

Growth and upconversion properties of erbium doped LiNbO_3 single crystal fibers

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Abstract Erbium (Er) doped LiNbO_3 (Er : LiNbO_3) single crystal fibers were grown free of cracks along the c-axis by micro-pulling down method. The Er^{3+} concentration was distributed homogeneously along the growth axis. The samples for optical characterization were cut from as-grown single crystal fibers and polished. When the 980nm light was incident on the sample, upconversion phenomena were observed at the green range of wavelength 510~570 nm. In addition, the intensity of upconversion was remarkably increased by increasing the concentration of Er_2O_3 dopant in as-grown Er : LiNbO_3 crystals.

1. Introduction

Erbium (Er) doped LiNbO_3 (Er : LiNbO_3) has recently gained attention through the development of light amplifier based on optical fibers [1]. And the work for near infrared (NIR) pumped blue/green lasers has been studying for the development of short-wavelength solid lasers [2], which have many technical applications including data storage, laser printing, underwater communications and full color laser display etc. [3]. LiNbO_3 is a very well-known crystal due to its unique physical properties of the ferro-electric material, which also shows piezo-electric, elastic-optic and photo-refractive effects [4, 5]. Some of these properties are drastically affected by the presence of impurities and the growth conditions [6]. Thus with a combination of the nonlinear optical properties of LiNbO_3 and the spectral properties of Er^{3+} , the crystal can simultaneously emit the second harmonic light through quasi-phase matching [7] and green light through upconversion at room temperature [2]. However it has a different physical mechanism between second harmonic generation and upconversion [8]. For such a optical properties, Er: LiNbO_3 single crystal fibers of high quality without subgrain boundaries are generally required. Yoon *et al.* [9] had developed the micro-pulling down (μ -PD) method. The characteristics of the method has high pulling down rate, low thermal strain compared with other growth method and it is possible to grow a crystal from incongruent melt composition [10].

In this work, we have grown Er : LiNbO_3 single

crystal fibers by the μ -PD method. Furthermore, this study was aimed at the dependence of the upconversion intensity on the doping concentration. We investigated the upconversion phenomena of green fluorescence in a Er: LiNbO_3 single crystal fibers exposed to light at the wavelength of 980nm which correspond to energy transitions of the Er^{3+} ions and compared the upconversion intensities under the two different conditions.

2. Experimental procedure

The starting materials were Li_2CO_3 and Nb_2O_5 powders of 99.99 % purity. They were thoroughly mixed in a ball mill at a congruent composition ($\text{Li}_2\text{O}_3/\text{Nb}_2\text{O}_5 = 48.6/51.4$). Doped materials were prepared by mixing the raw materials with 1 mol% and 3 mol% of Er_2O_3 (99.99 %).

Er : LiNbO_3 single crystal fibers were grown by the μ -PD method. Figure 1 shows a schematic diagram of μ -PD apparatus and growth conditions are summarized in Table 1.

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 to the tip pulled down at constant velocity. The alignment of the seed to the micro nozzle was controlled by the micro X-Y stage. Crystal diameter was maintained constant by controlling the temperature of the main and after heaters during growth process.

Several test plates (2 mm thick) were cut from as-

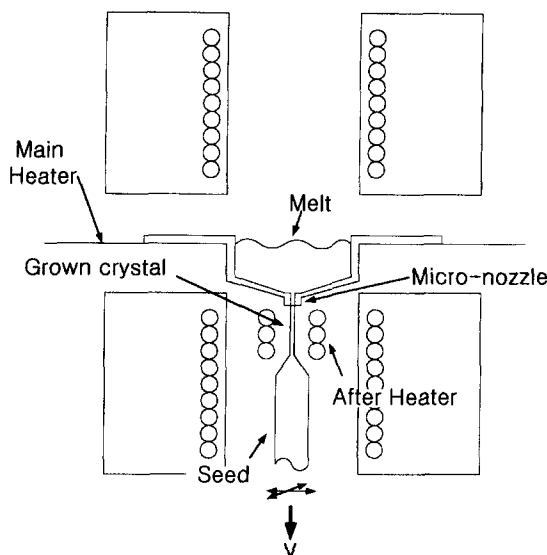


Fig. 1. Schematic diagram of m-PD apparatus.

