Selective optical bleaching of Cr^{3+} luminescence at low temperature in MgO codoped near stoichiometric $LiNbO_3$:Cr crystals

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Selective R-line emission of the Cr^{3+} ions in near stoichiometric $LiNbO_3$ crystals codoped with MgO has been studied at low temperature under excitation into the $^4A_2 \rightarrow {}^4T_1$ transition. The emission intensity of R lines associated with Cr^{3+} ions located in Nb^{5+} sites, $[Cr]_{Nb}$ centers, was observed to decrease with the illumination time, whereas those ascribed to other Cr^{3+} ions, such as those located in the Li site, $[Cr]_{Li}$ centers, are optically stable. The selective bleaching is explained by considering the photoinization of Cr^{3+} ions in Nb sites and the formation of Nb^{4+} complexes (small polaron).

$LiNbO_3$ doped with rare earth and transition metals is an interesting material for applications in linear and nonlinear optically active devices. In pure $LiNbO_3$ crystals of congruent composition (where the Li/Nb ratio is 0.946) an optically active dopant such as rare-earth or transition-metal ions are incorporated into the host matrix in the octahedral Li^+ lattice site.[1] In the case of Cr^{3+} ions, the as-grown crystal is uniformly green in color because of the broad absorption band in the visible region ascribed to transitions to the $^4T_1$ and $^4T_2$ energy levels.[2,3] Several different Cr^{3+} defect centers have been identified:[2,4,5] the center denoted γ-$[Cr]_{Li}$ corresponds to undisturbed Cr^{3+} in the Li^+ lattice site; the centers α-$[Cr]_{Li}$ and β-$[Cr]_{Li}$ which are perturbed by $[Nb]_{Li}$ and $[V]_{Li}$ (V: vacancy), respectively. In order to substitute the Nb^{5+} sites with Cr^{3+} ions additional codoping with other divalent cations, such as Mg^{2+} or Zn^{2+}, above a certain threshold corresponding with the composition of the $LiNbO_3$, is required. In the case of congruent composition this is ~4.5 mol %. At cation concentrations slightly higher than this concentration, there is an abrupt change in the crystal's color, from green to pink.[3] At these high concentrations of cations both optical and paramagnetic resonance techniques detected new Cr^{3+} centers, in coexistence with the $[Cr]_{Li}$ centers, which have been ascribed to Cr^{3+} ions located in the Nb^{5+} sites ($[Cr]_{Nb}$ centers).[3] The isotropic electron paramagnetic resonance (EPR) signal associated with a new center is explained considering that a Mg^{2+} ion close to the Cr^{3+} ion perturbs the center, producing a more cubic symmetry.[6,7] As the threshold value of ~4.5 mol % coincides with the concentration of Li^+ defect sites—Li^+ vacancy, $[V]_{Li}$, and antisites ($[Nb]_{Li}$, Nb^{5+} ion located in Li^+ vacancy) in congruent $LiNbO_3$ samples—it has been suggested that the appearance of the $[Cr]_{Nb}$ center starts when all Li^+ defect sites are filled by dopant divalent cations. In such circumstances, Cr^{3+} ions can be incorporated in both Li^+ and Nb^{5+} sites.[3]

In near stoichiometric $LiNbO_3$ samples, where the ratio of Li/Nb is ~1, the total number of defects (Li^+ vacancy and antisites) is expected to be much less and hence the cation concentration threshold is lower than in congruent samples. In fact, it has recently been reported that pink-colored near stoichiometric crystals can be grown by incorporating only 1 mol % of MgO in the melt.[8]

