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Detection of Cr^{3+} sites in LiNbO$_3$:MgO,Cr^{3+} and LiNbO$_3$:Cr^{3+}

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In this work, experimental results describing Cr^{3+} sites in LiNbO$_3$:Cr and LiNbO$_3$:MgO,Cr previously determined with electron-paramagnetic-resonance (EPR), electron-nuclear-double-resonance, and optical techniques, are correlated in terms of the formation of three chromium sites: Cr^{3+} ions in Li$^+$ and Nb^{5+} positions, and a Cr^{3+} (Nb^{5+})-Mg^{2+} center that only appears in the double-doped system. It is concluded that the majority of the unperturbed centers, Cr^{3+} (Li$^+$) and Cr^{3+} (Nb^{5+}), are forming close pairs and only a small fraction of Cr^{3+} (Li$^+$) ions are diluted into the crystal host, giving rise to an EPR signal.

The determination of the site location of dopant (rare-earth and transition-metal) ions in LiNbO$_3$ has come to be of great importance in understanding the nonlinear properties of this ferroelectric crystal. On the other hand, the doped system has to be codoped with 5% or more MgO in order to avoid the optical damage associated with the photorefractive effect.[1,2] In view of these results, in particular, the site location of Cr^{3+} ions has been the subject of special interest in order to understand the role played by these defects. In LiNbO$_3$:MgO, Cr^{3+}, by means of the electron-paramagnetic-resonance (EPR) technique, Corradi *et al.*[3] have identified the presence of two centers: one axial Cr^{3+} center with $D=0.4$ cm^{-1} and a different center giving an isotropic signal with $g=1.971$. These authors, by using electron nuclear double resonance (ENDOR), associated this second center with Cr^{3+} replacing Nb^{5+}, presumably perturbed by Mg^{2+} ions at various nearby locations. The axial EPR spectrum is the same as that which appears[4] in LiNbO$_3$ but doped with Cr^{3+}. Due to the significant differences with respect to the second Cr^{3+} center appearing in the double-doped system, they associated the axial spectrum to Cr^{3+} ions entering at Li$^+$ cation sites, at variance with Rexford, Kim, and Story,[4] where they assign the site to Nb^{5+}.

In a later work[5] Martin, López, and Aguilló-López observed the same two EPR spectra in their double-doped LiNbO$_3$:MgO, Cr^{3+} crystals. For the sake of comparison they also studied the single-doped system (but doped with Cr^{3+}). As expected, the new isotropic center was absent in LiNbO$_3$:Cr. They analyzed the EPR spectra according to the superposition model and concluded that both centers (axial and isotropic) are consistent with Nb^{5+} substitution, at variance with Corradi *et al.*, but in agreement with the assignment for the axial center of Rexford, Kim, and Story.

Now, optical spectroscopy (optical absorption and fluorescence) has recently been applied to study the Cr^{3+} site distribution in LiNbO$_3$:Cr^{3+} and LiNbO$_3$:MgO, Cr^{3+}. By means of site-selective spectroscopy[6] in the R-lines region (${}^4A_2 \Longrightarrow {}^2E$ transition of Cr^{3+}) it was shown that Cr^{3+} ions are replacing both Li$^+$ and Nb^{5+} cation sites in the single-doped system. On the other hand, the present authors carried out fluorescence experiments[7–9] in LiNbO$_3$:MgO, Cr^{3+}. Three Cr^{3+} sites were clearly observed in this system: the same Cr^{3+} (Li$^+$) and Cr^{3+} (Nb^{5+}) sites appear in LiNbO$_3$:Cr^{3+} and a different one associated to Cr^{3+} (Nb^{5+}) perturbed by close Mg^{2+} ions.

In a previous work[8] on the fluorescence spectrum of the double-doped system LiNbO$_3$:MgO, Cr^{3+} it was shown that the spectrum consists of peaks at 727.0 and 731.3 nm corresponding to the R lines ($\overline{E} \Longrightarrow {}^4A_2$ and $2\overline{A} \Longrightarrow {}^4A_2$ transitions, respectively) of the Cr^{3+} ion at a Li$^+$ site; one peak at 735.7 nm is assigned to the $2\overline{A} \Longrightarrow {}^4A_2$ transition for the Cr^{3+} ion at a Nb^{5+} site. The $\overline{E} \Longrightarrow {}^4A_2$ line for Cr^{3+} (Nb^{5+}) overlaps the intense $2\overline{A} \Longrightarrow {}^4A_2$ line of Cr^{3+} (Li$^+$) and cannot be resolved. Two other peaks at 739.1 and 741.1 nm were also found that correspond to the R lines of the Cr-Mg center.

