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Radiation defects in Dy^{3+} doped $LiNbO_3$ single crystals

S. M. Kaczmarek[a,*], T. Łukasiewicz[b,c], I. Pracka[c], R. Jabłoński[c], G. Boulon[d], B. Kaczmarek[c], S. Warchoł[c,e]

[a]*Inst. of Optoelectronics, M.U.T., 2 Kaliski Str., Warsaw, 01-489, Poland*
[b]*Inst. of Applied Physics, M.U.T., 2 Kaliski Str., Warsaw, 01-489, Poland*
[c]*Inst. of Elec. Materials Technol., 133 Wólczynska Str., Warsaw, 01-919, Poland*
[d]*Laboratoire de Phys.-Chimie des Materiaux Luminescentes, 6922 Villeurbanne cedex, France*
[e]*Inst. of Chem. and Nuclear Technics, 16 Dorodna Str., Warsaw, 01-415, Poland*

Abstract

Absorption measurements of the 'as grown', gamma irradiated and thermal annealed $LiNbO_3$ crystals doped with Dy^{3+} ions for several activator concentrations were performed. It was stated that the positions which the Dy^{3+} ions occupied in $LiNbO_3$ lattice depend on the dopant concentration. The large ion radius of Dy^{3+} ion causes it to locate in the interstital position as Dy^{2+}. Dy^{2+} ions, after exposure to gamma rays as well as thermal annealing, change their valency and become Dy^{3+}. The ESR measurements were performed for trivalent dysprosium. Changes in ESR lines before and after γ exposure at room temperature were not observed. © 1998 Elsevier Science S.A.

Keywords: Gamma-irradiation; Annealing; Ions position in lattice; Interstital positions

1. Introduction

The construction of waveguides as well as of electro-optic modulators and miniature bulk lasers has increased interest in high quality lithium niobate single crystals doped with rare earths [1]. Many reports indicate interest in activating optical glasses by Dy^{3+} ions for the purposes of 1.3 μm band fiber telecommunication [2]. In papers [3,4] authors report the absorption, emission and excitation spectra of Dy^{3+} doped $LiNbO_3$ (LN) and $SrLaGa_3O_7$ (SLGO) crystals. Laser action in Dy^{3+} activated solids has been only observed at the 3 μm band in a BaY_2F_6 crystal [5].

The aim of this work was to examine positions occupied in the LN lattice by Dy^{3+} ions with the use of gamma rays and annealing techniques and absorption measurements.

2. Experimental

The detailed description of the applied growth process is presented elsewhere in [6].

Gamma ray irradiation of the samples was performed with a ^{60}Co source at a rate of 1.5 Gy s^{-1} and dosage levels of the order of 10^5–10^6 Gy.

Thermal annealing was performed at 400°C and 800°C in air for 3 h for 'as grown' and gamma irradiated crystals.

2.1. Spectroscopic investigations

To obtain absorption coefficients in the range of 200–1100 nm, transmission spectra of the samples were measured before and after γ irradiation using a LAMBDA-2 Perkin-Elmer spectrometer. Samples of Dy doped (0.3 at.%, 1 at.% and 1.7 at.%) LN crystals with diameters of 10 mm and a thickness of 1–2 mm were cut out perpendicularly to the growth axis from the most homogeneous part of crystals. To omit scattering effects, samples in the form of a rod of 4 mm in diameter and length of about 50 mm were also subjected to spectroscopic investigations, both before and after gamma irradiation with a dose of 10^5 Gy. We also tried to obtain laser emission from the rods at 3 μm at room temperature, but we had no success.

Values of additional absorption, AA, (ΔK factors) due to the irradiation were calculated from the formula:

$$\Delta K(\lambda) = \frac{1}{d} \cdot \ln \frac{T_1}{T_2}, \quad (1)$$

where d is the sample thickness, T_1 and T_2 are the

*Corresponding author. Tel.: +48 22 6859019; fax: +48 22 6668950; e-mail: laslab@wat.waw.pl

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transmissions of the sample obtained before and after gamma irradiation, respectively.

2.2. ESR investigations

The samples, typically 3.5×3.5×2 mm, were measured in a BRUKER ESP-300 ESR spectrometer (X-band). The ESR lines were observed before and after gamma exposure of a 10^5 Gy dose in the temperature range from 4 to 300 K and microwave power from 0.002 to 200 mW.