Electron traps, in $LiNbO_3$ crystals, have been related to cation impurities as well as Nb^{5+} antisites and intrinsic Nb^{5+} ions. In the case associated with the Nb^{5+} ions the electron capture is expected to be delocalized onto the surrounding ions, forming a Nb^{4+} complex, which can be considered as a small polaron[9] involving either a regular Nb_{Nb} or a Nb_{Li} antisite. In an early work, it has also been suggested that Mg^{2+} ions are also an effective electron trap, forming Mg^+ complexes similar to the Nb^{4+} complex when the Mg^{2+} ions concentration is above the 4.5 mol %.[10] However, more recently it has been reported that in MgO and ZnO doped $LiNbO_3$, the electron trap is associated with the Nb^{5+} ions (antisites and intrinsic sites) and not with divalent cation impurities.[11]

The system of $LiNbO_3$:Cr:MgO doped with a cation concentration high enough to induce the coexistence of the two Cr^{3+} centers would therefore be a particularly interesting case to study the electron trapping property of this system. This paper reports preliminary results of the observed optical bleaching of the spectral lines of Cr^{3+} centers in near stoichiometric $LiNbO_3$:Cr (0.2 mol %) codoped with 2 mol % of MgO.

Near stoichiometric $LiNbO_3$ crystal doped with 0.2 mol % of Cr_2O_3 and with 2% of MgO in the melt was grown in air by the top-seeded solution pulling method at a pull rate of 0.3 mm/h. The as-grown boule shows a uniform pink color along the full length of the boule. Absorption spectra were measured with a Varian Cary-SE spectrophotometer. Emission spectra were excited using an Ar-ion laser at 514.5 nm.
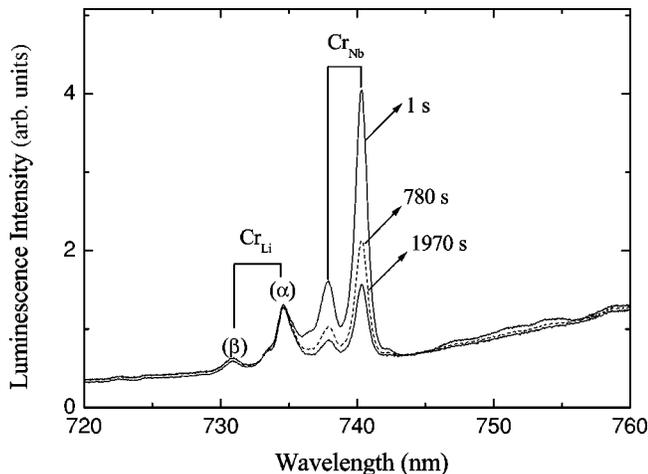
FIG. 1. 10-K photoluminescence spectra for different illumination time periods.

FIG. 2. Variation of the 740.3-nm R-line emission time decays as a function of excitation power density at 10 K.

The emitted light was dispersed in a SPEX 500M monochromator and detected with a Hamamatsu R-2949 photomultiplier or a charge-coupled device (CCD) array detector when a fast wavelength scan was required.

Figure 1 shows the emission spectra under continuous-wave (cw) 514.5-nm argon laser excitation (50 mW) at 20 K for different illumination time periods. The 514.5-nm wavelength excites the $^4A_2 \rightarrow {}^4T_1$ transition of the $[Cr]_{Nb}$ centers and also the $[Cr]_{Li}$ centers.[12] The R lines ascribed to the α- and β-$[Cr]_{Li}$ centers[2,4,5] are observed together with those associated with the $[Cr]_{Nb}$ center (ε in Macfarlane's notation[4]) centered at 740.3 and 738.0 nm. The emission of these two R lines has been previously reported in congruent MgO codoped LiNbO$_3$ and MgO codoped near stoichiometric LiNbO$_3$ crystals.[2,4] The emission of the R lines associated with γ centers is only observed at higher temperatures (>50 K).[5,12] It is important to note that, at difference with the spectra previously published, the intensity of the R lines ascribed to the $[Cr]_{Nb}$ center are initially more intense than that of the α-$[Cr]_{Li}$ center and decreases with increasing illumination time, whereas the emission intensity of the R lines ascribed to the α- and β-$[Cr]_{Li}$ centers remains constant. The emission intensity ratio of the two R lines ascribed to the $[Cr]_{Nb}$ center remains relatively constant as they decrease with increasing illumination time. This result clearly illustrates that a selective optical bleaching mechanism is taking place in this crystal system and is only related to this $[Cr]_{Nb}$ center. The previously published spectra are similar to our spectra after long-time excitation.

