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## Nd<sup>3+</sup> centres induced by ZnO or MgO codoping LiNbO<sub>3</sub>

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**Abstract.** Laser spectroscopy has been applied to systematically investigate the effect of MgO or ZnO codoping on the Nd<sup>3+</sup> centres formed in LiNbO<sub>3</sub>. Both codopant oxides produce the same effect, so two new Nd<sup>3+</sup> centres appear in both LiNbO<sub>3</sub>(MgO):Nd and LiNbO<sub>3</sub>(ZnO):Nd crystals. These new centres correspond to a small percentage (less than 1%) of Nd<sup>3+</sup> ions, which are displaced from Li<sup>+</sup> sites to a new lattice site. The possible sites for these Nd<sup>3+</sup> centres are discussed.

### 1. Introduction

Nd<sup>3+</sup> doped lithium niobate is a laser system with excellent perspectives for integrated optics [1]. In fact, the combination of the high gain of the Nd<sup>3+</sup> ion with the non-linear, electro-optic and acousto-optic properties of LiNbO<sub>3</sub> has allowed the development of small compact solid state lasers (minilasers), which incorporate several functions (self-*Q* switch, self-mode locking, self-frequency doubling, ...) in the laser crystal itself [2,3]. However, this crystal presents undesirable optical damage due to the photorefractive (PR) effect.

This damage can be greatly reduced by codoping with 5% or more of MgO [4] so that LiNbO<sub>3</sub>(MgO):Nd is the usual laser crystal. Moreover, the MgO additional codoping also influences other properties. In particular, the Nd<sup>3+</sup> ion distribution into different centres is affected as a result of MgO [5–7] codoping. This behaviour has also been reported for other rare earth and Cr<sup>3+</sup> ions in LiNbO<sub>3</sub> [8,9]. Thus, a full understanding of the map (structure and distribution) of the Nd<sup>3+</sup> centres in LiNbO<sub>3</sub>(MgO):Nd will help to improve the design and performance of this and other doped laser materials based on the LiNbO<sub>3</sub> host crystal.

Using laser spectroscopy (LS) it has been previously determined that the Nd<sup>3+</sup> ions are mainly distributed into three non-equivalent centres (denoted as Nd-1, Nd-2 and Nd-3)

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in  $\text{LiNbO}_3$ , while a new centre (denoted as Nd-Mg) appeared as a consequence of MgO codoping [5–7]. Combining Rutherford back-scattering (RBS)/channelling and LS the nature of the Nd-1, 2, 3 centres was tentatively interpreted as a result of three different off-centred positions from regular  $\text{Li}^+$  sites [10]. On the other hand, the nature of the Nd-Mg centres, i.e., the new centres induced by the codoping effect, is still an open question.

Recently Volk *et al* [11] have shown that the PR damage is also considerably reduced by codoping with 4% or more of ZnO. In principle, as in the case of MgO, it is expected that the  $\text{Nd}^{3+}$  centres should be affected by ZnO codoping. In fact, changes in the centre distribution of the trivalent ions have been reported in  $\text{LiNbO}_3(\text{ZnO}):\text{Cr}$  [12] and  $\text{LiNbO}_3(\text{ZnO}):\text{Er}$  [13].

In this work LS has been systematically applied to perform a comparative investigation on the  $\text{Nd}^{3+}$  centres formed in  $\text{LiNbO}_3(\text{ZnO}):\text{Nd}$  and  $\text{LiNbO}_3(\text{MgO}):\text{Nd}$  crystals. Thus, the effects of a different codoping on the  $\text{Nd}^{3+}$  centres can be established.

## 2. Experimental details

Congruent crystals ( $[\text{Li}]/[\text{Nb}] = 0.945$ ) of  $\text{LiNbO}_3$  were doped with 1% of Nd and 6% of MgO or 5% of ZnO in the melt. From these crystals, plate samples were cut perpendicular to the ferroelectric  $c$  axis to perform optical measurements.

