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Impurity sites of $\text{LiNbO}_3\text{:Er}^{3+}$ codoped with MgO or ZnO

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ABSTRACT

The optical properties of Er^{3+} doped LiNbO_3 , $\text{LiNbO}_3(\text{MgO})$ and $\text{LiNbO}_3(\text{ZnO})$ have been studied. Polarized absorption and laser excited luminescence spectra at liquid-He temperature show different structure dependent on the co-dopants (MgO, ZnO). The relationship between the optical characteristics and the impurity sites location is discussed.

1.-INTRODUCTION

LiNbO_3 crystals doped with rare earth ions have been extensively investigated in the last years due to their potential use in electro-optics and laser technology [1-3]. In particular, Er^{3+} and Nd^{3+} doped LiNbO_3 have been already demonstrated in active waveguides devices [4-6].

Although, pure LiNbO_3 crystals are damaged under high intensity illumination, the problem is greatly reduced codoping the material with MgO at a concentration of about 5% in the melt [7].

This additional doping not only affects the photorefractive characteristics of LiNbO_3 , but also the site location and the optical properties of the active ions, as it has been already observed in several rare earth doped $\text{LiNbO}_3(\text{MgO})$ crystals [3].

Recently, it has been reported that photorefractive damage in LiNbO_3 can be prevented by codoping with ZnO more efficiently than with MgO [8]. However, the effect on the optical properties of the rare earth dopants have not been studied yet

In this work, the effect of codoping LiNbO_3 with MgO or ZnO, on the optical properties of Er^{3+} ions is discussed through a comparative study of low temperature polarized absorption and luminescence experiments.

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2.-EXPERIMENTAL

Er doped LiNbO_3 , $\text{LiNbO}_3\text{:MgO}$ and $\text{LiNbO}_3\text{:ZnO}$ crystals were grown by the Czochralski method from grade I Johnson-Mathey powder. The erbium to niobium concentration was around 1% (molar fraction in the melt) in all cases. Magnesium and zinc oxide were incorporated in a ratio of 6% molar fraction in the melt.

Polarized absorption spectra were obtained by using a Cary 14 spectrophotometer and a calcite polarizer. Luminescence spectra were obtained under dye laser excitation and a multichannel analyzer detection.

Low temperature measurements were carried out with the crystal sample mounted at the cold station of a close-cycle helium cryostat.

3.-RESULTS AND DISCUSSION

The polarized absorption spectra of Er^{3+} ions in LiNbO_3 can be explained considering a C_3 symmetry for Er^{3+} ions. Nevertheless several multiplets exhibit a two-components structure which was initially interpreted as due to multisite occupancy [1]. Although the term "ion-site" has been extensively used in the literature to denote the different optical bands observed in rare earth doped LiNbO_3 , recent Rutherford Back Scattering (RBS) studies suggest that they may arise from slight distortions of a single lattice site, so that we shall adopt the term "optical centre" to label the different bands appearing in the optical spectra [9].

Polarized absorption measurements at low temperature show that MgO or ZnO codoping affects the impurity distribution, and favors the appearance of a single optical centre. This effect is observed in the different transitions of Er^{3+} ions in the visible and infrared range (350 nm - 1700 nm) and is illustrated in Figure 1 for the $^4I_{15/2} \rightarrow ^4S_{3/2}$ transition of $\text{LiNbO}_3(\text{ZnO})\text{:Er}^{3+}$.

This transition (see inset in Figure 1), exhibits two opposite polarization components $1 \rightarrow p$ (π -polarization) and $1 \rightarrow q$ (σ -polarization). It is apparent in Figure 1 that Er^{3+} doped crystals show a doublet structure (Er-1, Er-2), while the absorption bands for ZnO co-doped crystals are substantially narrower showing the appearance of a single band (Er-1). A similar result is obtained for MgO co-doped crystals [10].

Fig.1. Er^{3+} absorption spectra ($^4\text{I}_{15/2} \rightarrow ^4\text{S}_{3/2}$) for LiNbO_3 and $\text{LiNbO}_3(\text{ZnO})$.

While this narrowing of the absorption bands is the only major change detected for ZnO doped crystals, additional effects are observed in the case of MgO codoping. In this case, in a similar way to that observed for other rare earth doped crystals [3], new lines (Er-Mg) appear in the optical spectra.

The changes associated with the new Er-Mg lines, are better observed by laser excited luminescence experiments. Figure 2 shows the emission spectra associated to the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transition for Er^{3+} (dotted line) and Er-Mg (full line) crystals. The spectra are excited at wavelengths corresponding to Er-1 or Er-Mg bands, whose absorption spectra are depicted in the inset. The Er-Mg transitions are consistently shifted to lower energies either in absorption or emission.

Figure 2. Emission spectra ($^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) for Er-1 and Er-Mg excitation.

In relation to the origin of the different Er bands, although optical data cannot unambiguously identify the lattice location of the impurity, it can be concluded that the addition of photorefractive damage inhibitors (MgO or ZnO) favors Er-1 optical centres in relation to Er-2 centres.

These results are consistent with RBS experiments [11] which indicate a preferential location for Er^{3+} ions nearby Li^+ sites. This occupancy is almost total for MgO co-doped crystals, while a fraction of Er^{3+} ions are "randomly" located for crystals without co-doping. Although RBS results are not available for ZnO co-doped crystals, a similar explanation seems highly plausible.

In relation to the appearance of new lines in co-doped crystals it should be noted that only MgO induces these lines while they are absent in ZnO co-doped crystals. Only very recently, RBS and optical studies performed in Nd^{3+} doped $\text{LiNbO}_3(\text{MgO})$ [9], suggest the connection of these Mg-induced lines with the location of a fraction of rare earth ions at non-octahedral sites.

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