Therefore, the presence of three nonequivalent Cr^{3+} sites in the crystal codoped with MgO has been unequivocally ascertained by optical measurements. In principle, EPR spectroscopy should also show the same three Cr^{3+} centers. However, only two well-defined EPR spectra have been reported to date, the axial and the isotropic ones (Cr^{3+} at Nb^{5+} position, perturbed by Mg^{2+} ions).

It is important to point out that samples from the same block used for optical measurements[7–9] were used in the work of Martin, López, and Agulló-López.[5] As their experimental results are quite similar to those observed by Corradi *et al.*,[3] the same conclusions should be applied for the results obtained by both authors.

The isotropic EPR spectrum is clearly correlated with the emission R lines peaking at 739.1 and 741.1 nm of the Cr-Mg center because it only appears in the doubly doped system. However, at variance with the two nonequivalent Cr^{3+} (Li$^+$) and Cr^{3+} (Nb^{5+}) sites detected by optical spectroscopy, only one EPR axial spectrum has been observed. The assignment of this axial EPR spectrum with one of these centers is still the object of controversy; for Corradi *et al.*[3] this spectrum corresponds to Cr^{3+} at the Li^{+} site, while for Rexford, Kim, and Story[4] and Martin *et al.*[5] it should correspond to Cr^{3+} at the Nb^{5+} site.

Obviously there is a lack of agreement between the different spectroscopies about the Cr^{3+} site distribution. However, with this information at hand, and taking advantage of other experimental evidence, it is possible to make a coherent interpretation about the Cr^{3+} site distribution. Below we present a possible scheme to explain this apparent lack of agreement. Jia *et al.*[6] interpreted the broadening in the fluorescence spectra (R lines) of Cr^{3+} (Li^{+}) and Cr^{3+} (Nb^{5+}) centers as a consequence of the formation of Cr^{3+} (Nb^{5+})-Cr^{3+} (Li^{+}) dimers. Additionally they observed an energy shift in the time-resolved fluorescence spectra that supported this idea. These effects appear as a consequence of (Cr^{3+}-Cr^{3+})-ion superexchange interaction, which splits the ^{2}E and $^{4}A_2$ levels of the dimers. The effect of this interaction in the R-lines optical spectrum of the Cr^{3+} ion was evidenced a long time ago in chromium-doped $LaAlO_3$.[10] In $LiNbO_3$:Cr^{3+} the formation of Cr^{3+}-Cr^{3+} pairs has also been pointed out by Malovichko, Grachev, and Lukin[11] and Grachev, Malovichko, and Troitskii[12] by means of EPR spectroscopy. They assumed that only the nonclose pairs could be detected by EPR because of the close pairs the ground state is a singlet due to an antiferromagnetic coupling, with a constant $|J| \cong 400\ \mathrm{cm}^{-1}$. The spread in the optical spectrum, due to Cr-Cr pairs, depends on both coupling constants; J and J' for the ground and excited states, respectively. Now taking advantage of the emission spectrum shown in Ref. 8, the coupling constant for the excited state, $|J'|$, compatible with the width of the R-emission lines can be roughly estimated. Following the procedure used by Fergurson, Guggenheim, and Tanabe[13] the estimated value is $|J'| \simeq 390\ \mathrm{cm}^{-1}$. Thus, we can suppose that the majority of Cr^{3+} ions are forming close pairs, and only a small Cr^{3+} concentration is diluted inside the $LiNbO_3$ host. Therefore, this small fraction of diluted chromium ions is solely responsible for the EPR axial spectrum.