Laser spectroscopy experiments were carried out using a Ti-sapphire tunable laser (Spectra Physics, model 3900) as excitation source (resolution  $\leq 1 \text{ \AA}$ ). A 30 cm focal length monochromator followed by an Si photodiode was used to analyse the light emission. Excitation spectra were taken under broad-slit ( $\geq 25 \text{ \AA}$ ) emission conditions. This is equivalent to recording absorption spectra, but with the spectral resolution of the Ti-sapphire laser ( $\leq 1 \text{ \AA}$ ). All fluorescence (excitation and emission) spectra were taken at 5 K.

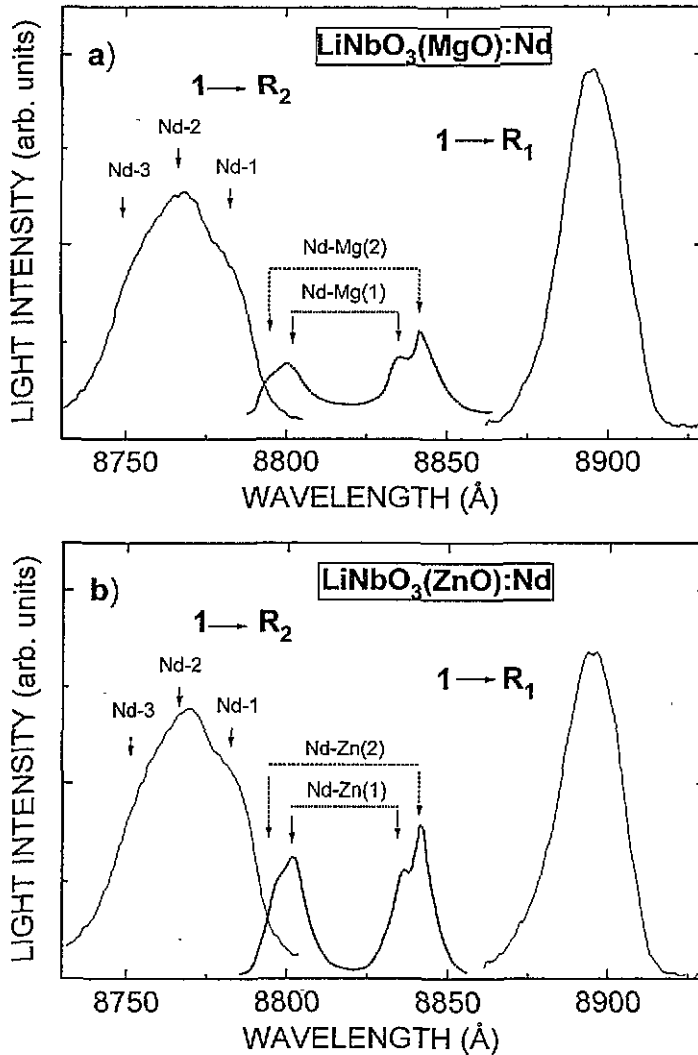
## 3. Experimental results and discussion

Figure 1 shows the 5 K excitation (absorption) spectra of the  $\text{Nd}^{3+}$  ion in the  ${}^4I_{9/2} \rightarrow {}^4F_{3/2}$  spectral region for the two crystals used in this work. This spectral region has been reported to be particularly suitable for detecting multicentres 6, 7, 10]. Due to the trigonal ( $C_3$ ) symmetry of regular lattice sites, the  ${}^4F_{3/2}$  state splits into two components ( $R_1$  and  $R_2$ ), so that the  ${}^4I_{9/2} \rightarrow {}^4F_{3/2}$  absorption consists of two bands associated with transitions from the lowest Stark component (denoted as 1) of the  ${}^4I_{9/2}$  state to the two Stark components of the  ${}^4F_{3/2}$  state.

The triplet structure observed over the  $1 \rightarrow R_2$  Stark transition (the spectrum shown as a full line) indicates the presence of the Nd-1, 2, 3 centres in both codoped crystals, which has also been observed in  $\text{Nd}^{3+}$  singly doped  $\text{LiNbO}_3$  crystals. Recently, the presence of additional centres of the same nature has been reported [14]. However their relative concentration is very small. On the other hand, this 'centre structure' is not so clearly resolved in the  $1 \rightarrow R_1$  transition. One way or the other, this structure is characterized by 'broad' bands.

