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LETTER TO THE EDITOR

Compositional effect on Cr³⁺ site distribution in MgO or ZnO codoped LiNbO₃:Cr congruent and stoichiometric crystals

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Abstract. In this letter optical and electron paramagnetic resonance (EPR) techniques are used to investigate the effect of stoichiometry changes on the site distribution of Cr³⁺ ions in LiNbO₃:Cr crystals with (or without) MgO or ZnO codoping. In congruent (Li_{0.95}Nb_{1.01}O₃) crystals codoped with MgO (ZnO) the Cr³⁺ ions begin to enter into the Nb⁵⁺ site for concentrations higher than 4.5% (4.7%). Below this MgO (ZnO) threshold Cr³⁺ ions enter only into the Li⁺ sites. However, for nominally stoichiometric (LiNbO₃) crystals, the threshold concentration is much lower (between 0 and 0.2% in our crystals). The use of Cr³⁺ ions as an optical and paramagnetic probe to evaluate the grade of stoichiometry is considered.

The optical absorption and luminescence properties of doped crystals are largely determined by the local site symmetry of the optically active ions. In recent years, the position in the lattice and local environment of rare earth and transition metal ions in congruent Li_{0.95}Nb_{1.01}O₃ crystals have been widely studied because of their potential use in electro-optic and integrated devices [1]. Through the combination of different experimental techniques an acceptable knowledge of the location of these ions in the lattice has been achieved. For congruent Li_{0.95}Nb_{1.01}O₃ crystals doped with rare earth ions only the Li⁺ sites have been reported to be occupied, irrespective of the MgO concentration [2, 3]. At variance, in chromium doped Li_{0.95}Nb_{1.01}O₃ samples two types of Cr³⁺ centre have been observed [4, 5]. These correspond to Cr³⁺ at Li⁺ or Nb⁵⁺ sites and are labelled Cr_{Li}³⁺ and Cr_{Nb}³⁺ centres, respectively. For codoped samples with MgO concentration levels below 4.5% only the Cr_{Li}³⁺ centres are observed; above the threshold value of 4.5% the Cr_{Nb}³⁺ centre appears together with the previous one. As the MgO concentration increases, the population of Cr_{Li}³⁺ centre decreases whereas that for Cr_{Nb}³⁺ increases [6]. A similar effect has been also observed for ZnO codoped congruent samples, the threshold in this case being 4.7% [7]. Above these threshold values, substantial changes in the optical properties take place. So, the colour of the crystals changes from green to pink, the absorption edge shifts and photorefractive damage vanishes [6, 7].

The existence of a threshold (at 4.5% of MgO or 4.7% of ZnO) for all the above effects established [6–8] the link between the redistribution of the Cr³⁺ centres and the intrinsic defects. In particular it depends on the number of Li⁺ sites available for substitution by Cr³⁺ ions. It has been shown [6, 7] that in codoped congruent crystals the available Li⁺

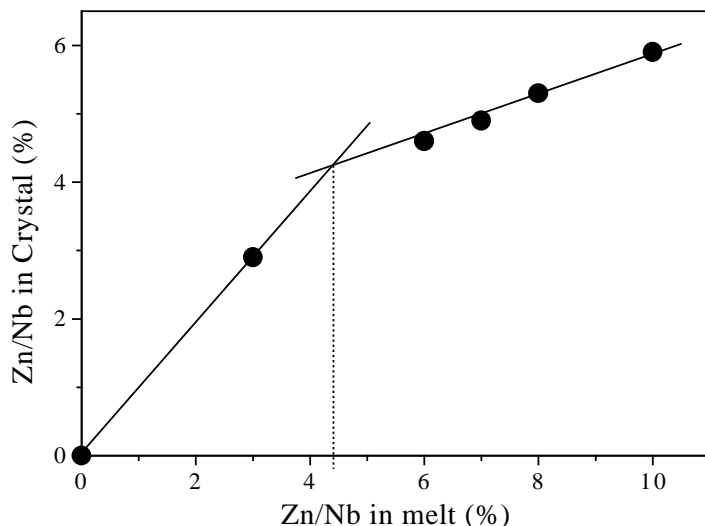


Figure 1. Dependence of the ZnO concentration measured in the crystal on the concentration added in the melt.

sites are preferentially occupied by Mg^{2+} (or Zn^{2+}) ions, resulting in a reduction in the $\text{Cr}_{\text{Li}}^{3+}$ centres as the MgO (or Zn) concentration increases. When all the available Li^+ sites are occupied by divalent cations, the Cr^{3+} ions substitute the Nb^{5+} ions resulting in the appearance of $\text{Cr}_{\text{Nb}}^{3+}$ centres.

