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Radiation Defects in LiNbO₃ Single Crystals Doped with Cr³⁺ Ions

Absorption and additional absorption of LiNbO₃ crystals doped with Cr³⁺ during growth or by diffusion process were investigated before and after γ -irradiation with a dose of 10⁵ Gy and also before and after proton irradiation with a fluency of 10¹⁴ cm⁻². It was found that chromium ions may be introduced into LiNbO₃ crystals also as Cr²⁺. ESR measurements of Cr:LiNbO₃ crystals irradiated by γ -rays and electrons were performed. Paramagnetic peak after γ and electron irradiation was observed, which vanishes after annealing at 400°C for 3h both in optical and ESR spectra. Mn²⁺ lines were also observed, which diminish after electron irradiation only.

Keywords: gamma, proton and electron irradiations; additional absorption; electron spin resonance; radiation defects; chromium valency

1. Introduction

Lithium niobate is an electro-optic material with a variety of applications. Recent developments include photorefractive devices (KRATZIG et al. 1988), waveguide substrates (ARMENISE et al. 1983), and self-frequency doubled and self-Q switched solid-state lasers (FAN et al. 1986). There is a growing interest in the characterization of transition-metal ion doped LiNbO₃ crystals because of their relevance to optoelectronic applications. Potential attraction of Cr as a laser active ion is that it has a broad emission spectrum and, combined with the electro-optic properties of lithium niobate, this offers the possibility of high-speed electro-optic tuning of the laser to produce a wavelength agile laser. Moreover, with Cr ions it is possible to pump the material with a laser diode at around 670 nm. However chromium-doped lithium niobate exhibits a short upper state lifetime, less than 1 μ s, compared to typical values close to 100 μ s for other Cr host materials (SCHEPS 1992)

Chromium is assumed to be incorporated in LiNbO₃ crystals mainly as Cr³⁺ (PHILIPS et al. 1972). KOVACS et al. 1988 suggested that chromium exists in Cr:LiNbO₃ crystals not only in 3-fold charged state, but also in 4-fold. The presence of Cr²⁺ ions is less probable. Earlier observations showed, however, that there are Cr³⁺ ions in oxide crystals irradiated by intense light or gamma rays (MARUYAMA et al. 1964).

Diffusion of the active dopant from a film or gas into the crystal offers the possibility of tailoring the doping profiles, avoiding important limitations imposed by a bulk doped substrate. Optical amplification and laser action in doped LiNbO₃ will preferably be obtained in locally diffusion-doped substrates, rather than bulk ones (ALMEIDA et al. 1995).

This paper reports electron spin resonance studies and optical measurements of lithium niobate single crystals doped in two different ways with Cr³⁺ ions: during crystal growth and by thermal diffusion.

2. Experimental

Single crystals of lithium niobate were doped with Cr³⁺ by two different methods. In the first, the dopant as a Cr₂O₃ was introduced into the starting charge of congruent melting composition with a ratio of Li/Nb=0.94 prior to synthesis at elevated temperature (1100°C). The charge material was melted in a platinum crucible and single crystals were grown by the Czochralski technique. The as-grown crystals were of „Y” orientation and had 70 mm diameter and length with dopant concentration of 0.3 at.% Cr. The crystals were then cut into specimens. In the obtained crystals uncontrolled Mn²⁺ impurity was observed.

The another method of Cr incorporation consisted in annealing undoped single-crystalline LiNbO₃ plates in powdered Cr₂O₃ at temperatures 750-1050°C for durations from 4 h to 30 h in an air atmosphere.

Thin samples polished on both sides were measured, before and after irradiation treatment, using LAMBDA-2 Perkin-Elmer and FTIR spectrometers. Additional absorption bands were obtained from the following equation:

$$\Delta K = (1/d) \ln(T_1 / T_2), \quad (1)$$

where K is absorption, ΔK is the additional absorption, d is the sample thickness, and T_1 and T_2 are transmissions of the samples before and after ionization treatment, respectively.

Two crystalline samples with the same concentration of Cr (0.3 at.%) were examined. One of them subjected to the following treatments was successive:

- (1) Irradiated with 10⁵ Gy of γ (⁶⁰Co source) at 300K.
- (2) Annealed at 400° C for 3 h in air.
- (3) Irradiated with 10⁵ Gy of γ at 300 K.
- (4) Irradiated with 10⁵ Gy of γ at liquid nitrogen temperature.

