

Optical properties of $\text{LiNbO}_3\text{:Zn}$ and $\text{LiNbO}_3\text{:Zn:Nd}$ fiber single crystals grown by micro-pulling down method

H.J.Lee, J.W.Shur, O.Nakamura^{}, D.H.Yoon^{**}*

School of Advanced Materials Science & Engineering,
Sungkyunkwan University, Suwon 440-746, Korea

^{*}OXIDE corporation, 1747 Mukawa, Hokuto, Yamanashi, Japan

^{**}Sungkyunkwan Advanced Institute of Nanotechnology (SAINT),
Sungkyunkwan University, Suwon 440-746, Korea

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The present interest in small compact diode pumped lasers has supported research on new solid state laser systems based on non-linear crystals. High quality LiNbO_3 fiber single crystals were grown by micro-pulling down method. It was found indirectly from the optical properties of the LiNbO_3 fiber single crystals that doping those with ZnO increases their photorefractive resistance. In addition, photoluminescence properties due to the addition of Nd_2O_3 dopant have been investigated.

Современный интерес к малогабаритным компактным лазерам с диодной накачкой стимулирует исследование новых твердотельных лазерных систем на основе нелинейных кристаллов. Методом микровытягивания выращены высококачественные волоконные монокристаллы LiNbO_3 . Из оптических свойств волоконных монокристаллов косвенным путем установлено, что их легирование ZnO приводит к повышению стойкости к фотоиндуцированной рефракции. Кроме того, исследованы фотолуминесцентные свойства, обусловленные присутствием Nd_2O_3 как легирующей примеси.

Lithium niobate LN (LiNbO_3) single crystal has been studied for various industrial applications such as holographic storage devices [1], solid-state lasers [2] or optical waveguides [3]. However, one serious disadvantage of undoped LiNbO_3 (LN) crystals is the photorefractive effect which occurs when they are irradiated with high-power laser beams, which restricts their utilization in optical device applications. Therefore, the suppression of the optical damage is a very important objective for LiNbO_3 optical devices. To provide an effective solution to this problem, the photorefractive resistance of the LiNbO_3 crystal needs to be improved by addition of ZnO or MgO. However, as with undoped LiNbO_3 , a dark trace is also induced in Mg-doped LiNbO_3 by a high-power laser beam [4]. Therefore, Volk

et al. [5] suggested the use of ZnO doped LiNbO_3 as a new photorefractive-resistant material that does not exhibit the darkening effect under irradiation from a laser beam with intensity of up to 120 MW/cm^2 . Another potential application of LN is in Nd^{3+} based compact diode-pumped self-frequency-doubled lasers which emits green radiation, useful for applications in optical data storage, undersea imaging, diagnosis in medicine, excitation sources to replace ion gas lasers for science and pumping of parametric oscillators and amplifiers [6].

In this work, the $\text{LiNbO}_3\text{:Zn}$ and $\text{LiNbO}_3\text{:Zn,Nd}$ fiber single crystals were grown by the micro-pulling down (μ -PD) method. The grown crystals were free of cracks and homogeneous distributions of