Table 1
Growth conditions of Er:LiNbO₃ single crystal fibers.

Starting materials	Li ₂ CO ₃ , Nb ₂ O ₅ , Er ₂ O ₃
Melt composition (Er : Li : Nb)	1 : 48.6 : 52.4, 3 : 48.6 : 52.4
Crucible	Pt, 2×0.5×0.5 cm ³
Nozzle diameter	0.5 mm
Pulling-down rate	0.5~2 mm/min
Pulling-down axis	<001>
Crystal Diameter	0.3~0.5 mm
Atmosphere	Air

grown fiber crystals and polished for optical characterization. The fluorescence spectra were recorded with a SPEX/fluorolog-T2 spectrofluorometer system. It was obtained with a pulsed 980 nm Xenon lamp and the single monochromator. All spectral measurements were performed at room temperature. Er³⁺ compositional distribution in the samples was determined by electron probe microanalysis (EPMA).

3. Results and discussion

The Er:LiNbO₃ single crystal fibers were grown with Er₂O₃ concentrations of 1 and 3 mol%. The crystals were transparent, changing from colorless to pink in color depending on increase of the Er³⁺ concentration in crystal. The crystals had a uniform shape and were grown free of cracks.

Figure 2 shows the distribution of Er³⁺ ions along

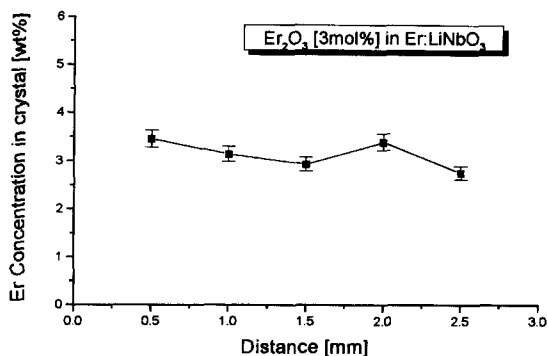


Fig. 2. Distribution of Er³⁺ ions along the grown c-axis.

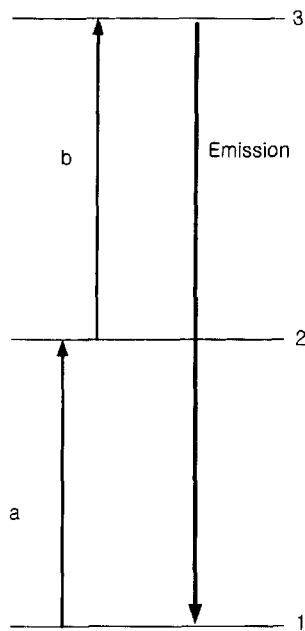


Fig. 3. Sequential two-photon absorption upconversion in a three-level ion.

the grown c-axis in 3 mol% Er₂O₃ doped crystals. The concentrations of Er³⁺ are almost identical to the initial melt composition, which means that the very little segregation occurred during crystal growth. This is probable because the nature convection was restricted in the micro-nozzle and the Er₂O₃ constituent in Er:LiNbO₃ melt became unity along the growth axis leading to the homogeneous composition throughout the fiber [11].

Figure 3 shows the upconversion process described using three-level ions. Sequential two-photon upconversion relies on two photons at different wavelength, a and b, to populate the upper emitting level of the ions. Pho-

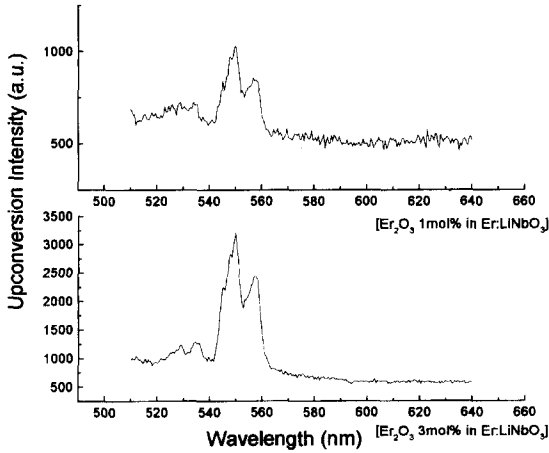


Fig. 4. Emission spectrum of upconversion phenomena; (a) 1 mol% Er₂O₃ doped crystal (b) 3 mol% Er₂O₃ doped crystal.

ton a promotes the ground state ion to the metastable intermediate state, while photon b promotes the ion from the metastable state to the upper emitting level [12].

