{3+}$  is helpful and reveals the presence of two non-equivalent optical sites. Site-selective fluorescence spectroscopy confirms the presence of at least two  $\text{Ho}^{3+}$  sites which could be related, as in other rare-earth-doped  $\text{LiNbO}_3$  crystals, to a  $\text{Li}^+$  and a  $\text{Nb}^{5+}$  lattice site, although this point must be confirmed using other techniques.

The appearance of the new crystal-field site when co-doping with MgO, which is needed to avoid photorefractive damage in the host crystal, has also been detected by absorption measurements.

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