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Invited Paper

Change of optical properties of $LiNbO_3$ fiber single crystals by addition of rare-earth elements

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Rare earth doped lithium niobate, $LiNbO_3$ (LN) have received a renewed attention because of the availability of a broad range of laser sources as the pump sources because their emission wavelength 1.34 µm (Nd^{3+}) and 1.54 µm (Er^{3+}) are quite useful in the optical communications. In this study, rare-earth doped LN single crystal with stoichiometric composition fibers were grown by the micro-pulling down (µ-PD) method which is advanced method of crystal growth. The grown crystal fibers were investigated about the homogeneity and change of the photoluminescence (PL) for active ions in the crystals according to influence on adding of rare-earth. The grown fiber crystals were had no crack and sub-grain boundary and good optical properties.

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1. Introduction

Lithium niobate, $LiNbO_3$ (LN), is a material that combines excellent electro-optic, acousto-optic and non-linear properties with the possibility of rare earth or transition metal doping. The material can be used in bulk or it is possible to prepare low-loss optical waveguides [1]. Especially, erbium (Er_2O_3, Er) doped LN has been proposed as a very useful material for optical storage, optoelectronics, and waveguide devices [2]. The crystal can simultaneously emit the second harmonic light through quasi-phase matching [3] and green light through up-conversion at room temperature [4] with a combination of the nonlinear optical properties of LN and the spectral properties of Er. For such a optical properties, Er doped LN single crystals of high quality without sub-grain boundaries are generally required.

Also, because of their high electro-optical and nonlinear coefficients, the LN single crystals doped with Nd^{3+} rare-earth (RE) ions offer the interesting possibility of making CW, self Q-switched or self frequency-doubled compact diode-pumped mini-lasers suitable for integrated optics emitting in the infrared or in the green region [5-6]. But Nd^{3+} ion based lasers and amplifiers have been shown to reduce the optical quality and make difficult the growth of crystals sharing high optical quality and high Nd^{3+} concentration. Because the congruent composition is different from the stoichiometric composition, the LN of the composition which escaped from the congruent composition is very difficult to be grown to a single crystal without defect [7].

Recently, certain materials have attracted attention for a new generation of high speed, efficient, multi-functional optical devices. Among these materials, small-diameter long-length bulk crystals are of considerable interest for miniaturization and high efficiency. In particular, fiber single crystals have already received attention as attractive materials for a variety of electro-optical application [8-10] because of because of the high surface-volume ratio, the long interaction length and the high crystal quality [11-12].

Consequently, in this study, RE (Nd or Er) doped LN fiber single crystals with stoichiometric composition fibers were grown by the micro-pulling down (µ-PD) method which is advanced method of crystal growth. The optical properties on the RE doped LN fiber single crystals have been observed by the measurements of transmission and photoluminescence (PL) spectra.

2. Experimental

It has been reported for several years that the interface electric field influences solute partitioning leading to an electric field-dependent effective solute partition coefficient [13-14]. This is peculiar to the growth by the µ-PD method which accompanies a significantly high temperature gradient at the solid-liquid interface.

In the frame work of the “micro crystal project”, since 1992, the development and broad application of single crystalline fiber growth by the “micro-pulling down (µ-PD)” method was established at Fukuda laboratory of Tohoku university. The method, described for the first time by Yoon and Fukuda etc. for the growth of oxide fiber single crystals [15-21].

The crystal growth method, called the μ-PD method, involves growing single crystals through a micro-nozzle by pulling in the downward direction, as shown Fig. 1. This growth equipment consists of a 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 single crystal was formed by attaching the seed crystal to the tip of the micro-nozzle and slowly pulling it downward with a constant velocity. The alignment of the seed and the micro-nozzle was controlled by the micro X-Y stage. The crystals were grown in air atmosphere. The growth rate was varied from 12 to 90 mm/h.

The configuration of the micro-nozzle and after-heater makes it easy to control the liquid-solid interface temperature and the crystal diameter. In this way the growth conditions can be kept constant and it is reasonable to assume that it is possible to continue growing until the melt is all consumed.

One of the greatest advantages of the μ-PD method is the very high growth rate. Because of the absence of natural convection in the very thin nozzle, a diffusion-controlled regime with high composition homogeneity is created.

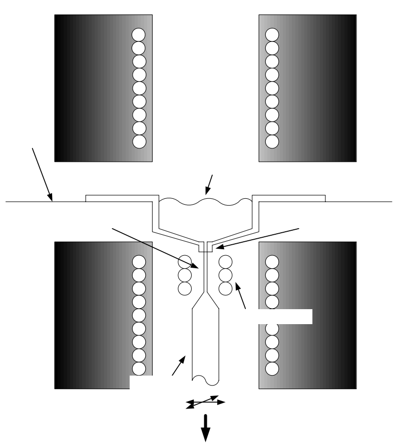

Fig. 1. Schematic diagram of the μ-PD apparatus.