The other sample was irradiated by protons with energy of 21 MeV and fluency of 10¹⁴/cm² with the use of a cyclotron.

The ESR spectra of these crystals were measured before and after γ (10⁵ Gy) or electron (from 10¹⁴ to 5x10¹⁶ electrons cm⁻²) with the use of Van de Graaff accelerator) irradiation, performed at room temperature. These spectra were recorded at 9.4 GHz over a temperature range from 4 K to 300 K using a BRUKER ESP300 X-band spectrometer.

3. Results and discussion

3.1. Optical measurements

The absorption spectra of Cr:LiNbO₃ (0.3 at.% Cr³⁺) single crystal are presented in Fig. 1a. Curve 1 shows the fundamental absorption edge for LiNbO₃ doped with 0.3 at. % Cr during growth is equal to $\lambda = 350$ nm. Two broad vibronic absorption bands centered at 464 and 659 nm and narrow line centered at 730 nm can be distinguished. GARCIA-SOLE et al. shown that there are ⁴A₂→⁴T₁, ⁴T₂ transitions, and narrow line, the so-called R line (⁴A₂→2A(²E) and ⁴A₂→E(²E) transitions) which is observed at room temperature as one line at about 730 nm (two lines at 724 and 726 nm observed at 20 K). The latter appears as a consequence of a splitting in the ²E level because of the combined effect of spin-orbit interaction and a trigonal distortion. The observed structure is a consequence of the presence of two nonequivalent Cr³⁺ ion positions. The peaks around 724 and 726 nm correspond to the ⁴A₂→E(²E) transition of Cr³⁺ ions in Li⁺ and Nb⁵⁺ sites, respectively. It means that Li⁺ and

Nb^{5+} sites are always occupied (GARCIA-SOLE et al. 1993). This conclusion confirms a weak ($<0.4 \text{ cm}^{-1}$) absorption at 2870 nm band, connected with the presence in $\text{Cr}:\text{LiNbO}_3$ crystal of OH ions.

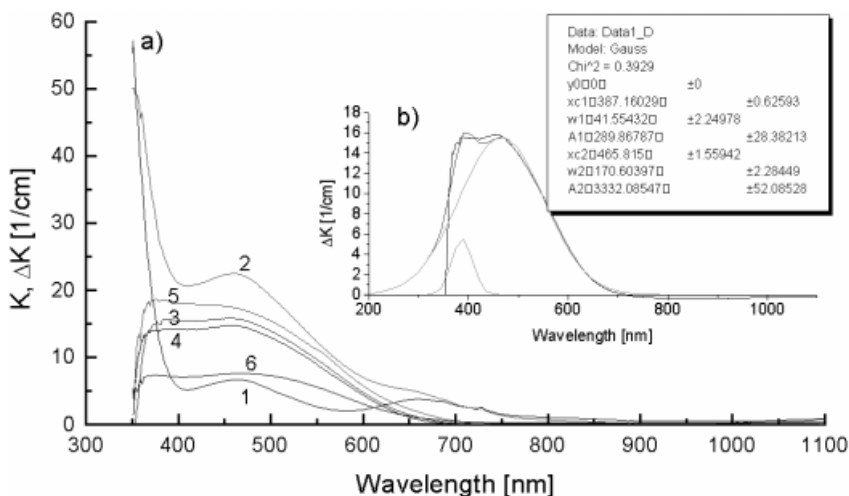


Fig. 1: (a). $\text{Cr}^{3+}:\text{LiNbO}_3$ absorption (1) before and (2) after γ irradiation with a dose of 10^5 Gy , and (3-6) AA bands after (3-5) γ and (6) proton irradiations. (b). Gaussian distribution of AA bands for $\text{Cr}:\text{LiNbO}_3$ crystal after γ irradiation

Fig. 1 also shows absorption (curve 2) and additional absorption bands after ionization of $\text{Cr}:\text{LiNbO}_3$ crystal with: gamma rays with a dose of 10^5 Gy (curves 2, 3), with the same γ dose after annealing of previously irradiated sample at 400°C for 3h (curve 4), with the same γ dose but irradiated at 77K (curve 5) and with protons with fluency of 10^{14} cm^{-2} and energy of 21 MeV (curve 6). It can be seen that defects introduced into $\text{Cr}:\text{LiNbO}_3$ crystal by different types of ionization are of the same type. Two additional absorption bands can be distinguished: first centered at about 387 nm and second one centered at about 464 nm (Fig. 1b). The first one is probably connected with F-center (FRUKACZ et al. 1996), while the second one seems to be associated with a valency change of Cr^{3+} ions.