3. Results

3.1. Spectroscopic investigations

In Fig. 1 results of absorption (curve No. 1) and AA measurements after 10^5Gy (curve No. 2) and 10^6Gy (curve No. 3) exposure to gamma rays of Dy^{3+}: LN (0.3 at%) plate with a thickness of 2.96 mm are shown. In the range of electron transitions of the Dy^{3+} ion, no more transition bands are observed. Intensity of AA band in the UV range increases with increase in gamma dose.

The 'as grown' Dy:LN rod with a length of 57 mm and 4 mm in diameter containing 1 at.% of Dy^{3+} was γ-exposed with a dose of $\gamma_1 = 10^5$ Gy and next annealed in an air atmosphere at a temperature of 800°C for 3 h and again exposed to the same dose of gamma rays – γ_2. Results of absorption and AA measurements are shown in Fig. 2. As one can see, the concentration of Dy^{2+} ions in the Dy:LN crystal is almost equal to the concentration of Dy^{3+} (curve No. 3). We think that Dy^{2+} ions take up interstitial positions because the effect of gamma rays and annealing at 800°C are the same, i.e. an increase of the Dy^{3+} concentration.

Exposure with gamma rays usually decreases valency of a dopant due to capture of a Compton electron. If the opposite effect is observed it means that ionization of the Dy ion takes place and, in our opinion, this is possible for ions in interstital positions. Annealing of the crystal does not change the shape of AA in the range of electron transitions of the dysprosium ion but removes colour centres in the UV and visible parts of the spectrum (curve No. 5). Repeated exposure of the rod to gamma rays reproduces colour centres and slightly decreases AA in the range of electron transitions (curve No. 6).

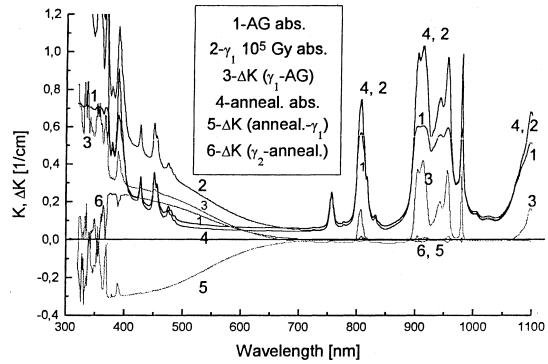

Fig. 2. Absorption and AA bands after both gamma and annealing treatment of Dy:$LiNbO_3$ (1 at.%) rod (l=57 mm): 1='as grown' (AG) crystal; 2=γ_1 10^5 Gy absorption; 3=ΔK (γ_1-AG); 4=absorption after annealing at 800°C; 5=ΔK (anneal.-γ_1); 6=ΔK-(γ_2-anneal.).

To omit scattering and absorption effects the 'as grown' Dy^{3+}:LN plate with a thickness of 3.02 mm containing 1 at.% Dy^{3+} was γ-exposed to a dose of 10^5 Gy and next annealed in an air atmosphere at temperature of 400°C for 3 h and again exposed to the same dose of gamma rays. AA bands as a result of γ-irradiation and the annealing processes are shown in Fig. 3. AA bands with maxima at 375 and 475 nm in the UV and visible range of the spectrum as well as the band connected with the recharging effect of $Dy^{2+} \rightarrow Dy^{3+}$ can be clearly distinguished. Annealing of the plate at 400°C removes the first two colour centers (however not entirely) but the AA band related to the dysprosium recharging effect remains unchanged. Repeated exposure of the annealed sample makes the increase of an absorption in the UV and visible range significantly higher than the level obtained after exposure

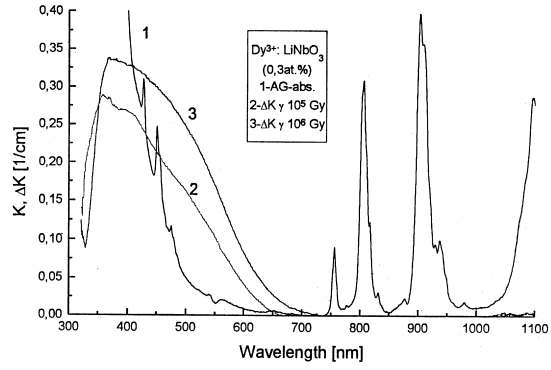

Fig. 1. Absorption (1) and AA bands in γ-irradiated (2=10^5 Gy, 3=10^6 Gy) Dy^{3+}:$LiNbO_3$ (0.3 at.%) plate with a thickness of 3.02 mm.