Figure 2 shows the dependence of the 740.3-nm R-line emission time decays as a function of excitation power density. These intensity decay curves show a bleaching of the emission intensity of 33% and 86% for ~3.3 and ~6 W/mm^2 excitation power density, respectively, and reaching a similar "plateau" level for long illumination time, suggesting some sort of equilibrium condition was reached. After a dark period of several minutes at 10 K, a recovery of only a few percent of the luminescence intensity is observed, whereas a full recovery is obtained only after heating the sample up to room temperature.
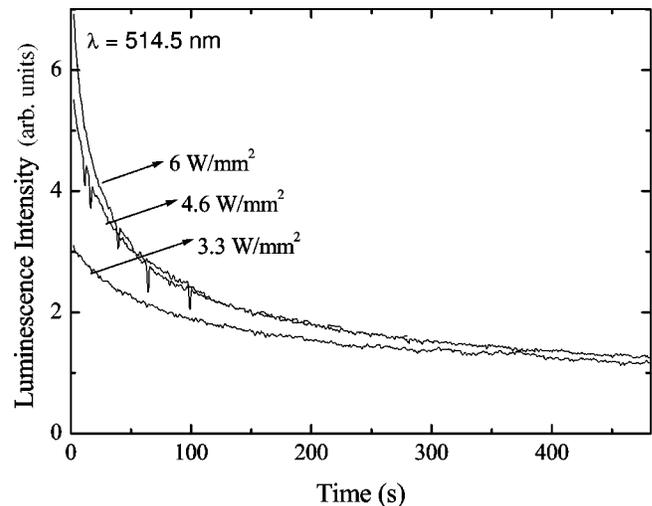
Figure 3 shows the absorption spectra before and after illumination (~1 h) with the 514.5-nm argon laser line at 10 K. In this experiment the front and back surfaces of the crystal are masked showing only an aperture of ≈2 mm in diameter. The laser beam was expanded in order to obtain uniform illumination over the aperture, which was subsequently used for the absorption measurements. An illumination power density of ~1 W/mm^2 was estimated. The absorption spectrum before bleaching is essentially due to the broad absorption bands ascribed to $[Cr]_{Li}$ and $[Cr]_{Nb}$ centers.[12] The presence of $[Cr]_{Li}$ centers in the overall spectrum only becomes more noticeable after subtracting the contribution of the absorption due to this $[Cr]_{Nb}$ center. Figure 3 shows that after illumination at 514.5 nm the optical absorption due to this $[Cr]_{Nb}$ center decreases, which is in agreement with the bleaching behavior observed of the R-line emission associated with this center. However, the bleaching magnitude is less than that reported in Fig. 1 for the R lines, due to the different illumination light power density used in the two experimental setups. It is important to note that a broadband
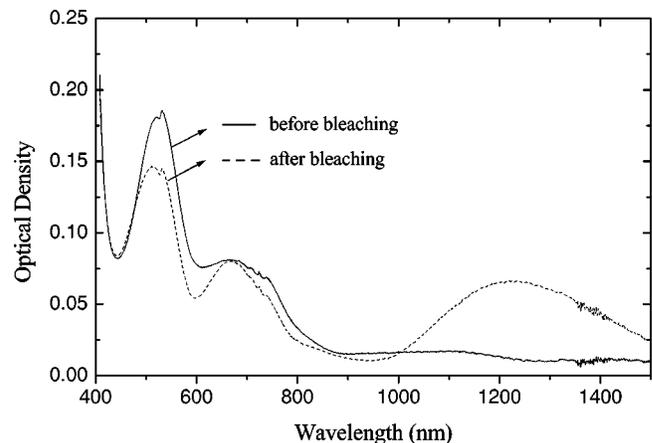
FIG. 3. Absorption spectra before and after illumination with the 514.5-nm argon laser line at 10 K (power density ~1 W/mm^2).

