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SITE SELECTIVE SPECTROSCOPY OF Nd^{3+} AND Cr^{3+} SITES IN $LiNbO_3$ CRYSTALS CODOPED WITH Mg^{2+} IONS

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Abstract - The fluorescence properties of Nd^{3+} in $Nd : MgO : LiNbO_3$ and Cr^{3+} in $Cr : MgO : LiNbO_3$ systems have been systematically studied after site selective laser excitation. Three kinds of sites have been detected for the active (Nd^{3+} or Cr^{3+}) ions. Two sites correspond to the active ion located in Li^+ and Nb^{5+} lattice positions, and also appear in the singly (without MgO) doped systems. Codoping with Mg^{2+} ions induce the appearance of a new site for the active ion, together with a decreasing in the Li/Nb occupation ratio.

1. Introduction.

The understanding of the optical properties of transition metal and rare earth ions in $LiNbO_3$ has gained a considerable interest after demonstration of laser action in miniature and waveguide devices of $Nd : MgO : LiNbO_3$ crystals (1,2). These materials appear very promising because they can exploit the laser properties of the active ion together with the non-linear characteristic of $LiNbO_3$, making possible the development of self-frequency doubled lasers. For these applications the addition of about 5 mol % of MgO is necessary to reduce the so called "optical damage", due to the photorefractive effect (3).

Site location of the active ion can play an important role in the optical and laser properties of this ion-host combination. In fact, preliminary studies in $LiNbO_3 : Nd, Mg$ have shown the formation of a new Nd^{3+} site in comparison with the sites appearing in the singly doped system (3).

In this work laser-site selective spectroscopy has been used to study the fluorescence bands of Nd^{3+} and Cr^{3+} active ions, which appear in $LiNbO_3 : MgO : Nd$ and $LiNbO_3 : MgO : Cr$, respectively. The interest in the last system lies in the possibility of using this material as broadly tunable laser, due to broad emission band of Cr^{3+} ion (5). Special emphasis is put in the spectral regions of laser interest.

2. Experimental.

The crystals used in this work were grown by Czochralski method. Singly doped crystals had an active ion to Niobium concentration ratio of 0.33 %. In doubly doped samples this ratio was 0.15 % and MgO was incorporated in a ratio of 5 mol %. Samples were cut perpendicular to the c axis.

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Figure 1: a) Partial energy level diagram for Nd^{3+} in LiNbO_3 . b) $R_1 \rightarrow 1$ emission line for $\text{LiNbO}_3 : \text{Nd}$ (dashed line) and $\text{LiNbO}_3 : \text{Nd, MgO}$ (full line) ($T = 10\text{K}$).

Emission spectra were excited by laser radiation; Ar^+ ion, dye, $\text{Nd}:\text{YAG}$ or Ti:Sapphire lasers. Emitted signal was sent to an EMI-9958-QB photomultiplier or Si-photodiode, depending on the studied spectral region. Resolution was of $1.6 \text{ \AA}$ in the best cases.

3. Results.

The procedure for studying the formation of new active (Nd^{3+} or Cr^{3+}) sites in both ($\text{LiNbO}_3 : \text{Nd} : \text{MgO}$ and $\text{LiNbO}_3 : \text{Cr} : \text{MgO}$) systems has been to compare the fluorescence (excitation and emission) spectra of singly and doubly doped samples.

$\text{LiNbO}_3 : \text{Nd, MgO}$

Nd^{3+} ion presents a rich absorption spectrum due to various transitions between stark energy levels of different terms inside the $4f^3$ configuration of the ion. Figure 1a shows a partial diagram showing the relevant energy levels responsible for luminescence. The low temperature emission spectrum of this ion consists in two set of lines corresponding to transitions from the low component of the $4F_{3/2}$ term to the $4I_{11/2}$ and $4I_{9/2}$ lower terms. The $R_1(4F_{3/2}) \rightarrow 1(4I_{9/2})$ line is well isolated in the emission spectrum and can be used for site selective spectroscopy.

Figure 1b shows the $R_1 \rightarrow 1$ emission spectra, at 10 K, for both singly and doubly doped systems. The peaks denoted as Nd-1 and Nd-2 have been previously associated with Nd^{3+} ions entering Li^+ and Nb^{5+} lattice sites, respectively (4). In addition the doubly doped system shows a new $R_1 \rightarrow 1$ emission band (labelled as Nd-Mg) at higher energy, which was associated with the formation of a new Nd^{3+} site perturbed by a close Mg^{2+} ion. It should be noted as the $\text{Nd-1}/\text{Nd-2}$ ratio for doubly doped samples decreases because of Mg^{2+} ions are preferentially entering Li^+ sites.