As for the available Li^+ sites, two models for the intrinsic defects associated to the Li deficiency of congruent crystals have been reported (see [6] and references therein). In both models the Li deficiency gives rise to antisite defects, i.e. Nb^{5+} ions located in Li^+ sites ($\text{Nb}_{\text{Li}}^{5+}$). However, the mechanisms for total charge compensation are different. The Li-site vacancy model proposes a number of Li^+ vacancies together with antisites at the Li^+ sites and all Nb^{5+} sites occupied by Nb^{5+} , whereas, the Nb-site vacancy model proposes only antisites at the Li^+ sites and a number of Nb^{5+} vacancies at the Nb^{5+} sites. In both models the available Li^+ sites (Li^+ vacancies and/or antisites) amount to a concentration of 4.6%.

This letter extends the previous study for congruent crystals to nominally stoichiometric ones codoped with MgO or ZnO. In this case a much lower threshold value (0.2% or less) has been found for our crystals. This is explained by the dependence of the intrinsic defect concentration on the stoichiometric grade of the crystals.

Congruent ($\text{Li}_{0.95}\text{Nb}_{1.01}\text{O}_3$) and nominally stoichiometric (LiNbO_3) crystals will be named hereafter as C and S crystals, respectively. They were grown in air by the Czochralski method. The S crystals were grown from congruent composition melts with the addition of 7% weight of K_2O [9]. With this composition the error in the stoichiometric grade is evaluated to be around 0.15 mol%. Codoped crystals were grown by adding up to 10% of MgO or ZnO.

The Cr/Nb and Zn/Nb ratios were determined using the total reflection x-ray fluorescence technique (TRXFT). The Mg concentration was determined by the energy dispersive x-ray (EDX) technique.

Optical absorption spectra were obtained with a Hitachi 345 spectrophotometer. Details about the EPR measurements are described in [5].

Figure 1 shows the ZnO concentration in the crystal versus the concentration in the melt

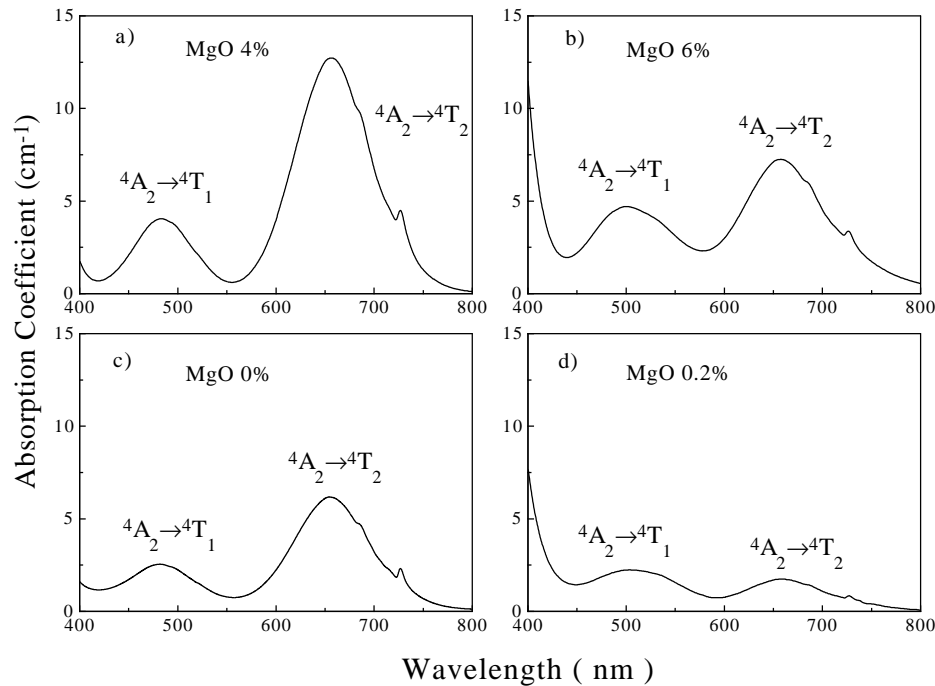


Figure 2. Absorption spectra measured at room temperature of: (a) congruent composition $\text{LiNbO}_3\text{:Mg:Cr}$ crystal (Mg and Cr concentrations in the crystal are 4% and 0.07%, respectively), (b) congruent composition $\text{LiNbO}_3\text{:Mg:Cr}$ crystal (Mg and Cr concentrations in the crystal are 6% and 0.07%, respectively), (c) nominally stoichiometric $\text{LiNbO}_3\text{:Cr}$ crystal (Cr concentration in the crystal is 0.032%) and (d) nominally stoichiometric $\text{LiNbO}_3\text{:Mg:Cr}$ crystal (Mg and Cr concentrations in the crystal are 0.2% and 0.013%, respectively).