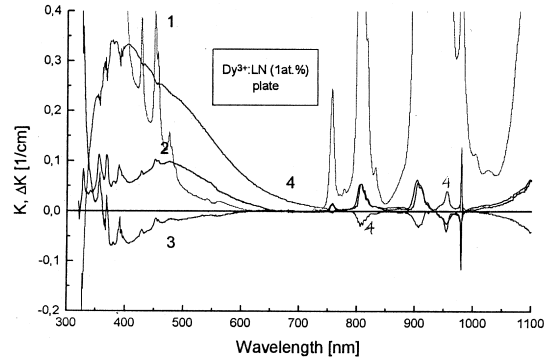

Fig. 3. Absorption and AA bands in Dy^{3+} (1 at.%) doped $LiNbO_3$ crystal plate with a thickness of 3.02 mm after both gamma and annealing treatments. 1=AG-absorption; 2= γ 10^5 Gy AA bands; 3=400°C AA bands; 4−γ 10^5 Gy AA bands.

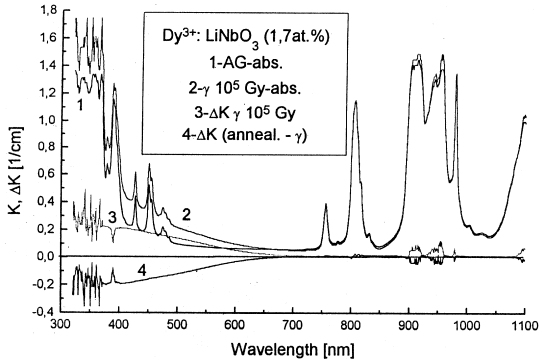

Fig. 4. Absorption and AA bands in Dy:$LiNbO_3$ (1.7 at.%) crystal (rod with $l=51$ mm and $\phi=4$ mm) for both gamma and annealing treatments: 1='as grown' crystal; 2=γ 10^5 Gy absorption; 3=ΔK after γ; 4=ΔK(anneal.-γ).

of an 'as grown' crystal and the recharging effect in the reciprocal direction $Dy^{3+} \rightarrow Dy^{2+}$ is observed.

Thus, independent of sample thickness, after γ-exposure of the Dy^{3+}:LN (1 at.%) crystal, AA bands are observed related to a recharging effect of the type: $Dy^{2+} \rightarrow Dy^{3+}$.

In Fig. 4 the results of a 10^5Gy gamma ray exposure followed by annealing at 800°C of Dy^{3+}:LN(1.7 at%) rod with a length of 51 mm and 4 mm in diameter are shown. Similarly as for the Dy^{3+}:LN (1 at%) crystal, in the range of electron transitions, AA bands appear but with much lower intensity ($\approx$0.1 cm^{-1}) than was observed before.

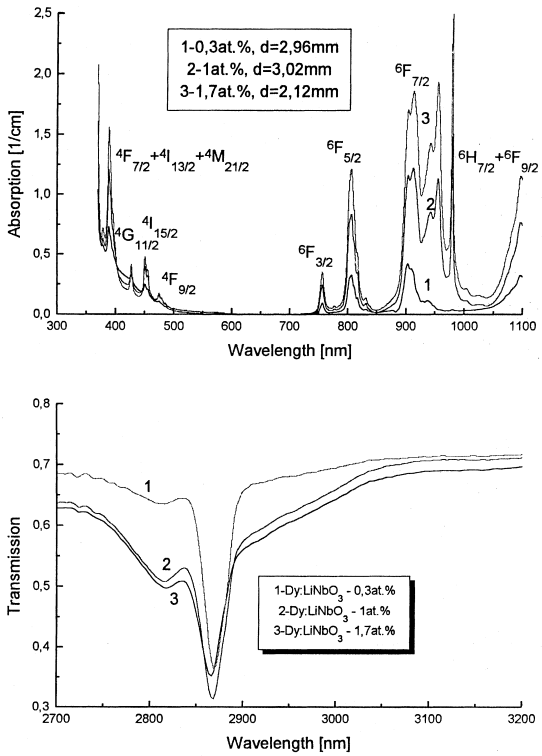

Fig. 5. Absorption spectra (transitions from $^6H_{15/2}$ ground state of Dy^{3+} ion) for LN crystal doped with Dy^{3+} ions with a concentration of: 0.3 at.% (1), 1 at.% (2) and 1.7 at.% (3).