Therefore there are three Nd^{3+} sites in $\text{LiNbO}_3 : \text{Nd, Mg}$ with different emission spectra. Figure 2 shows the fluorescence (excitation and emission) spectra of these sites in the spectral

Figure 2: Excitation and emission spectra of $Nd-1$ and $Nd-2$ (dashed line) and $Nd-Mg$ (full line) sites, taken on the $LiNbO_3:Nd,MgO$ sample ($T = 10K$).

region of interest for laser applications, $R_1(^4F_{3/2}) \rightarrow ^4I_{11/2}$ transitions. The excitation spectrum of the $Nd-Mg$ site (full line) is well separated from that of $Nd-1$ and $Nd-2$ sites (dashed line). Therefore $Nd-Mg$ site can be selectively excited and its $R_1 \rightarrow ^4I_{11/2}$ emission spectrum appears also shown in figure 2. At variance, the overlapping between $Nd-1$ and $Nd-2$ sites leads to emission spectra which can not be completely resolved.

The emission lifetime corresponding to each Nd^{3+} site has also been measured giving a value of $95\mu s$ for $Nd-1$ and $Nd-2$ sites and being reduced to $75\mu s$ for new $Nd-Mg$ site. This result suggests that $Nd-Mg$ site is emitting more efficiently than $Nd-1$ and $Nd-2$ sites. On lasing this material, it should be taken into account what center is the responsible for laser action. In fact, this could explain why it is necessary to change the pumping wavelength to get two different laser polarized lines at $1.085\mu m$ and $1.093\mu m$ in $Nd:MgO:LiNbO_3$ miniature lasers (1).

$LiNbO_3:Cr,MgO$

The experimental results obtained for the $LiNbO_3:Cr,Mg$ systems are similar to the above described using the Nd^{3+} ion as active center.

$LiNbO_3:Cr$ is an intermedial crystal field material (near to the cross-over of Cr^{3+} (6)) and then the emission of this ion consists in the $^4T_2 \rightarrow ^4A_2$ broad luminescence, useful for tunability, and the $^2E \rightarrow ^4A_2$ sharp emission.

Figure 3 shows the emission spectra for the singly (dashed line) and doubly doped (full line) crystals under excitation with light into the $^4T_1 \rightarrow ^4A_2$ broad band. The $^4T_2 \rightarrow ^4A_2$ vibronic emission band (useful for tunability) is slightly different for both systems, the peak position being shifted to lower energies for the $Cr:MgO:LiNbO_3$. However the best information on multisites can be obtained from the $^2E \rightarrow ^4A_2$ sharp emission. This transition, which appears split in two components labelled as R_1 and R_2 in order of decreasing energy, is very sensitive to slight changes in the local environment. The main $^2E \rightarrow ^4A_2$ peaks have been associated (7) with the R_1 emission of $Cr-1(Li^+)$ and $Cr-2(Nb^{5+})$ sites. The small peak at higher energy is the R_2 emission peak of the $Cr-1(Li^+)$ site. As in the $LiNbO_3:Nd,Mg$ system, codoping with Mg^{2+} ions induces the appearance of two new peaks which are the R_1 and R_2 components of a new Cr^{3+} center, induced by the proximity of Mg^{2+} ions. This new site has been denoted as $Cr-Mg$ site.

Figure 3: Emission spectra (10 K) of $\text{LiNbO}_3 : \text{Cr}$ (dashed line) and $\text{LiNbO}_3 : \text{Cr, MgO}$ (full line) samples.

Lifetime of the ${}^4T_2 \rightarrow {}^4A_2$ vibronic emission changes from $10\mu\text{s}$ for the singly doped crystal to $17\mu\text{s}$ for the doubly doped one. The lifetime of the R_1 emissions are $400\mu\text{s}$ for $\text{Cr} - 1$ and $\text{Cr} - 2$ sites, and $500\mu\text{s}$ for $\text{Cr} - \text{Mg}$ site. This variation can be explained by considering spin-orbit admixing between the 4T_2 and 2E levels as in the case of Cr :doped garnets (8).

Finally, we have to mention that the effect of adding Mg^{2+} ions to the Cr doped LiNbO_3 also affect the absorption spectrum of Cr^{3+} shifting the ${}^4A_2 \rightarrow {}^4T_1$ and ${}^4A_2 \rightarrow {}^4T_2$ vibronics bands to the red. This results explain why the green single crystals become pink after codoping with Mg^{2+} ions.

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