for C crystals as determined by TRXFT. Two stages appear in the figure which indicate the presence of different mechanisms in the Zn incorporation. It is observed that in the concentration range from 0% to about 4.5% the effective distribution coefficient, K_{eff} , is close to 1 whereas above this concentration level K_{eff} decreases, reaching an average value of 0.3. Similar K_{eff} values were also observed for MgO codoped crystals. This result is in good agreement with the two proposed cation-vacancy models for the non-stoichiometry of LiNbO_3 , where the total concentration of Li^+ sites available for substitution is 4.6% in C crystals.

Figure 2 shows the room temperature absorption spectra for various crystals: (a) congruent codoped $\text{Li}_{0.95}\text{Nb}_{1.01}\text{O}_3\text{:Mg(4%):Cr(0.07%)}$; (b) congruent codoped $\text{Li}_{0.95}\text{Nb}_{1.01}\text{O}_3\text{:Mg(6%):Cr(0.07%)}$; (c) stoichiometric $\text{LiNbO}_3\text{:Cr(0.032%)}$ and (d) stoichiometric codoped $\text{LiNbO}_3\text{:Mg(0.2%):Cr(0.013%)}$. All the spectra consist of two broad bands that have been attributed to the vibronic transitions ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ associated with Cr^{3+} ions [1, 6]. Figures 2(a) and 2(c), which correspond to C composition with Mg content below the threshold and to S compositions, respectively, show identical spectral features indicating that the same type of Cr^{3+} centre is present in both compositions. The lower absorption intensity in spectrum 2(c) is a consequence of the lower Cr concentration in the S crystal [8]. Figures 2(b) and 2(d), corresponding to C and S compositions with MgO concentrations above a certain threshold, show an overall decrease in the absorption intensity and a shift of the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ transition to lower energy when compared with the

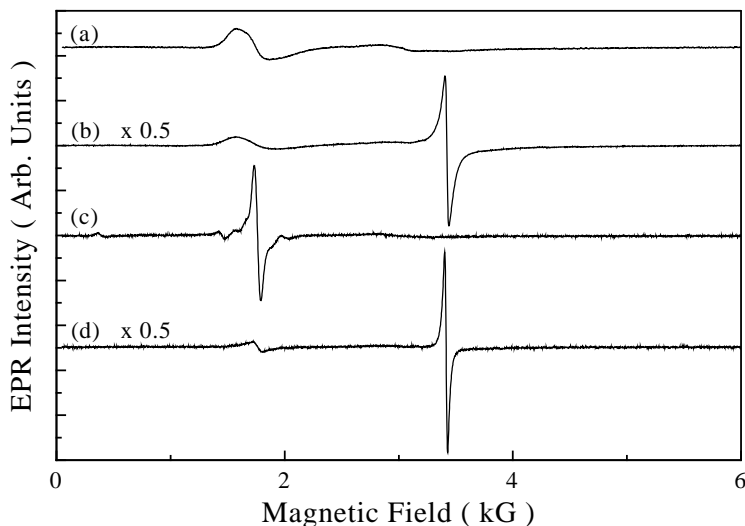


Figure 3. EPR spectra measured at room temperature with the magnetic field perpendicular to the crystal c axis. Parts (a), (b), (c) and (d) of the figure correspond to the same samples as in figure 2.

spectra shown in figures 2(a) and 2(c). In addition, the ${}^4A_2 \rightarrow {}^4T_2$ vibronic band is slightly broadened on the low energy side. These changes have been previously attributed to the appearance of Cr_{Nb}^{3+} centres [6, 8]. The low overall absorption intensity can be explained by the smaller oscillator strength associated with the Cr_{Nb}^{3+} centre in relation to the Cr_{Li}^{3+} centre [8]. The data of figure 2 clearly demonstrate the redistribution of the population of both Cr^{3+} centres in relation to the concentration of the Mg (or Zn) codopant, which in turn is related to the concentration of the available Li^+ sites in the crystals.

Figure 3 shows the room temperature EPR spectra corresponding to the four samples shown in figure 2. For the C sample codoped with MgO below the threshold (figure 3(a)), the EPR spectrum consists only of the EPR signal attributed to Cr_{Li}^{3+} centres [5]. Otherwise, for C samples codoped with MgO above the 4.5% threshold (figure 3(b)) the EPR spectrum associated with Cr^{3+} ions located in Nb^{5+} sites is clearly observed together with that due to the Cr_{Li}^{3+} centres [6]. In the S samples without MgO codoping (figure 3(c)) only the EPR signal attributed to the Cr_{Li}^{3+} centre is detected. At variance, in the MgO codoped (0.2%) S sample (figure 3(d)), the EPR spectrum consists almost exclusively of the signal associated with Cr_{Nb}^{3+} centres, even though a weak signal from the Cr_{Li}^{3+} centres still remains.

