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Site selective spectroscopy and RBS/channeling in optically active ion doped LiNbO_3 crystals

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INTRODUCTION

LiNbO_3 is a non-linear crystal with a variety of possible applications as a host laser matrix. Doping with laser active centers can lead to small compact lasers (minilasers) including several functions (self-frequency doubling, self-Q switching, waveguides ...) required in integrated optics [1]. The presence of non-equivalent centres (multicentres) has been recently ascertained for a number of ion-doped LiNbO_3 systems [2]. However, the structure and lattice location of these multicentres are still being subject of controversy.

According to that, several optically active ion-doped LiNbO_3 crystals have been investigated by using, in parallel, two quite different techniques. By site selective spectroscopy (SSS) we can determine the number of non-equivalent multicentres as well as their spectroscopic properties. By Rutherford backscattering spectrometry (RBS)/channeling the lattice site(s) occupied by the dopant ions can be determined [3].

Combining these two techniques on the same crystals we have studied the Nd^{3+} , Pr^{3+} and Yb^{3+} multicentres and their lattice location in the LiNbO_3 host.

EXPERIMENTAL

Congruent LiNbO_3 crystals doped either with (0.2 %, 0.5%) Pr, (1 %) Nd or (0.5 %) Yb were grown by the Czochralski technique. SSS was performed exciting either with a Ti-Sapphire laser or with a N_2 pumped pulsed dye laser. RBS/Channeling experiments with He^+ ions were carried out in a 2 MV Van de Graaff accelerator of the Institut de Physique de Lyon. The same samples were used in the SSS and RBS experiments, so that possible

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variations from crystal to crystal were discarded.

RESULTS

Figure 1 shows the 15 K optical spectra (absorption-Pr and Yb³⁺ or excitation-Nd-) corresponding to single transitions between defined Stark

Figure 1

levels (states indicated in the figure) for the three ions investigated in this work. Thus the structure appearing in these bands indicates the presence of, at least, three non-equivalent centres for the Nd³⁺ and Yb³⁺ ions and four for the Pr³⁺ ions. These centres can be selectively excited with the adequate laser photon energy, so that the energy levels of each individual centre can be obtained. Polarization spectroscopy reveals a main C₃ symmetry for all the centres.

In principle the structure of LiNbO₃ permits three possible octahedral locations; Li⁺, Nb⁵⁺ or a free intrinsic octahedron, all of them having C₃ symmetry. By RBS/channeling the occupied site can be determined comparing the angular scans of Nb⁵⁺ with those of the dopant ions along relevant directions (channels) [3].

Figure 2

Figure 2 shows the angular scans for Nb and Nd ions along the $\langle 0001 \rangle$, $\langle 04\bar{4}5 \rangle$ and $\langle 02\bar{2}1 \rangle$ channels. The projection of the lattice structure on planes perpendicular to these directions have also been displayed. The similar $\langle 0001 \rangle$ scans for Nd (full dots) and Nb (open dots) indicate that the Nd^{3+} ions lie, as expected, in the mentioned octahedral positions (all screened by Nb ions). The scan along the $\langle 04\bar{4}5 \rangle$ channel excludes the location in the free octahedron, which should produce a flux peak in the Nd yield due to the mid-channel position of these sites. The different $\langle 02\bar{2}1 \rangle$ angular scans for Nb and Nd indicate that Nd^{3+} ions are located in Li octahedra. However the anomalous shape of this Nd angular scan suggests that these ions are not located in regular Li^+ sites. Rather these angular scans have been explained supposing a shifting from the regular Li^+ site along the c axis for the dopant ions [3].

Figure 3

DISCUSSION

The spectroscopic results indicate the presence of three non-equivalent (or more) sites for the investigated dopant ions. In all of them the dopant ions are in C_3 local symmetry and (for Nd and Pr) only the Li-octahedrons are occupied. However the angular scans along some specific channels reveal non regular Li^+ sites. Thus the non equivalent centres of the dopant ions can be explained as a result of different off-centred positions in the Li octahedron. Figure 4 shows the dependence of the $|B_2^0|$ trigonal crystal field parameter as a function of the displacement from the regular Li^+ position,

calculated as in ref. [4]. Positive, $x > 0$, shifting leads to a more cubic

Figure 4

octahedral environment whereas negative, $x < 0$, shifting produces a less cubic octahedral symmetry (higher trigonal crystalline field). Therefore the non equivalent multicentres for a determined ion are a consequence of different off-centres positions of the ion in the Li octahedron. The reason for these different off-centre positions has to be related to presence of defects associated to the non-stoichiometry of $LiNbO_3$; Nb antisites, $Nb^*(Nb^{5+}$ ions in Li^+ sites) and Nb vacancies, Nb_v , [5]. In fact the formation of Nb^*-Nb_v complexes has been reported to be more energetically favorable than the diluted Nb^* and Nb_v defects [6]. Thus the formation of the non equivalent $M^{3+}(Li)-Nb_v$ and $M^{3+}(Li)$ complexes, M^{3+} being the dopant ion ($M = Nd, Pr$ or Yb), could give place to the different M^{3+} multicentres. However, at the present time, a definite structure for these centres can not be given.

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