Curves 3 and 4 show that $\text{Cr}:\text{LiNbO}_3$ single crystal is resistant to γ -irradiation influence. Irradiation of the crystal at nitrogen temperatures (curve 5) does not introduce any other additional absorption bands and increase in the additional absorption value is rather small. Curve 6 shows additional absorption bands after proton irradiation with a fluency of 10^{14} cm^{-2} . The shape and position of these bands are the same as for gamma rays.

From the fact that the existence of the second band does not depend on the kind of irradiation and that the most probable process during proton irradiation should be LiNbO_3 ionization, it may be concluded that in $\text{Cr}:\text{LiNbO}_3$ crystal lattice there is a certain amount of Cr^{2+} ions (perhaps of higher concentration than Cr^{3+}). This conclusion is confirmed by the value of additional absorption in $\text{Cr}:\text{LiNbO}_3$ after irradiation ($10\text{-}20 \text{ cm}^{-1}$). For example, for lithium niobate single crystals doped with Fe and Cu the value is relatively low ($2\text{-}5 \text{ cm}^{-1}$). The additional absorption bands appearing after γ , electron or proton irradiation vanish after an annealing of $\text{Cr}:\text{LiNbO}_3$ crystals in air.

Fig. 2 depict changes in the optical absorption of diffusion doped LiNbO_3 crystals as a function of diffusion temperature in the range of $750\text{-}1050^\circ\text{C}$. The 650 nm band is observed.

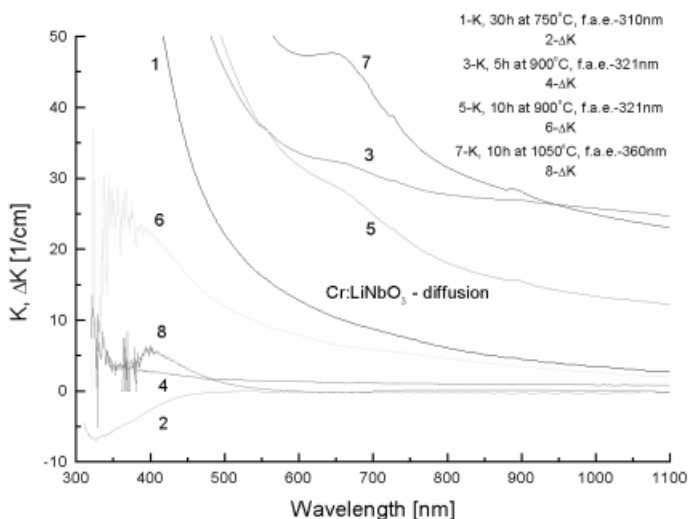


Fig. 2: (1, 3, 5, 7) absorption and (2, 4, 6, 8) AA bands in diffusion doped Cr³⁺:LiNbO₃ crystals after γ irradiation

The shape and intensity of additional absorption after γ irradiation with a dose of 10^5 Gy is also presented. Irradiation processes were used to check if there exist changes in the defect structure of LiNbO₃ crystals with diffusion temperature.

It is evident that with an increase in diffusion temperature the process of Cr incorporation into LiNbO₃ lattice is more effective but simultaneously the crystals exhibit higher and higher optical density. A shift in the maximum of additional absorption band from 330 nm to 380 nm and very clear decrease in its intensity for diffusion at the optimal temperature 1050°C is also seen.

The value of the additional absorption after γ irradiation for Cr:LiNbO₃ crystals doped during growth or by diffusion suggests high level of defect content in the crystals.