Figure 1 also reveals the presence of new  $\text{Nd}^{3+}$  centres in the codoped crystals. This is manifested by the appearance of new  $1 \rightarrow R_1$ ,  $R_2$  excitation bands (see the spectrum shown as a broken line), which are not present in the singly doped  $\text{LiNbO}_3$  crystals. These centres have been labelled as Nd-Mg and Nd-Zn centres in figure 1. It should be mentioned that the latter bands have been enlarged by a factor of 10. In fact these bands could not be observed in the optical absorption spectra.

At this point, it is important to point out two aspects related to these new centres. The



**Figure 1.** 5 K excitation spectra of the Nd<sup>3+</sup> centres: Nd-1,2,3 centres, full line and  $\lambda_{em} = 1080$  nm; Nd-Mg (Nd-Zn) centres, broken line (scale enlarged by a factor of 10) and  $\lambda_{em} = 1092$  nm. (a) LiNbO<sub>3</sub>(MgO):Nd. (b) LiNbO<sub>3</sub>(ZnO):Nd.

first is the similar excitation spectra of Nd-Mg and Nd-Zn centres, which is an indication that in both centres the Nd<sup>3+</sup> ions are located in very similar crystalline fields, but different from that of the Nd-1, 2, 3 centres. The second relevant aspect is the clear doublet structure appearing in the  $1 \rightarrow R_1$  excitation bands. Indeed, this structure indicates the existence of two non-equivalent Nd-Mg or Nd-Zn centres in each codoped crystal.

Hereafter these centres will be denoted as Nd-Mg(1) (11 318 cm<sup>-1</sup>), Nd-Mg(2) (11 309 cm<sup>-1</sup>), Nd-Zn(1) (11 314 cm<sup>-1</sup>) and Nd-Zn(2) (11 306 cm<sup>-1</sup>) according to their corresponding  $1 \rightarrow R_1$  excitation peak, in which there is a better resolution than in the  $1 \rightarrow R_2$  excitation bands.

The Nd-Mg and Nd-Zn centres were selectively excited by pumping with adequate laser radiation in order to gain additional information about the energy levels associated

with them. In fact these site selective fluorescence experiments allowed us to assign the  $1 \rightarrow R_1 R_2$  transitions of each centre, as displayed in figure 1. Figure 2 shows, as a representative example, the  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  emission spectra obtained for the Nd-Zn(1) and Nd-Zn(2) centres. This spectral region is the more relevant for laser applications. As expected the Nd-Mg centres present emission spectra, not given by the sake of brevity, quite similar to those of the Nd-Zn centres.

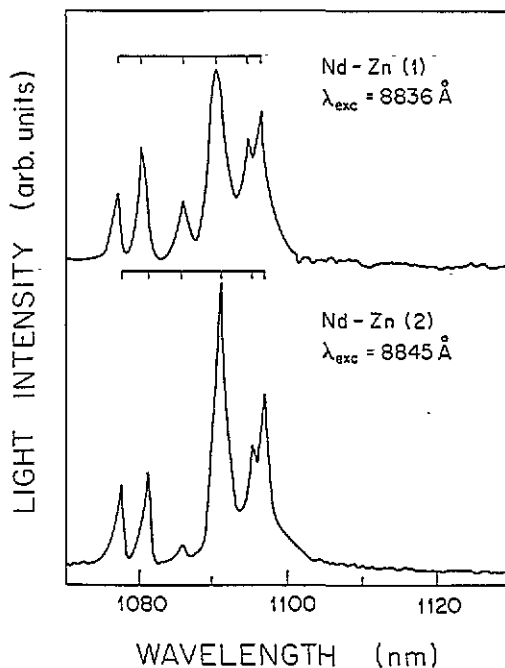


Figure 2. 5 K selective emission spectra (the  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  transition) corresponding to the Nd-Zn centres. Marks indicate the Stark structure in the  ${}^4I_{11/2}$  state.

From the set of selective fluorescence (excitation and emission) spectra the Stark multiplets and barycentres of the  ${}^4I_J$  and  ${}^4F_{3/2}$  states can be determined for the Nd-Mg and Nd-Zn centres.