centered at 1200 nm (~1 eV) emerged after 514.5 nm illumination. A similar absorption band has been reported in MgO and ZnO doped LiNbO$_3$ crystals and has been ascribed to a small polaron (Nb^{4+}) formed by a trapped electron.[11] Although Nb^{4+} polarons have also been reported located in antisites, however in the present case this possibility is discarded because in near stoichiometric LiNbO$_3$:Cr:MgO crystals the expectation of much reduced intrinsic defects suggest a very low concentration of antisites. Furthermore, the absorption bands ascribed to antisite polaron is at 1.6 eV.[13]

In previous works it has been established that the high-energy side of the broad $^4A_2 \rightarrow {}^4T_1$ transition overlapped with the charge transfer region in MgO and ZnO codoped LiNbO$_3$:Cr crystals.[3] Taking this into account, the optical bleaching of Cr^{3+} ions could be achieved if a stable electron trap is involved in the process. As commented above, electron traps together with the Nb^{4+} complexes can be formed in MgO doped congruent LiNbO$_3$ crystals when the cation concentrations exceed the 4.5% threshold. It is therefore not unreasonable that a similar situation is found in near stoichiometric crystals, but at a lower MgO concentration.

The structure suggested by EPR and electron-nuclear double-resonance (ENDOR) measurements for this [Cr]$_{Nb}$ center is a Cr^{3+} ion substituting into a Nb^{5+} site with a Mg^{2+} ion in close proximity forming a Cr^{3+}-Mg^{2+} complex.[7] The precise position of the Mg^{2+} ion is undetermined: however, a theoretical calculation by Yang *et al.*[14] suggested the Mg^{2+} ions may enter the structural vacancy sites on the [111] axis above the Cr^{3+} ions. If the high-energy band of the [Cr]$_{Nb}$ centers is photoexcited, the ionized electron could be trapped by the Nb^{5+} ions, resulting in the formation of small polarons (Nb^{4+} complex) and Cr^{4+}-Mg^{2+} complexes. This is supported by the presence of the absorption band centered at 1200 nm ascribed to small polarons and the decrease of the concentration of the initial Cr^{3+}-Mg^{2+} complexes.

In a first approximation calculation, taking $N(t)$ to be the ε-[Cr]$_{Nb}$ center concentration and the intrinsic Nb^{5+} ions the unique electron traps, the time dependence (dN/dt) under illumination can be written as

$$dN(t)/dt = -\sigma(\lambda)I(\lambda)DN(t) + kN'(t), \tag{1}$$

where $\sigma(\lambda)$ the absorption cross section of the [Cr]$_{Nb}$, $I(\lambda)$ the light intensity, D a factor proportional to the decay time of the $^4T_1 \rightarrow {}^4A_2$ radiative transition, and k the Nb^{4+} thermal ionization coefficient. $N_0 = N(t) + N'(t)$ is the initial concentration of [Cr]$_{Nb}$ centers where $N(t)$ is the [Cr]$_{Nb}$ center concentration and $N'(t)$ is the concentration of the Nb^{4+} complex. The analytical solution of Eq. (1) is