3.2 ESR results

Additional ESR lines are observed after electron or γ irradiation of Cr:LiNbO₃ single crystals (see Figs 3 and 4) in comparison with the ESR lines for the crystals prior to irradiation. Fig. 3 shows additional ESR lines at temperature 24 K formed in LiNbO₃:Cr crystal after irradiation with electrons (fluency $5 \cdot 10^{16}$ particles cm⁻²) on the Cr³⁺ background (Siu et al. 1991). The curve „a” was obtained for magnetic field orientation $H \perp c$ while curve „b” for $H \parallel c$. The numbers „1” and „2” denote positions of Al₂O₃:Cr³⁺ standard lines. Fig. 4 shows additional ESR spectrum in Cr:LiNbO₃ crystal after γ -irradiation recorded at 24 K. The direction of magnetic field was chosen in such a way that irradiation defect was clearly seen. From Figs. 3 and 4 it is obvious that the same type of paramagnetic defects appear after both types of radiations.

Because Mn lines in Cr:LiNbO₃ crystals are not distinguishable at 24 K (REXFORD 1972), we investigated them at a temperature of 40 K. Two different types of influence of ionizing radiations are observed with respect to Mn²⁺ lines. Fig. 5 shows normal spectrum (prior to irradiation) and a new additional ESR spectrum for field H rotated around c axis about 90°. Besides the typical Cr lines, Mn²⁺ lines are seen which diminish after electron irradiation. This means that there is a change in the Mn valency after electron irradiation (may be ionization effect: Mn²⁺ → Mn³⁺).

Fig. 3: ESR spectra of Cr:LiNbO₃ crystal after electron irradiation with a fluency of 5×10^{16} cm⁻² and energy of 1 MeV measured at 24 K: (a) H⊥c and (b) H||c. (1) and (2) denote positions of Cr³⁺:Al₂O₃ standard lines.

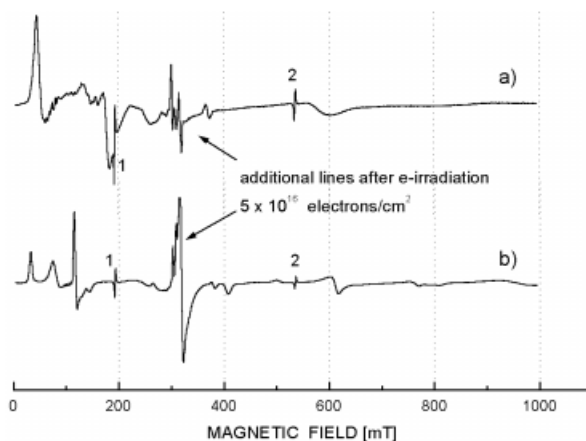


Fig. 4: ESR spectrum of Cr:LiNbO₃ crystal after γ irradiation with a dose of 10^5 Gy measured at 24 K. The field H is rotated around c axis by about 20°.

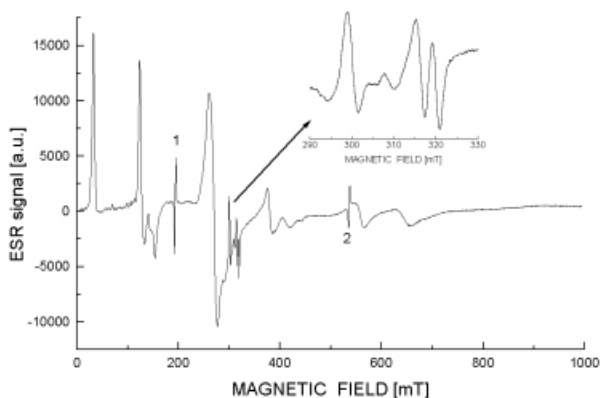
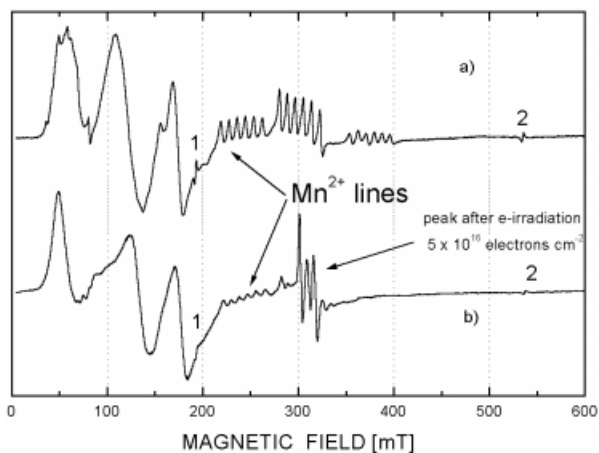


Fig. 5: ESR spectrum of Cr:LiNbO₃ crystal (a) before and (b) after electron irradiation with a fluency of 5×10^{16} cm⁻² and energy of 1 MeV measured at 40 K. The field H is rotated around c axis by about 90°.