We now focus our attention on the  ${}^4F_{3/2}$  state. This state splits only by deviations from the cubic symmetry, so the amount of its splitting gives a measure of the trigonal ( $C_3$ ) crystalline field around the  $Nd^{3+}$  ions in the different centres. On the other hand, the barycentre position of the  ${}^4F_{3/2}$  state is useful in comparing the lattice sites occupied by the  $Nd^{3+}$  ions forming the different centres [10].

Figure 3 shows the amount of splitting and the barycentre (measured from the  ${}^4I_{9/2}$  barycentre) of the  ${}^4F_{3/2}$  state for each Nd-Mg and Nd-Zn centre. For the sake of comparison, the above values reported for the Nd-1, 2, 3 centres have been included in this schematic figure. It can be seen that the latter centres have the same barycentre and only differ in their trigonal splitting. This is in agreement with three different off-centred positions inside the  $Li^+$  octahedron for the  $Nd^{3+}$  ions of the Nd-1, 2, 3 centres [10].

Figure 3 also reveals that the Nd-Zn and Nd-Mg centres have (within experimental uncertainty) the same  ${}^4F_{3/2}$  barycentre (black squares), which is different from the barycentre of the Nd-1, 2, 3 centres. This fact might indicate that the  $Nd^{3+}$  ions forming the Nd-Mg and Nd-Zn centres enter the same lattice site, but not the  $Li^+$  octahedron (which is the site

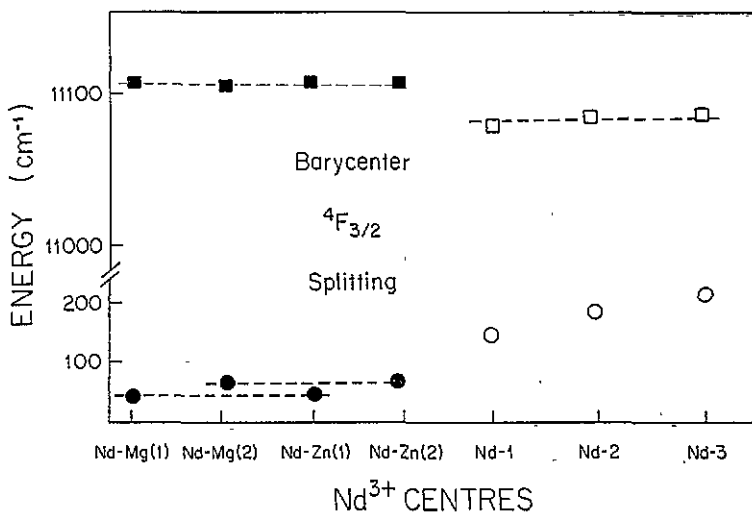


Figure 3. The splitting and barycentre of the  ${}^4F_{3/2}$  state for the Nd<sup>3+</sup> centres.

occupied by the Nd-1, 2, 3 centres). Therefore, according to the structure of LiNbO<sub>3</sub>, three possible sites are candidates for these centres: a Nb<sup>5+</sup> octahedron, an empty octahedron or an empty tetrahedron. Unfortunately, optical spectroscopy alone does not allow us to determine the lattice site related to the Nd-Mg and Nd-Zn centres.

On the other hand, the relative concentration of Nd-Mg and Nd-Zn centres must be a very low fraction (around less than 1%) of the total Nd concentration, as inferred from the low excitation (absorption) intensity in relation to the Nd-1, 2, 3 centres. Because of this fact, it is not possible to determine the lattice position by RBS/channelling, as was done for the case of the Nd-1, 2, 3 centres [10].

In spite of the difficulty of determining the lattice site occupied by the Nd<sup>3+</sup> ions in the Nd-Mg and Nd-Zn centres, some conclusions related to these centres can be advanced from our spectroscopic results.

(i) ZnO and MgO codoping affect the Nd<sup>3+</sup> distribution in the same way. In both cases the formation of new centres is favoured.