In order to clarify the nature of the Cr^{3+} center [Cr^{3+} (Li^{+}) or Cr^{3+} (Nb^{5+})] associated to the axial EPR spectrum, the absorption spectrum (in the R-lines region) of $LiNbO_3$:Cr^{3+} can give us useful help. This spectrum is shown in Fig. 1. The main peaks at 724 and 726.6 nm are associated with the same $^{4}A_2 \Longrightarrow \bar{E}(^{2}E)$ transition of Cr^{3+} (Li^{+}) and Cr^{3+} (Nb^{5+}) centers, respectively. Assuming that the oscillator strength of this transition is similar for both centers, the optical density has to be proportional to the concentration of each type of Cr^{3+} ion. Thus, Fig. 1 indicates that the concentrations for both kinds of sites are similar. However, there are more Cr^{3+} ions (about 14%) occupying Li^{+} sites than Cr^{3+} ions replacing Nb^{5+} ions. This excess of Cr^{3+} (Li^{+}) is not paired, and therefore it should be diluted into the $LiNbO_3$ matrix.

In this scheme the Cr^{3+} (Li^{+}) sites should be responsible for the axial EPR spectrum found in both $LiNbO_3$:Cr^{3+} and $LiNbO_3$:MgO, Cr^{3+} systems. This idea is in accordance with the assignment made by Corradi *et al.*[3] but at variance with the assignment of Rexford, Kim, and Story[4] and Martin, López and Agulló-López.[5]

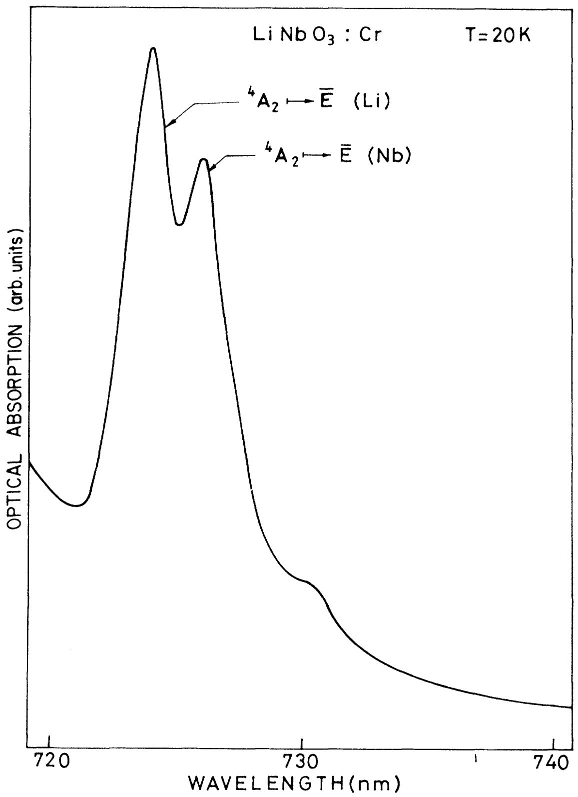

FIG. 1. R-lines absorption spectrum observed for $LiNbO_3$:Cr.

In the double-doped system, the absorption coefficient at 724 nm [Cr^{3+} (Li^{+})] diminishes with respect to the peak at 726.6 nm [Cr^{3+} (Nb^{5+})], the former peak [Cr^{3+} (Li^{+})] then being only slightly higher than the latter [Cr^{3+} (Nb^{5+})]. Consequently, the axial EPR spectrum should be strongly reduced in the sample codoped with magnesium, as experimentally observed.[3,5]

In summary, the results about site location obtained by EPR and ENDOR are consistent with the results obtained by optical spectroscopy, if one assumes that Cr^{3+} (Li^{+})-Cr^{3+} (Nb^{5+}) close pairs (not detected by EPR) and Cr^{3+} (Li^{+}) centers are formed in $LiNbO_3$: Cr. Codoping with MgO produces a different center, which is related to Cr^{3+} (Nb^{5+}) perturbed by Mg^{2+} ions. The Cr^{3+} (Li^{+})-Cr^{3+} (Nb^{5+}) close-pair centers are missed in the EPR spectrum due to an antiferromagnetic coupling. On the other hand, crystal-field effects on the optical spectrum are dominant and Cr^{3+} (Li^{+}) and Cr^{3+} (Nb^{5+}) sites are identified separately and can be associated with two defined optical spectra.

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