Figure 4 shows when the 980 nm light was incident on the sample, green fluorescence spectra were observed with an incident power of 450 W (Xenon Lamp). It was observed that the fluorescence peak was strong with increasing the Er₂O₃ concentration. It shows that the Er:LiNbO₃ really possesses strong upconversion emission, at the green light of wavelength 510~570 nm. Among the peaks, the 550 nm peak was the most intense one.

The dominant peaks around 550 nm were due to the ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition, whereas the small peaks around 530 nm were due to the ${}^2H_{11/2} \rightarrow {}^4I_{15/2}$ transition. For the same pump intensities, the measured fluorescence intensity for the 3 mol% Er₂O₃ doped crystals was about 3.5 times larger than that for the 1 mol% Er₂O₃ doped crystals.

Figure 5 shows the upconversion mechanism for sequential two-photon absorption of Er³⁺ ions in Er:LiNbO₃ crystals. The ground-state-absorption (GSA) and the excited-state-absorption (ESA) refer to photon wavelengths corresponding to the ${}^4I_{15/2} \rightarrow {}^4I_{11/2}$ and ${}^4I_{11/2} \rightarrow {}^4F_{7/2}$ transitions, respectively, where ${}^4I_{15/2}$ is the ground state and ${}^4I_{11/2}$ is the metastable state, and the emission from ${}^4S_{3/2}$ produces visible radiation. It is characterized that the ESA ions decay through rapid non-radiation processes from the ${}^4F_{7/2}$ level to the ${}^4S_{3/2}$ level in upconversion phenomena [13]. In Er:LiNbO₃ crystals, it is believed that the green upconverted fluorescence

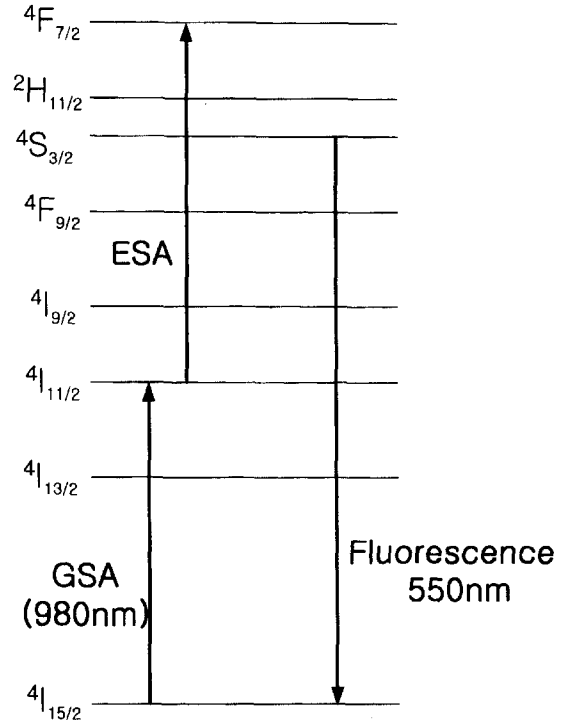


Fig. 5. Energy level structure of Er³⁺ ions in LiNbO₃ crystals.

corresponding to the ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions of Er³⁺ ions was emitted.

4. Summary

LiNbO₃ single crystal fibers doped with a high concentration of Er₂O₃ were grown free of cracks by micro-pulling down method. And it was demonstrated the visible dual-wavelength light generation in Er:LiNbO₃ and observed green upconverted fluorescence when the samples were exposed to the light with 980 nm wavelength. For the 980 nm exposure the dominant mechanism for the upconverted fluorescence was proved to be the sequential two-photon excitation. The intensity of upconversion was increased by increasing the concentration of Er₂O₃ in Er:LiNbO₃. Thus, it is expected that the Er³⁺ concentration in LiNbO₃ had an effect on the intensity of upconversion.

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