(ii) The fine structure observed in the excitation spectra related to the Nd-Mg (Nd-Zn) centres indicates two similar but non-equivalent environments for the Nd<sup>3+</sup> ions giving place to the Nd-Mg1 (Nd-Zn1) and Nd-Mg2 (Nd-Zn2) centres. They differ in their crystal field splitting, as can be seen in figure 3 (black circles). This fact, recently observed for other centres in LiNbO<sub>3</sub> [8], is probably due to different local charge compensating mechanisms of the Nd<sup>3+</sup> ions in these centres.

(iii) In spite of the difference between the ionic radii of Mg<sup>2+</sup> (0.65 Å) and Zn<sup>2+</sup> (0.74 Å) ions, the Nd-Mg and Nd-Zn centres are very probably the same, i.e., the Nd<sup>3+</sup> ions forming these centres have the same local structure, as can be noted from their quite similar  ${}^4F_{3/2}$  splitting and barycentre. This might be an important indication that the effect of MgO or ZnO codoping is to remove a small percentage (less than around 1%) of Nd<sup>3+</sup> ions from the Li<sup>+</sup> site to another lattice site. Also, as mentioned before, the Nd-1, 2, 3 excitation bands are broader than those of the Nd-Mg (Nd-Zn) centres, pointing then to a lattice site less sensible to strain broadening/lattice disorder effects for these latter centres.

As we said previously, optical spectroscopy alone does not allow us to determine the

lattice site occupied by the  $\text{Nd}^{3+}$  ions in the Nd-Mg (Nd-Zn) centres. However, the spectroscopic differences with respect to the Nd-1,2,3 centres allow to advance some conclusions.

As mentioned before, the crystal field splitting of the  ${}^4F_{3/2}$  state is larger for the Nd-1,2,3 centres than that of the Nd-Mg or Nd-Zn centres. Now, if the  $\text{Nd}^{3+}$  ions were to occupy the  $\text{Nb}^{5+}$  octahedron, as this one is less distorted than the  $\text{Li}^+$  octahedron, one might think of this as the reason for a smaller splitting. On the other hand, as the Nb-O distances are smaller than those of Li-O one would expect, on the basis of a point charge model, a splitting of other  ${}^4I_j$  multiplets of the Nd-Mg (Nd-Zn) centres at least as large as those of the Nd-1,2,3 centres, but however these latter have been reported to be larger [7]. Then the possibility of  $\text{Nd}^{3+}$  ions occupying the  $\text{Nb}^{5+}$  octahedron sites might be ruled out.

The two possible assignments left are the empty octahedron and empty tetrahedron. However, the very narrow optical bands of the Nd-Mg/Nd-Zn centres in comparison to those of the Nd-1,2,3 centres could indicate a non-octahedral site for the former ones. In fact a similar behaviour has been reported to occur for  $\text{Tm}^{3+}$  doped yttrium scandium gallium garnet [15]. In this crystal both dodecahedral and octahedral sites were occupied and the bandwidth of the optical bands was broader for the latter sites. Therefore the Nd-Mg/Nd-Zn centres formed in the codoped  $\text{LiNbO}_3$  crystal should be consistent with the occupation of tetrahedral empty sites by  $\text{Nd}^{3+}$  ions. This conclusion is also in agreement with the suggestions made through RBS/channelling experiments [8].

In order to confirm this possible assignment, experiments dealing with light polarization and higher Mg/Zn concentrations are now in progress.

#### 4. Conclusions

Experimental results reveal that the  $\text{Nd}^{3+}$  dopant ions are distributed in at least five centres in both  $\text{LiNbO}_3(\text{MgO}):\text{Nd}$  and  $\text{LiNbO}_3(\text{ZnO}):\text{Nd}$  crystals: three centres that also appear in the singly doped crystal (Nd-1,2,3 centres) and two centres formed as a consequence of codoping (Nd-Mg(1,2) or Nd-Zn(1,2)). The spectroscopic parameters of the Nd-Mg and Nd-Zn centres are practically the same, indicating that MgO or ZnO codoping removes a small percentage (around 1%) of  $\text{Nd}^{3+}$  ions from the  $\text{Li}^+$  site to another lattice site, likely the empty tetrahedron of the  $\text{LiNbO}_3$  structure.

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