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EPR spectroscopy of Yb^{3+} in $LiNbO_3$ and Mg:$LiNbO_3$

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Abstract

Electron paramagnetic resonance (EPR) experiments have been carried out on congruent crystals of $LiNbO_3$ doped with Yb and crystals codoped with Mg. Crystals without Mg codoping show a complex spectrum which is attributed to slightly different centers of Yb^{3+} located at the Li^+ site. In samples codoped with Mg a new ytterbium spectrum is detected in addition to those observed in crystals without codoping. This new Yb^{3+} center is compared to additional centers observed for Er^{3+} and trivalent transition metal ions (particularly Cr^{3+}) in $LiNbO_3$ heavily doped with Mg or Zn. On these grounds the new center can be attributed to Yb^{3+} located at the Nb^{5+} site of $LiNbO_3$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Insulators; Crystal growth; Point defects; Electronic states (localized); Electron paramagnetic resonance

1. Introduction

Yb-doped $LiNbO_3$:MgO has proved to be an excellent system for compact solid state lasers with self-frequency doubling [1,2]. Although nominally pure $LiNbO_3$ crystals are damaged under high intensity illumination due to the photorefractive effect, the problem is greatly reduced by codoping the material with MgO at a concentration of about 5% [3].

The optical properties of doped crystals are largely determined by the local site symmetry of the optically active ions. The space group of $LiNbO_3$ is *R3c*, the cationic sites and structural vacancy site all having point symmetry C_3 with the trigonal axis along the crystal *c*-axis. In recent years, the position in the lattice and local environment of transition metal and rare earth (RE) ions in congruent $LiNbO_3$ crystals have been widely studied because of their interesting applications. Additional doping with MgO or ZnO (about 6%) affects the optical properties of the active ions, as has been observed by optical methods in several rare earth codoped crystals [4,5]. Moreover, for RE ions only the Li^+ sites have been reported to be occupied irrespective of the MgO concentration [6], except for a recent report on Mg:$LiNbO_3$ codoped with Er ions [7].

In order to propose models for local environments of impurities, electron paramagnetic resonance (EPR) spectroscopy has proved to be a powerful tool. In recent works, the EPR spectra of Er^{3+} in congruent $LiNbO_3$ have been assigned to either a unique defect with axial symmetry [8] or several defects on Li^+ sites next to Li^+ vacancies [9]. On the other hand, in the case of some trivalent transition metal and rare earth (Er) ions in crystals codoped with MgO, ZnO or CaO above a concentration threshold of around 4.6%, new EPR spectra have been observed with respect to crystals without codoping and attributed to the impurity ion on the Nb^{5+} site [10–14]. In the present work we studied the EPR spectra of Yb^{3+} in congruent $LiNbO_3$ crystals with and without MgO codoping to investigate whether the addition of Mg influences the Yb^{3+} spectra, as is the case for other impurity ions.

2. Experimental

Yb-doped $LiNbO_3$ and $LiNbO_3$:MgO congruent crystals were grown by the Czochralski method from grade I Johnson-Matthey powder. The ytterbium to niobium concentration was around 1.2 and 0.5% (molar fraction in the melt) for the $LiNbO_3$ and $LiNbO_3$:MgO crystals, respectively. For the latter crystal a 6% molar fraction of magnesium oxide was added to the melt. Crystals were

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oriented by means of a number of Laue X-ray diffraction patterns and samples for EPR measurements were cut from them.

EPR spectra were recorded by means of Bruker EleXsys E580 and Bruker ESP 300E X-band spectrometers. Measurements were carried out in the temperature range 7–10 K using continuous flow liquid-helium cryostats (Oxford Instruments ESR 900). The samples were mounted on a Bruker programmable goniometer ER218PG1 to obtain angular dependence of the spectra.

3. Results and discussion

The EPR spectrum of Yb-doped congruent $LiNbO_3$ crystals (without Mg codoping) shows an intense broad line when the magnetic field ***B*** is parallel to the ferroelectric *c*-axis (Fig. 1). Despite the low resolution of the spectra, which is typical of congruent $LiNbO_3$ crystals [15], the observed line results from a superposition of various lines, as can be deduced from the angular dependence of the spectrum (see Figs. 1 and 2). Moreover, two hyperfine satellites with a splitting of about 670 G are observed for orientations of ***B*** close to the *c*-axis (Fig. 1). This doublet can be attributed to the ^{171}Yb isotope [16,17], having 14% natural abundance and nuclear spin $I = 1/2$. The expected sextet for the 16% abundant ^{173}Yb isotope ($I = 5/2$) is too weak to be observed.