Another type of interaction is seen in Fig. 6. After γ irradiation paramagnetic peak is also observed but now the intensity and the shape of Mn²⁺ lines for Cr:LiNbO₃ crystal practically do not change as compared to unirradiated crystal (compare Figs 6a and 6b). This means that γ radiation does not influence the valency of Mn in LiNbO₃ lattice.

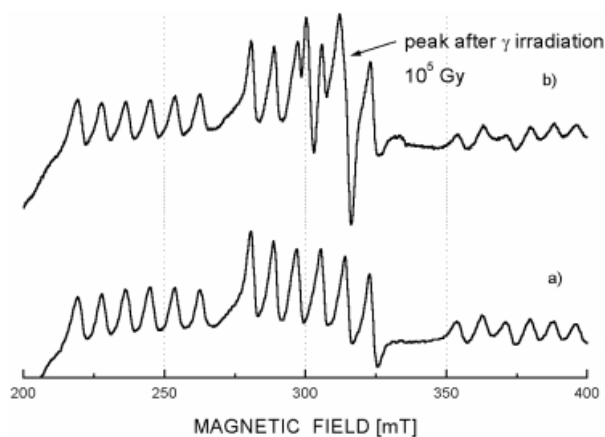


Fig. 6: ESR spectrum of Cr:LiNbO₃ crystal (a) before and (b) after γ irradiation with a dose of 10^5 Gy measured at 40 K. The field H is rotated around c-axis by about 90° .

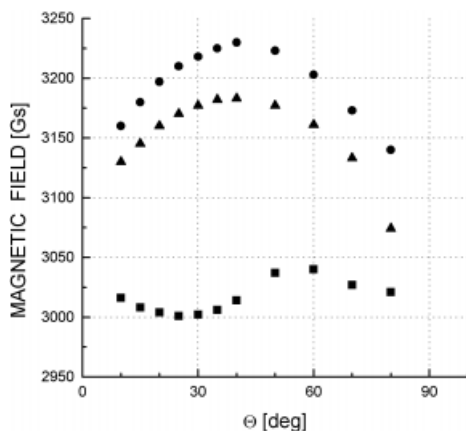


Fig. 7: Angular dependence of ESR lines of the paramagnetic peak obtained in Cr:LiNbO₃ crystals after γ irradiation with a dose of 10^5 Gy

Fig. 7 presents the angular dependence of ESR lines observed as a paramagnetic peak after γ irradiation. The dependence in the case of electron irradiation is of the same type. The angular dependencies are unambiguous due to the overlapping of Cr and paramagnetic peak lines. For this reason determination of peak localization was not done.

Paramagnetic peak observed for Cr:LiNbO₃ crystals in ESR spectrum after electron, proton or gamma irradiation vanishes after annealing the crystals in air at a temperature of 400°C for 3 h. Additional measurements should be made to explain the nature and localization of the peak.

4. Conclusions

High values of additional absorption after γ or proton irradiation of LiNbO₃:Cr crystal doped during growth or diffusion suggests high level of its defect structure.

The γ irradiation, independently of the temperature and proton irradiation, leads to the appearance of additional absorption bands in Cr:LiNbO₃ single crystal with maxima at 387 and 465 nm. The first one is characteristic for LiNbO₃ crystals and is connected probably with defects of F type center [FRUKACZ et al. 1996]. The second one exists in the range of electron transitions characteristic for Cr³⁺ ions and suggests that a change in Cr

concentration takes place after irradiation. In $\text{LiNbO}_3:\text{Cr}$ crystal lattice there exists certain amount of Cr^{2+} ions (perhaps of higher concentration than Cr^{3+}).

With an increase in diffusion temperature the incorporation of Cr into LiNbO_3 lattice is more intensive but immediately the crystals exhibit higher optical density. The shifting of maximum of additional absorption band after γ irradiation from 330 nm to 380 nm and a very clear decrease in its intensity for diffusion at optimal temperature 1050°C is observed in diffusion doped $\text{Cr}:\text{LiNbO}_3$ crystals. This means better conditions of diffusion with an increase in temperature. Thus the strongest factor which controls the diffusion process is found to be the temperature.

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