Moreover, the temperature gradient along the growth axis near the nozzle is about 300 ℃/mm, enabling growth rates much faster than the Czochralski (CZ) method.

In this study, the rare-earth doped LN single crystal fibers were grown by the μ-PD method from a stoichiometric melt containing with Nd_2O_3 or Er_2O_3 of 1 and 3 mol%. The starting materials were prepared by mixing Li_2CO_3 and Nb_2O_5 powders at a stoichiometric composition of Li/Nb=1. They were then doped with 1 and 3 mol% Nd_2O_3 or Er_2O_3, respectively. All raw materials (Li_2CO_3, Nb_2O_5, Nd_2O_3 and Er_2O_3) were 99.99% purity.

The raw materials were melted in the Pt crucible and allowed to pass through the micro nozzle. The single crystal fibers were formed by attaching the seed crystal, which was pulled down at a constant velocity. Crystal diameter was maintained constant by controlling the temperature of the main and after heaters during the growth process. The prepared materials were loaded in a Pt crucible with a micro nozzle at a bottom and heated up to 1150℃ to melt. The pulling down rate was 0.3~0.5 mm/min and growth direction was z-axis. The transmission peaks and photoluminescence (PL) spectra were measured using a UV/VIS/NIR spectrophotometer, laser Raman and PL spectrometer (SPEX 1403).

3. Results and discussion

Using the μ-PD method, RE doped LN fiber single crystals of 1 mm in diameter were grown along the z-axis. Fig. 2 shows typical as-grown LN fiber single crystal which are represented with microscopic detail magnification of 1 mm diameter grown along the z-axis. We have grown crack-free z-oriented RE doped LN crystals with length up to 50 mm and high diameter constancy using the μ-PD method. Homogeneous colorlessness over the whole length and uniform diameter independent of the growth directions can be shown.

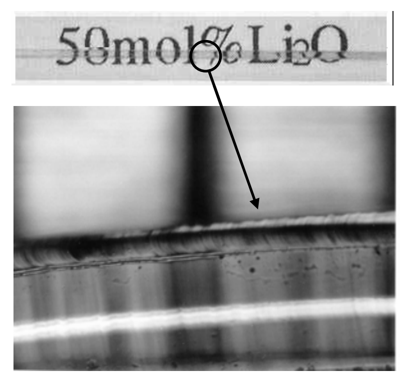

Fig. 2. Photograph of z-oriented LN fiber single crystal with diameters of 1 mm grown from the melt with 50 mol% Li_2O

Also, the crystals grown were free of cracks from the stoichiometric composition (50 mol% Li_2O).

3. 1. The optical properties of Nd doped LN fiber single crystals

The Nd doped stoichiometric LN fiber single crystals were grown by μ-PD method. For the stoichiometric composition, the best single crystal fiber was obtained with pulling-down rate equal to 0.3 mm/min. The Nd doped LN fiber single crystals grown from the melts of stoichiometric composition were transparent from colorless to blue in color depending on the increase of Nd concentrations and represent 45~50 mm length with 1 mm in diameter. The surface was very flat and smooth, and diameter was almost constant. Also, the grown LN fiber single crystals were crack free and not contained visible defects.

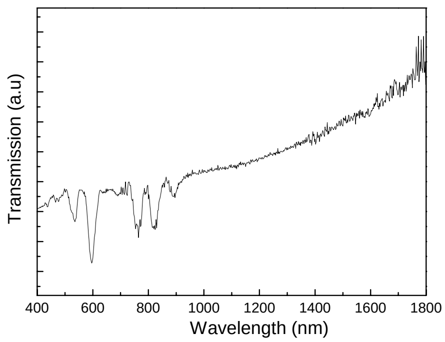

Fig. 3. The transmission spectra of Nd doped LN fiber single crystal.

The optical properties according to Nd^{3+} ions concentration in LN fiber single crystals were measured by laser system that the source was non-polarized light. The incident light inputted toward the growth direction. The transmission spectra of Nd doped LN fiber single crystal was shown in Fig. 3.

Fig. 4 shows PL spectra of 1 and 3 mol% Nd doped stoichiometric LN fiber single crystals in the wavelength range of 800~900 nm. The double spectrometer technique was used to measure the fluorescence spectra and performed at room temperature, using an Ar-ion laser as an excitation source.