As the orientation of ***B*** changes from parallel to perpendicular to the crystal *c*-axis the complex broad line splits into several components that move close together (Fig. 1). Although the existence of Yb^{3+}–Yb^{3+} dimers cannot be rejected, the observed splitting could not be explained as line pairs due to dipole–dipole interaction between two Yb^{3+} ions. Therefore, apart from the weak hyperfine lines, we can attribute the components to various slightly different Yb^{3+} centers. At least one of them must have axial symmetry along the *c*-axis, since the most intense line does not move in angular variation on the plane perpendicular to the *c*-axis (Fig. 2). On the contrary, other less intense lines clearly change their position in this angular variation (Fig. 2). This implies that the other centers must have different sets of principal axes, probably with symmetry lower than axial, assuming that the impurity enters the cationic sites or the intrinsic vacancy site. Accurate deconvolution of the spectra could not be achieved due to the low resolution. However, the most intense line is well fitted considering an axial defect along the *c*-axis with effective spin $S' = 1/2$ and the following g values: $g_\parallel = 4.70 \pm 0.03$ and $g_\perp = 2.70 \pm 0.02$. The other less intense lines must have slightly different sets of principal axes and g values.

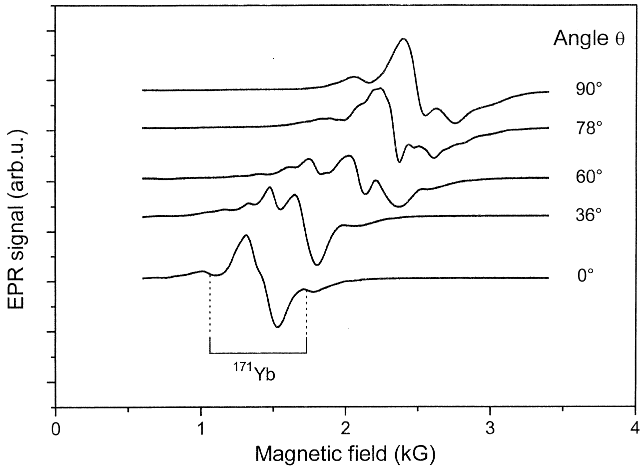

Fig. 1. Angular dependence of the EPR spectrum of Yb-doped $LiNbO_3$ measured at 8 K. The magnetic field is rotated in a plane that contains the crystal *c*-axis and forms an angle θ with this axis. The stick diagram in the lower part of the figure depicts the hyperfine doublet of ^{171}Yb for $\theta = 0°$.

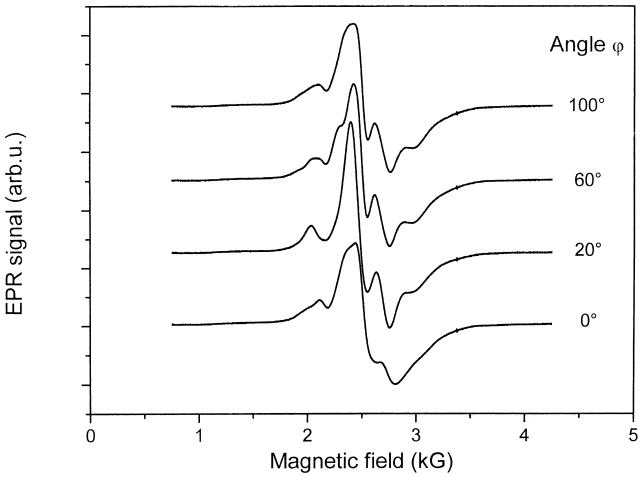

Fig. 2. Angular dependence of the EPR spectrum of Yb-doped $LiNbO_3$ measured at 8 K. The magnetic field is rotated in a plane perpendicular to the crystal *c*-axis and forms an angle φ with the *a*-axis.

The given $g_\parallel$ value is coincident with that measured by means of magnetic circular dicroism for Yb^{3+} in congruent $LiNbO_3$ [18] and both $g_\parallel$ and $g_\perp$ are in good agreement with those reported by Burns et al. for the only axial Yb^{3+} center previously observed [19]. Moreover, the mean g value $(g_\parallel + 2g_\perp)/3$ is 3.37, very close to those obtained for Yb^{3+} in other hosts [17]. Therefore, we associate the various lines with Yb^{3+} with slightly different surroundings. It is reasonable to suppose that Yb^{3+} occupies the Li^+ site, analogously to other trivalent impurities [9–14], also in agreement with Rutherford backscattering (RBS) spectrometry measurements [6]. A similar proposal has recently been made for Er^{3+} in congruent $LiNbO_3$, where the different Er^{3+} centers were attributed to the effect of nearby Li vacancies in various positions [9]. It should be pointed out that charge compensation can easily be achieved in congruent $LiNbO_3$ crystals in different ways [9–14] due to the large number of intrinsic defects present in this non-stoichiometric material.