Table. Growth conditions of LN:Zn and LN:Zn,Nd fiber single crystals

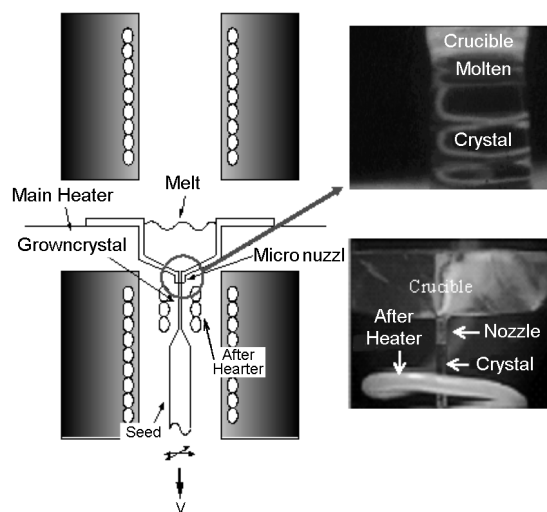
Starting materials	Li_2CO_3 , Nb_2O_5 , ZnO , Nd_2O_3
Stoichiometric composition ($\text{Li}_2\text{CO}_3\text{:Nb}_2\text{O}_5\text{:ZnO}$)	50:50:1, 50:50:2, 50:50:3
Congruent composition ($\text{Li}_2\text{CO}_3\text{:Nb}_2\text{O}_5\text{:ZnO}$)	48.6:51.4:1, 48.6:51.4:3, 48.6:51.4:5
Zn:Nd:LN ($\text{Li}_2\text{CO}_3\text{:Nb}_2\text{O}_5\text{:ZnO}:\text{Nd}_2\text{O}_3$)	50:50:1:0.3, 50:50:3:0.3
Crucible	Pt
Nozzle diameter	1.0 mm
Pulling-down rate	Average 0.5 mm/min
Pulling-down axis	<001>
Crystal diameter	0.8-1.0 mm
Atmosphere	Air

the ZnO and Nd_2O_3 dopant concentration were observed by electron probe analysis (EPMA). The change of the IR transmission spectra and photoluminescence properties with increase of ZnO and Nd_2O_3 dopant contents was investigated for the grown crystal fibers.

Li_2CO_3 , Nb_2O_5 , and dopants powders of 99.99 % purity were used as starting materials. Zn:LN and Zn:Nd:LN fiber single crystals were grown using μ -PD method. The μ -PD method is described in [7] in detail. This method is characterized by the high pulling rate and the low thermal strain which differ from other growth methods [7], and it is possible to grow stoichiometric single crystals from incongruent melt composition [8]. The growth conditions are summarized in Table.

Fig. 1 shows a schematic diagram of the μ -PD apparatus. This growth equipment consists of a Pt crucible directly heated resistively, an after-heater made from Pt wire, an annealing furnace, and a crystal lowering mechanism containing a micro X-Y stage. The crystal diameter was kept constant by controlling the temperature of the crucible and after-heater during the growth process.

The concentrations in the fiber single crystals were determined by EPMA (JEOL JXA-8900R) and the defects were observed by optical microscopy. The IR transmission spectra of the crystals were obtained using a Fourier Transform Infrared spectrophotometer (FT-IR, Bruker IFS-66/S) at room temperature. The PL spectra were measured using a laser Raman and photoluminescence spectrometer (SPEX 1403) and PL measurements were divided into three wavelength ranges.

Fig. 1. Schematic diagram of μ -PD apparatus.

The $\text{LiNbO}_3\text{:Zn}$ fiber single crystals of near-stoichiometric and congruent compositions were successfully grown by the μ -PD method. The fiber crystals were 20-30 mm in length at a diameter of 0.8-1.0 mm. The grown crystals had a uniform shape and their diameter was almost constant. The grown crystals were transparent and changed from colorless to yellow with increasing ZnO concentration. Fig. 2(a) and (b) shows the distribution of the Zn concentration in ZnO doped near-stoichiometric and congruent LiNbO_3 fiber single crystals along the growth c-axis. The distributions of 1, 2 and 3 mol.% ZnO in the near-stoichiometric LiNbO_3 crystals are shown in Fig. 2(a), while Fig. 2(b) shows the composition distribution of 1, 3 and 5 mol.% ZnO in the congruent LiNbO_3 crystals. The EPMA results revealed that the ZnO concentration was very similar to the initial melt composition. This means that very little