In Fig. 5 the values of the absorption bands for three Dy^{3+}:LN plates with a thickness of 2 mm and dopant concentrations of: 0.3 at%, 1.0 at% and 1.7 at% are shown. As seen from the figure, the spectra of those samples differ significantly. Intensity of transition, e.g., for about 900 nm in the case of the LN crystal containing 0.3 at%, is much higher than for the other 970 nm. For higher concentrations of dysprosium, these relationships change.

3.2. ESR investigations

Dy^{3+} ions ($4f^9$) have ground multiplets $^6H_{15/2}$ and there are two isotopes, 161 and 163, with nuclear spin $I=5/2$ and abundance 19.0% and 2.49%, respectively. The central line observed corresponds to other isotopes with $I=0$. We depicted angular dependence of the ESR lines in the x–z plane at a temperature of 5 K. Moreover we have investigated changes in ESR lines for $H\|z$ and $H\|x$ vs. temperature [7]. We have obtained: $g_{(1)x}=2.56(1)$, $g_{(1)z}=4.43(1)$, $g_{(2)x}=6.67(1)$, $g_{(2)z}=1.23(1)$.

Changes in ESR lines before and after γ irradiation of the samples investigated at room temperature were not observed which does not mean that there is no rise in Dy^{3+} concentration after γ exposure.

4. Discussion

The influence of a ^{60}Co γ-radiation, electron-radiation (3.5 MeV) and heat treatment on the optical properties of LN crystals containing rare-earth dopants was investigated earlier [8,9]. It has been stated that introducing trivalent dopants alone (Tm^{3+}, Er^{3+} or Fe^{3+}) into an LN crystal causes an increase in $\Delta K(\lambda)$ in comparison with nominally pure crystals. The $\Delta K(\lambda)$ increases for γ-irradiated LN crystals in the dose interval of 10^3–10^6 Gy achieved values 0.4–0.5 cm^{-1}. Our investigations led to the same results obtained for Dy^{3+} doped LN crystals.

By inducing the range of electron transitions of Dy^{3+} ions by gamma rays, AA bands show that the concentration of these ions increases after γ-exposure. The mechanism for the formation of colour centres (375 nm, 475 nm) in a Dy:LN crystal is the same as for other LN crystals which indicates that recharging processes of growth defects located in the absorption spectrum close to the short-wave absorption edge dominate (F-type centers and a transition of the niobium ions to a lower valent state; hole centers O^- localized near the cation sublattice defects; biopolarons and the recharge of doping ions or complex associates consisting of an oxygen vacancy and impurity). Change in the dysprosium valency in the LN crystal is clearer than for other types of rare earths. It could be that it is connected with the large difference in ion radii between Dy^{3+} and Li^+ and Nb^{5+} ions. The large ion radius of the Dy ion causes it to locate in the interstitial

position as Dy^{2+}. In the case of a dysprosium concentration of 0.3 at.%, dopant ions take the place of Li^{+}. For concentration ~1 at.% the dopant takes the place of Li^{+} as well as the interstitial positions.

5. Conclusions

Rare-earth elements used as dopants in LN crystals may take the positions of Li^{+}, Nb^{5+} or occupy interstitial sites [10]. Rutherford backscattering measurements only show occupation of the center Li^{+} [11]. After gamma irradiation of 1 at.% Dy^{3+}:LN crystals an additional absorption is observed in the region of electron transitions of the Dy^{3+} ion. The same phenomenon is observed in the annealed crystal (800°C, 3 h, air). It shows two possible positions for dysprosium in the crystal structure: as a Dy^{3+} ion at Li^{+} or Nb^{5+} sites and as a Dy^{2+} ion located at interstitial sites. Dy^{2+} ions after exposure to gamma rays as well as thermal annealing, change their valency and become Dy^{3+}. In this way the effective concentration of Dy^{3+} increases. In the case of the higher concentration of dysprosium ions in the crystal, i.e., above 1 at.%, Dy^{2+} ions are also present but their quantity is much lower.

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