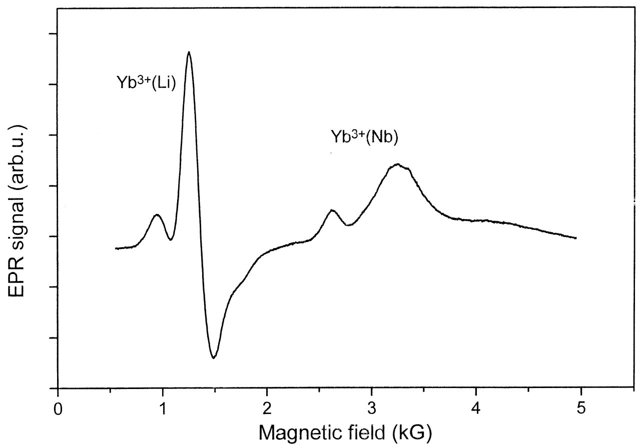

Fig. 3. EPR spectrum of Yb-doped $LiNbO_3$:MgO measured at 7 K with the magnetic field parallel to the crystal *c*-axis. Each group of lines is labeled with the corresponding Yb^{3+} center (see text).

On the other hand, the spectrum of congruent $LiNbO_3$ crystals codoped with 6% MgO for $\boldsymbol{B} \| c$ again shows the above complex line together with a new broad line of similar structure (Fig. 3). Fig. 4 shows the angular dependence of both broad lines in the codoped sample. The line attributed to Yb^{3+} in the Li^+ site has identical spectral features to those observed in $LiNbO_3$:Yb^{3+} without codoping (Fig. 1) and is well fitted with the g values given above. However, this line now shows worse resolution.

The new broad line shows axial symmetry, but has a very different angular dependence, with $g_\| < g_\perp$, in contrast to the other line. The principal g values which best fit the new line are $g_\| = 1.9 \pm 0.1$ and $g_\perp = 2.8 \pm 0.1$. It is interesting to note the different mean g value (2.5) with respect to the other center (3.37). However, this mean g value has also been observed for Yb^{3+} in several hosts [17] and can be understood if the new center has a ground doublet different to that for the above centers. These features suggest that the new line must be attributed to a new center of Yb^{3+} located at a different lattice position.

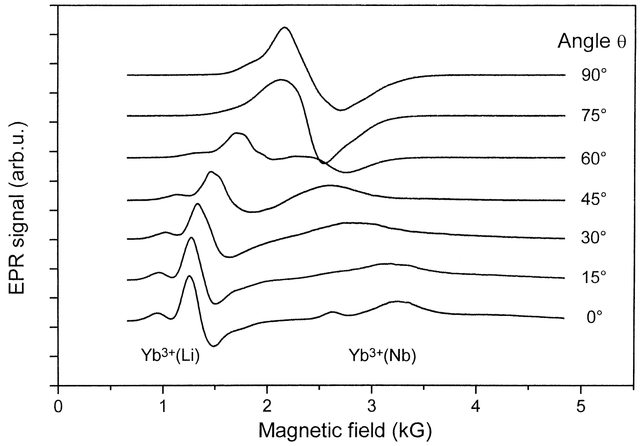

Fig. 4. Angular dependence of the EPR spectrum of Yb-doped $LiNbO_3$:MgO measured at 7 K. The magnetic field is rotated in a plane that contains the crystal *c*-axis and forms an angle θ with this axis.

To go deeper into the nature of this new center it is interesting to compare our EPR results for ytterbium with those for other trivalent ions in codoped crystals. Transition metal ions have already been studied by means of EPR in $LiNbO_3$ codoped with MgO, ZnO or CaO. In crystals containing Mg above the concentration threshold, a new EPR center (coexisting with the old one) has been observed for Ti^{3+} [14], Fe^{3+} [13] and Cr^{3+} [10]. All of these new centers have been attributed to the impurity occupying the Nb^{5+} site as the divalent impurity preferentially occupies the Li^+ site, whereas the old centers are associated with the Li^+ site. Moreover, the electron nuclear double resonance (ENDOR) technique has confirmed the assignment of the new Cr^{3+} center to the Nb^{5+} site [20]. Also, a new Er^{3+} center recently reported in MgO or ZnO co-doped $LiNbO_3$ has been attributed to Er^{3+} at the Nb site [7]. Therefore, in view of the analogies found in the EPR spectra of Yb^{3+} and the above trivalent impurities in MgO-codoped $LiNbO_3$, we also attribute the new EPR line to a Yb^{3+} center at the Nb^{5+} site [Yb^{3+}(Nb^{5+}) center, as shown in Figs. 3 and 4]. However, one has to bear in mind the lack of resolution of the EPR signal, which may obscure the existence of several centers with slightly different g values for this site, as observed above for crystals without codoping (Figs. 1 and 2).

Finally, it should be noted that the proposal here remarked for RE ions occupying the Nb^{5+} site in codoped crystals is based on EPR results. This contradicts to some extent the results of RBS experiments on several RE ions in $LiNbO_3$ [6]. In that study, only the Li^+ site has been proposed to be occupied by the RE ions in crystals with and without MgO codoping. We believe the explanation of this fact should be found in the different relative concentrations of the centers depending on the specific growing conditions of the crystals analyzed and codopant added. Also, one should consider the different sensitivity of the EPR and RBS techniques.

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