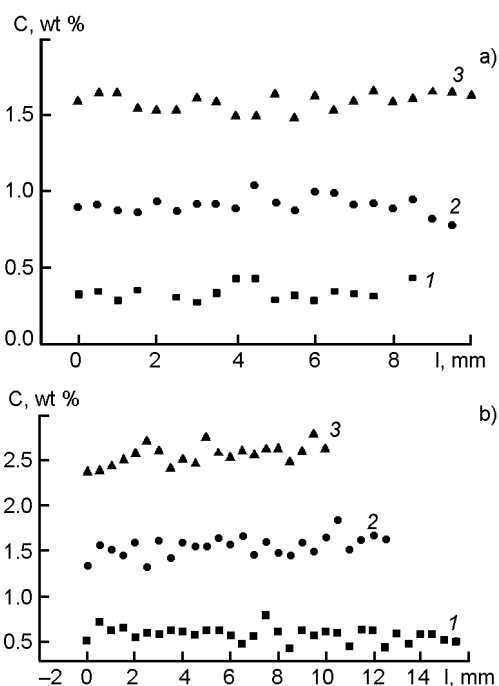


Fig. 2. Distribution of ZnO concentration in the LiNbO_3 fiber single crystals along the growth c-axis: a - stoichiometric crystals doped SLN: 1- 1 mol. %, 2 - 2 mol. %, 3 - 3 mol. %; b - congruent crystals doped CLN: 1- 1 mol. %, 2 - 3 mol. %, 3 - 5 mol. %.

segregation occurred during crystal growth, because of the restricted convection in the micro-nozzle and the shape of the flat solid-liquid interface. A flat solid-liquid interface is established with a meniscus of narrow width and the same diameter as the crystal under the micro-nozzle. The axial temperature gradient at the solid-liquid interface was about $300^\circ\text{C}/\text{mm}$ and was controlled by adjusting the temperature of the Pt after-heater. The configuration of the micro-nozzle and after-heater makes it easy to control the shape of the flat liquid-solid interface and its temperature [9].

The optical transmission spectra of the crystals were measured using an FT-IR spectrophotometer. Fig. 3(a) shows the OH^- absorption peaks of the near-stoichiometric LiNbO_3 fiber single crystals obtained by adding 1, 2 and 3 mol.% ZnO. The OH^- absorption peak of the undoped LiNbO_3 crystal was located at 3485 cm^{-1} and the doping of the LiNbO_3 crystal with 1 mol.% ZnO appeared only to change the absorption band intensity without resulting in any OH^- absorption band shift (OH^- absorption band: 3483 cm^{-1}). The OH^- absorption bands of the 2 and 3 mol.% doped LiNbO_3 fiber sin-

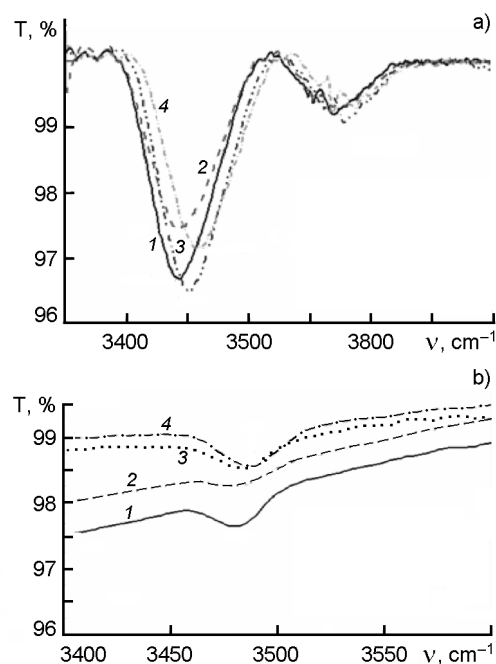


Fig. 3. IR absorption band of ZnO doped - a - nearstoichiometric crystals doped SLN: 1- undoped, 2- 1 mol. %, 3 - 2 mol. %, 4 - 3 mol. %; b - congruent LiNbO_3 fiber single crystals doped CLN: 1- undoped, 2 - 1 mol. %, 3 - 3 mol. %, 4 - 5 mol. %.

gle crystals were shifted to 3505 and 3518 cm^{-1} , respectively. On the other hand, Fig. 3(b) represents the OH^- absorption peaks of the congruent LiNbO_3 fiber single crystals with 1, 3 and 5 mol.% ZnO. The OH^- absorption peaks of the undoped and 1 and 3 mol.% ZnO doped LiNbO_3 fiber single crystals were all located at approximately 3478 cm^{-1} . However, in the case of the 5 mol.% ZnO doped LiNbO_3 fiber single crystals, the OH^- absorption peak shifted to 3487 cm^{-1} .