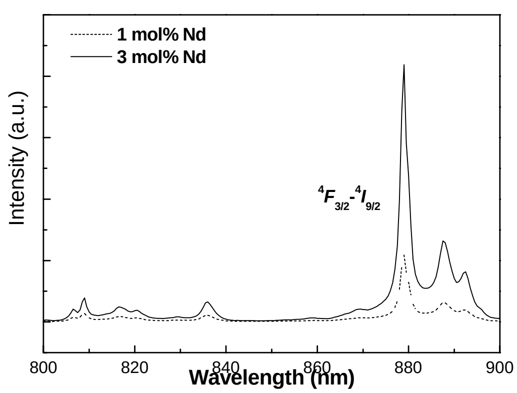

Fig. 4. PL spectra of the 1 and 3 mol% Nd doped LN fiber single crystals.

The intensity peaks of PL spectra of the 3 mol% Nd doped LN fiber single crystal was stronger than that of 1 mol% Nd doped LN single crystal fiber in the same wavelength range. It was the same as other wavelength range. The strongest intensity peaks of PL spectra were discovered in the wavelength range around 880 nm. This intensity peak was due to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition.

Fig. 5 (a) and (b) show fluorescence spectra of the 3 mol% Nd doped stoichiometric LN fiber single crystals in the wavelength range of 900~1250 and 1250~1700 nm.

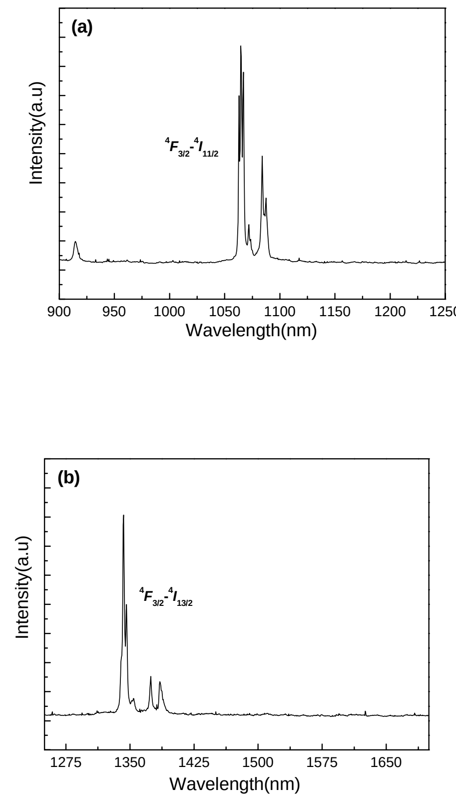

Fig. 5. PL spectra of the Nd 3 mol% doped stoichiometric LN fiber single crystals: (a) 900~ 1250 nm wavelength; (b) 1250~ 1700 nm wavelength.

The strongest intensity peaks of fluorescence spectra were discovered in the wavelength around 1060 and 1340 nm, respectively. In other wards, the strongest intensity peaks of PL spectra around 1060 nm wavelength range was due to the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition and that around 1340 nm wavelength range was due to the $^4F_{3/2} \rightarrow {}^4I_{13/2}$ transition, separately.

3. 2. The optical properties of Er doped LN fiber single crystals

The Er doped fibers were used to prove the physical mechanism of two-photon as well as excited-state absorption under near-infrared (NIR) diode laser excitation [22-25]. And room temperature green up-conversion lasers were developed by pumping Er-doped fibers with infrared (IR) lasers [26-28]. The doping of LN is an interesting task because it enables the combination of the optically active Er^{3+} ions with the excellent nonlinear, electro-optical and acousto-optical properties of this material [29].

The Er doped LN fiber single crystals with stoichiometric composition were grown by μ-PD method. The crystals were transparent, but the colors of grown crystals were changed from colorless to pink depending on increase of the Er concentration in the crystal. The grown LN fiber single crystals had a uniform shape (1 mm in diameter, 30~40 mm in length) and were grown free of cracks.

The transmission spectra at room temperature are shown in Fig. 6. Several energy bands are observed in the grown LN fiber single crystals. The observed energy bands are due to the f_{11} electronic configuration of Er^{3+} ions, it is the transition from the ground state $^4I_{15/2}$ to the excited states which are created from the $^4f_{11}$ electron configuration.