It is to be noted that the EPR lines for the S samples are clearly narrower than for the C ones suggesting a much more regular and homogeneous crystal structure. This behaviour can be attributed to the reduction of intrinsic defects, which could cause strain and local distortions in the environment of the Cr centres.

Similar results to that shown in figure 3 were obtained for C and S $LiNbO_3:Cr$ crystals codoped with ZnO.

The presented observations confirm that for C composition, where Li^+ sites are available for substitution, Cr^{3+} ions enter these sites preferentially giving rise to the Cr_{Li}^{3+} centres. When divalent codopant cations, such as Mg^{2+} or Zn^{2+} , are present they occupy the available Li^+ sites with preference over Cr^{3+} ions, resulting in a reduction in the amount of Cr_{Li}^{3+} centres. Above the threshold concentration, where all these Li^+ sites are filled

in, the Cr^{3+} ions have to compete with the divalent cations for the Li^+ or the Nb^{5+} sites. Now their preference is to substitute the Nb^{5+} ions resulting in the appearance of $\text{Cr}_{\text{Nb}}^{3+}$ centres. Accordingly, in a totally stoichiometric crystal one would expect to detect only $\text{Cr}_{\text{Nb}}^{3+}$ centres as no available Li^+ sites would be present. The observation of $\text{Cr}_{\text{Li}}^{3+}$ centres in our S samples (without codopant) suggests that they have not achieved the desired total stoichiometric composition. However, the small amount of codopant required to enhance the population of the $\text{Cr}_{\text{Nb}}^{3+}$ centre shows that they must be very close to stoichiometry.

The results obtained in this work agree better with the Li-site vacancy model than with the Nb-site vacancy one. This is because, in the second model, one would expect the $\text{Cr}_{\text{Nb}}^{3+}$ centre to appear below the threshold value as there are Nb^{5+} sites (the Nb^{5+} vacancies) available for Cr^{3+} ions.

In conclusion, the present data show that the changes in the optical properties of the $\text{LiNbO}_3:\text{Cr}$ crystals must be attributed to the relative population of the $\text{Cr}_{\text{Li}}^{3+}$ and $\text{Cr}_{\text{Nb}}^{3+}$ centres, which is directly related to the number of available Li^+ sites depending on the grade of stoichiometry and codoping. The closer to the S composition the more homogeneous the crystal structure and the better the crystal quality. This is especially desirable in many optoelectronic devices. The use of the Cr^{3+} centres as a probe could provide a simple and effective method to evaluate the stoichiometric grade of this material. This could be done even for the more stoichiometric LiNbO_3 crystals since the sensitivity of the EPR technique in detecting the $\text{Cr}_{\text{Nb}}^{3+}$ centres has a detectable limit of about 0.001%, equivalent to 10 ppm defects.

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References

- [1] Sohler W 1993 *Proc. 11th Ann. Conf. on European Fibre Optics Communications and Networks (EFOC & N'93) (The Hague, July 1993)*
- [2] Macfarlane P I, Holliday K, Nicholls J F H and Henderson B 1995 *J. Phys.: Condens. Matter* **7** 9643–56
- [3] Rebouta L, Da Silva M F, Soares J C, Santos M T, Diéguez E and Agulló-López F 1995 *Radiat. Eff. Defects Solids* **136** 137–9
- [4] Corradi G, Söhte H, Spaeth J-M and Polgár K 1991 *J. Phys.: Condens. Matter* **3** 1901–8
- [5] Martín A, López F J and Agulló-López F 1992 *J. Phys.: Condens. Matter* **4** 847–53
- [6] Díaz-Caro J, García-Solé J, Bravo D, Sanz-García J A, López F J and Jaque F 1996 *Phys. Rev. B* **54** 13 042–6
- [7] Torchia G A, Sanz-García J A, Díaz-Caro J, Jaque F and Han T P J *Chem. Phys. Lett.* at press
- [8] Díaz-Caro J, García-Solé J, Martínez J L, Henderson B, Jaque F and Han T P J *Opt. Mater.* at press
- [9] Malovichko G I, Grachev V G, Kokonyan E P, Schirmer O F, Betzler K, Gather B, Jermann F, Klauer S, Schlarb U and Wöhlecke M 1993 *Appl. Phys. A* **56** 103–8