The OH^- absorption peaks were confirmed to be almost same for the undoped near-stoichiometric LiNbO_3 (3485 cm^{-1}) and the 5 mol.% doped the congruent LiNbO_3 (3487 cm^{-1}). As a result of this experiment, the near-stoichiometric LiNbO_3 fiber single crystals showed the better photorefractive resistance than the congruent LiNbO_3 . This phenomenon provides convincing proof that the Zn^{2+} ion dopant initially enters into the Li sites rather than the Nb sites because of the change in the misfit compensation in the LiNbO_3 crystal [10]. In the near-stoichiometric LiNbO_3 fiber single crystal, Zn^{2+} ions can occupy the Nb sites at even a little amount of ZnO dopant, while Zn^{2+}

ions in the congruent LiNbO_3 fiber single crystal can substitute for Nb sites at over 5 mol.% ZnO doping because of the change of misfit compensation. The Zn^{2+} ions substitute for the Nb_{Li} ions and then, when the ZnO doping level exceeds the threshold point, extra Zn^{2+} ions substitute for Nb_{Nb} . The Zn^{2+} ions which occupy the Nb sites form strongly negatively charged $(\text{Zn}_{\text{Nb}})^{3-}$ ions in the LiNbO_3 crystal. As a result, the decreased positive ions can improve the optical conductivity of the photoelectrons. This means that the OH^- absorption band spectra can shift to a higher energy when the negatively charged $(\text{Zn}_{\text{Nb}})^{3-}$ ions are formed in the LiNbO_3 crystal. It is therefore to conclude that the threshold levels of ZnO doping the near-stoichiometric and the congruent LiNbO_3 fiber single crystals were measured to be of the order of 2 and 5 mol.%, respectively.

The 1 and 3 mol.% ZnO co-doped LN:Nd fiber single crystals of stoichiometric composition were successfully grown by μ -PD method. The crystals had a size of 0.8–1 mm in diameter and about 25 to 30 mm in length. The crystals were transparent and blue. Fig. 4(a) shows a PL spectrum of LN:Nd co-doped with 1 and 3 mol.% ZnO single crystal fibers in the range of 800–900 nm. The double spectrometer technique was used to measure the PL properties at room temperature, using an Ar-ion laser as the exciting source. The excited Nd^{3+} ions were initially excited to upper energy level and then dropped to the metastable state. The PL intensity from the sample doped with 3 mol.% ZnO was stronger than that of the sample doped with 1 mol.% ZnO at the same wavelength. The strongest intensity peak was found in the wavelength range around 880 nm. This peak is due to the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition. Figs. 4(b) and (c) show PL spectra of LN:Nd single crystal fibers co-doped with 3 mol.% ZnO in the range 1000–1100 and 1300–1400 nm. The strongest intensity peaks are found in the wavelength ranges around 1065 and 1340 nm, respectively. The peak around 1065 nm is due to the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition and that around 1340 nm, to the ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ transition.

Thus, using the μ -PD method, LN:Zn and LN:Zn,Nd fiber single crystals were grown to confirm the optical properties. The distribution of the ZnO concentration in the LiNbO_3 fiber single crystals was homogeneous along the growth c -axis. The near-stoichiometric