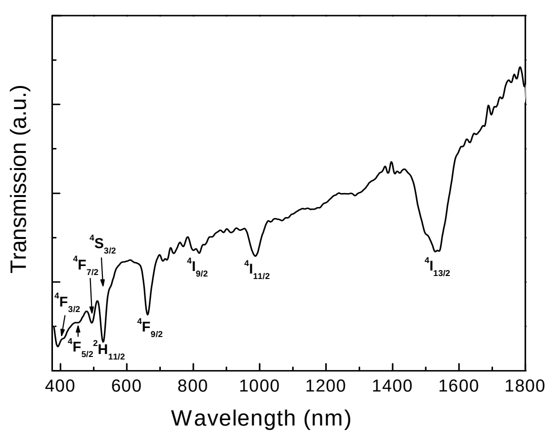

Fig. 6. The transmission spectra of Er doped LN fiber single crystal.

Also, the double spectrometer techniques were used to measure the PL properties. The PL spectrometry was performed at room temperature, using the 514 nm line of an Ar-ion laser as an excitation source. Fig. 7 (a) and (b) shows the PL spectra of Er 1 and 3 mol% doped stoichiometric LN fiber single crystals. In Fig. 7 (a) and (b), the PL spectra of ranges 520~540, 545~565, 650~680, 840~880 and 1500~1570 nm were observed and each peaks corresponded to the transitions of the energy levels of $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$ and $^4I_{13/2}$ to the ground state of $^4I_{15/2}$. The strongest peaks of intensities were discovered in the green wavelength range of 545~560 nm and IR wavelength range of 1525~1575 nm. These peaks around 550 and 1530 nm were due to the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions. The intensities of the PL spectra were increased by the increase of Er concentration.

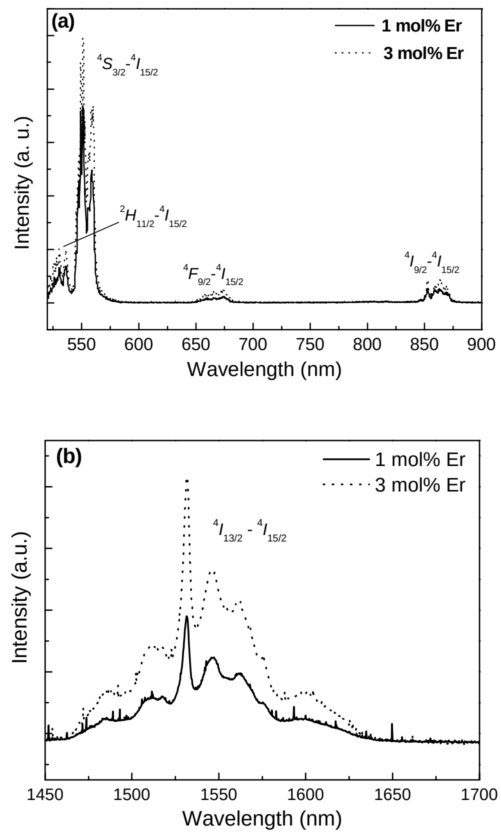

Fig. 7. PL spectra of 1 and 3 mol% Er doped stoichiometric LN fiber single crystals.

From this study, the changes of energy levels of LN fiber single crystals were confirmed by the addition of RE (Nd and Er) elements. In case of The Nd doped LN fiber single crystals, the strongest intensity peaks of PL spectra were discovered in the wavelength range around 880, 1060 and 1340 nm, respectively. Also, in case of The Er doped LN fiber single crystals, the strongest peaks of intensities were discovered in the wavelength range of 550 and 1530 nm. In accordance with these results, the applications of various fields of UV-visible lasers, telecommunications, display, etc. are expected.

4. Conclusions

The grown rare-earth doped stoichiometric LN fiber single crystals by μ-PD had no crack and sub-grain boundary and good optical properties. In case of the Nd doped LN fiber single crystals, the transmission spectra of the grown LN single crystals were measured in the range 530~ 540, 590~ 600, 755~ 765, 805~ 825 and 885~ 900 nm. And the PL spectra were measured in the range of 870~900, 1050~1100 and 1320~1400 nm. The strongest intensity peaks of PL spectra were discovered in the wavelength range around 880, 1060 and 1340 nm, respectively. These peaks were 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. The PL spectra of the grown fiber single crystals were increased by addition of Nd^{3+} ions in the same wavelength range. Also, in case of the Er doped LN fiber single crystals, several energy bands are observed in the transmission spectra. The PL spectra of green wavelength range (from 520 to 565 nm), red wavelength range (from 650 to 680 nm) and IR wavelength range (from 1450 to 1650nm) were observed. It can be known that the emission peaks of 530, 550, 660 and 1530 nm correspond to the $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$ and $^4I_{13/2}$ transitions to the $^4I_{15/2}$ ground state, respectively. The intensities of the PL spectra were increased by the increase of Er concentration.

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