$$N = A + B \exp[-(t/\tau_0)], \tag{2}$$

where

$$A = kN_0/(\sigma DI + k),$$

$$B = I\sigma DN_0/(\sigma DI + k),$$
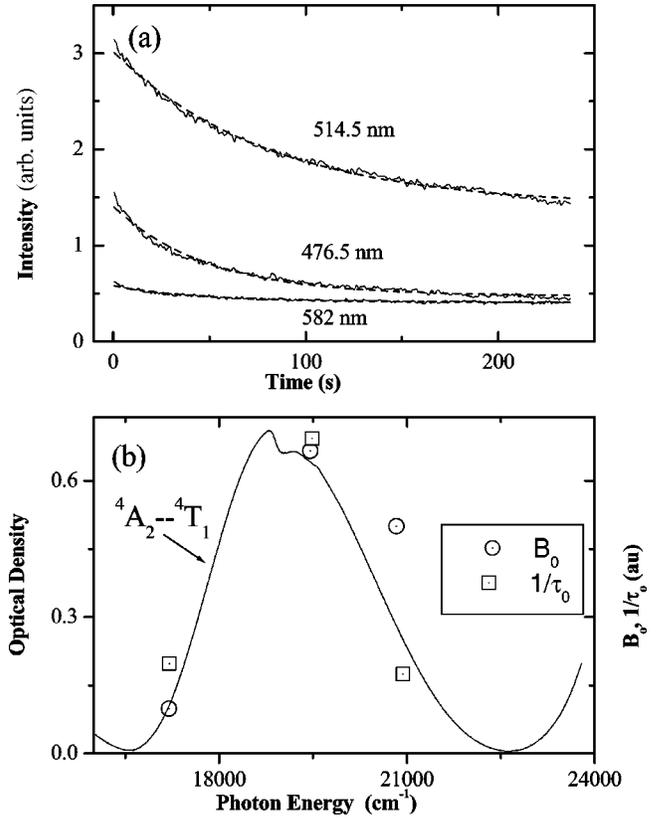
FIG. 4. (a) Variation of the luminescence decay curves of the *R*-line emission with the illumination wavelengths. (b) Dependence of the B_0 and $1/\tau_0$ parameters. The line corresponds to the optical density of the sample before bleaching.

$$1/\tau_0 = I\sigma D + k. \tag{3}$$

The luminescence intensity $L(t)$ is given by

$$L(t) = I\sigma(\lambda)N(t) = A_0 + B_0 \exp[-(t/\tau_0)], \tag{4}$$

where the expression for the A_0 and B_0 parameters is

$$A_0 = \sigma IkN_0/(\sigma DI + k),$$

$$B_0 = I^2\sigma^2 DN_0/(\sigma DI + k), \tag{5}$$

and the expression for $1/\tau_0$ is unchanged.

Figure 4(a) shows the luminescence decay curves of the *R*-line emission (740.3 nm) of the [Cr]$_{Nb}$ center at 10 K for three different excitation wavelengths with the same excitation power (~3.3 W mm^2). An acceptable fit to the experimental decay curves is achieved using expression (4). According to expression (5) and considering that $\sigma DI > k$ (for a weak thermal recovery), both parameters B_0 and $1/\tau_0$ are proportional to σ and therefore they have to follow the form of the broadband associated with the $^4A_2 \rightarrow {}^4T_1$ transition of the [Cr]$_{Nb}$ centers. This is presented in Fig. 4(b) where the variation of B_0 and $1/\tau_0$ as a function of the excitation wavelengths is plotted along with the high-energy absorption broadband of the [Cr]$_{Nb}$ centers.

In summary, this preliminary study revealed the following important points: (i) the photoionization of Cr^{3+} ions is

only effective when the active ion is located in the Nb^{5+} site forming a $[Cr]_{Nb}$ center; (ii) the role played by cations such as Zn^{2+} and Mg^{2+} in the optical stability is twofold: forcing the substitution of Cr^{3+} ions in the Nb^{5+} sites and destroying the Nb^{5+} antisites; (iii) the presence of the absorption band centered at 1200 nm and the bleaching of the $[Cr]_{Nb}$ center seems to give more evidence for the polaron electron trap model; (iv) a single exponential decay function described in the simple model used in this work can explain the general characteristic of the observed bleaching behavior.

Finally, this work reinforced the role of the Cr^{3+} ions as a successful optical probe for the study of defect structure especially in $LiNbO_3$ crystal.

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