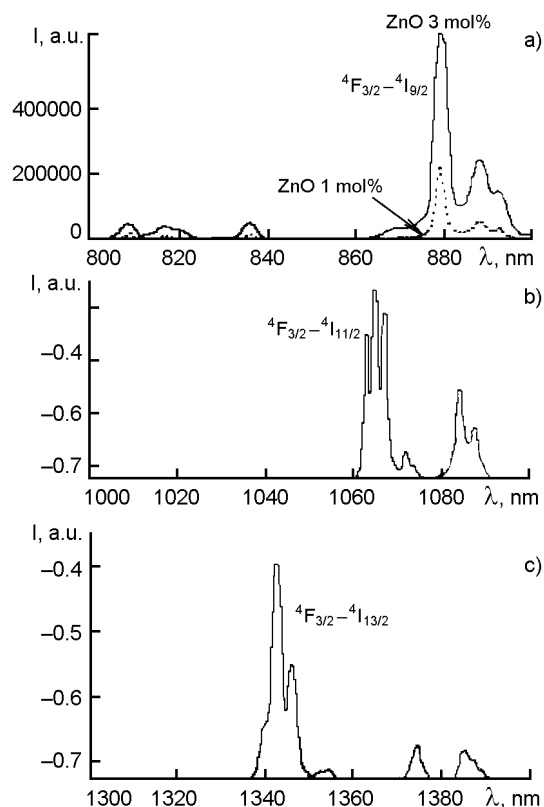


Fig. 4. Photoluminescence spectra of the LiNbO_3 :Nd co-doped with ZnO fiber single crystals: (a) 800–900 nm; (b) 1040–1100 nm; (c) 1300–1400 nm wavelength.

LiNbO_3 fiber single crystals have shown a better photorefractive resistance than the congruent LiNbO_3 , because of the almost same OH^- absorption peaks in undoped near-stoichiometric and 5 mol.% doped congruent LiNbO_3 fiber single crystals. The threshold levels for the ZnO doped near-stoichiometric and congruent LiNbO_3 fiber single crystals were confirmed to be of the order of 2 and 5 mol.%, respectively.

In addition, the PL spectra of LiNbO_3 :Zn,Nd fiber crystals were measured in the range of 800–900, 1000–1100 and 1300–1400 nm. The most intense peaks were at the wavelengths around 880, 1065 and 1340 nm, these peaks being due to the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$, ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ transition, respectively. Also, the intensity of PL from the grown crystals was increased by addition of ZnO.

References

1. F.H.Mok, *Opt. Lett.*, **18**, 915 (1993).
2. L.F.Johnson, A.A.Ballman, *J. Appl. Phys.*, **40**, 297 (1969).

3. M.N.Armenise, C.Canali, M.D.Sario et al., *Mater. Chem. Phys.*, **9**, 267 (1983).
4. T.Y.Fan, A.Cordova-Plaza, M.J.F.Digonnet et al., *Opt. Soc. Amer.*, **B3**, 140 (1986).
5. T.R.Volk, V.I.Pryalkin, N.M.Rubinina, *Opt. Lett.*, **15**, 996 (1990).
6. J.Capmany, D.Jaque, J.A.Sanz Garcia et al., *Opt. Commun.*, **161**, 253 (1999).
7. D.H.Yoon, P.Rudolph, T.Fukuda, *J. Cryst. Growth*, **144**, 207 (1994).
8. K.Imai, M.Imaeda, S.Uda et al., *J. Cryst. Growth*, **177**, 123 (1997).
9. D.H.Yoon, I.Yonenaga, T.Fukuda et al., *J. Cryst. Growth*, **142**, 339 (1994).
10. S.Kawakami, E.Ishii, A.Tsuzuki et al., *Mater. Res. Bull.*, **21**, 463 (1986).

**Оптичні властивості волоконних монокристалів
LiNbO₃:Zn and LiNbO₃:Zn:Nd,
що вирощені методом мікровитягання**

Г.Дж.Лі, Дж.У.Шур, О.Накамура, Д.Г.Юн

Сучасний інтерес до малогабаритних компактних лазерів з діодною накачкою стимулює дослідження нових твердотільних лазерних систем на основі нелінійних кристалів. Методом мікровитягання вирощено високоякісні волоконні монокристали LiNbO₃. З оптичних властивостей волоконних монокристалів непрямым шляхом встановлено, що при їх легуванні ZnO підвищується стійкість до фотоіндукованої рефракції. Крім того, досліджено фотолюмінесцентні властивості, обумовлені присутністю Nd₂O₃ як легувальної домішки.