

## Single crystal growth and effects of stoichiometry and dopant ( $Mg^{2+}$ ) on the properties in $LiNbO_3$

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### $LiNbO_3$ 단결정 성장과 결정의 특성에 대한 화학양론성과 첨가물( $Mg^{2+}$ )의 영향

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**Abstract** The effect of dopant and stoichiometry on the physical and optical properties of  $LiNbO_3$  were studied. We prepared three samples, undoped, MgO doped  $LiNbO_3$  with congruent composition and near-stoichiometric  $LiNbO_3$ . Dielectric constant and transmittance in UV/VIS/IR light range were measured. The results showed that the features for high [Li]/[Nb] were similar to those for low [Li]/[Nb] but with high [Mg].

**요 약** 본 연구에서는 floating zone 법에 의해서 고용조성의 순수한  $LiNbO_3$ 와 MgO가 5 mol% 첨가된  $LiNbO_3$  단결정을 육성하였다. 화학양론조성의  $LiNbO_3$ 는 순수한  $LiNbO_3$ 를 VTE(vapor transport equilibration) 법에 의해 처리하여 준비하였고 위의 세 결정을 기본으로 하여 결정의 화학양론비와 첨가물( $Mg^{2+}$ )에 따른  $LiNbO_3$ 의 물성변화를 조사하였다. 공용조성의  $LiNbO_3$ 에서 높은 농도의 MgO 첨가는 화학양론조성  $LiNbO_3$ 와 유사한 특성을 보였다. Curie 온도는 공용조성의 순수한  $LiNbO_3$ 의 1145°C에서 1200°C 이상으로 상승되었고 가시광선 영역의 흡수단의 위치도 단파장쪽으로 10 nm 이상 이동하였다. MgO가 첨가된 결정의 OH 흡수밴드의 위치는 40 nm 정도 단파장 영역으로 크게 이동하였다.

### 1. Introduction

$LiNbO_3$  (LN) is one of the most important ferroelectric materials for surface acoustic wave (SAW) devices because of its excellent piezoelectric and acoustic properties [1]. Ferroelectricity in this crystal was discovered as early as 1949, and large single crystal was grown successfully from melt by Czochralski technique in 1965.  $LiNbO_3$  possesses a high Curie temperature (1210°C). It has high mechanical quality factor (Qm) and low acoustic losses, and has turned out to be an excellent material for high-frequency transducer and SAW devices. Recently,  $LiNbO_3$  single crystal has been targeted as an expected useful material for electro-optic devices. Bulk crystals used for optical use will require higher quality to prevent optical damage than SAW materials.

However, photorefractive effect remains a problem for the usage of lights in visible region. In order to suppress the photorefractive effect, doping of MgO in  $LiNbO_3$  has been mainly studied (Bryan *et al.*; Furukawa *et al.*) [2, 3].  $LiNbO_3$  has a wide solid solution range (45~51 mol%  $Li_2O$ ). The properties of  $LiNbO_3$  is very sensitive to [Li]/[Nb] ratios and the effect of nonstoichiometry on the defect structure of  $LiNbO_3$  is still under investigation.

In this study, we investigated optical properties of undoped and MgO doped  $LiNbO_3$  with congruent composition and near-stoichiometric  $LiNbO_3$  to clarify the effect of stoichiometry and dopant on the physical and optical properties of  $LiNbO_3$ .

### 2. Experimental procedures

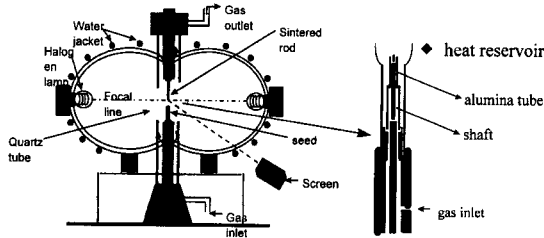


Fig. 1. Schematic illustration of the features of floating zone apparatus and heat reservoir.

The anisotropy of thermal expansion along the  $c$ -axis and  $a$ -axis in  $LiNbO_3$  [4] making the crystal fragile during cooling, was stabilized by a heat reservoir using an alumina tube [5] (Fig. 1). The starting materials were high purity (99.99 wt%)  $Li_2CO_3$ ,  $Nb_2O_5$ ,  $MgO$ . The growth rate was 3 mm/hr and the rotation rate for both the  $c$ -axis seed and the feed rod was 30 rpm in the opposite directions. Growth was accomplished with an argon ambient gas (0.6~0.9 l/min) and annealing treatment was done in oxygen atmosphere at 1000°C for 20 hrs after growth.

In order to investigate the homogeneity of the grown crystals, ordinary refractive index was measured. For the preparation of a near-stoichiometric  $LiNbO_3$  crystal, VTE (vapor transport equilibration) method [6, 7] was used. A purely grown congruent  $LiNbO_3$  crystal was converted to the stoichiometric composition in  $LiNbO_3+Li_3NbO_4$  powder at 1050°C for 150 hrs by the in-diffusion of  $Li_2O$ . Undoped, 5 mol%  $MgO$  doped crystals with congruent composition and stoichiometric crystal were cut and polished and analyzed by FT-IR and spectrophotometer. The value of the dielectric constant was measured in a frequency range of 100 kHz with increasing temperature by HP 4194A impedance/gain-phase analyser.

### 3. Results and discussions

The resulting crystals were 27 mm in length and 6~7 mm in diameter. Undoped crystal was colorless, clear and transparent, while 5 mol%  $MgO$  doped crystal was slightly of a milky color. Figure 2 shows the refractive indices along the solidification fraction ( $g = 0.1, 0.4, 0.9$ ) in the crystal. Variations of refractive indices were around  $10^{-3}$  order along the growth direction within the experimental error.

Figure 3 shows the measured dielectric constant with increasing temperature. At specific temperature,

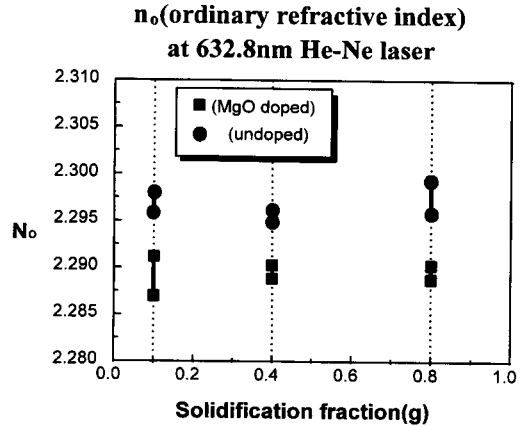


Fig. 2. The ordinary refractive indices of grown crystals along the solidification fraction.

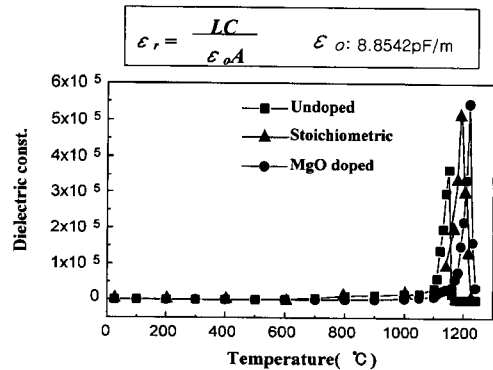


Fig. 3. The dielectric constant of grown crystals with increasing temperature.

the dielectric constant value increased abruptly. Phase transition from ferroelectric to paraelectric occurs at this temperature. The Curie temperatures of stoichiometric sample and  $MgO$  doped sample were much higher than that of the undoped congruent sample. The Curie temperature of the stoichiometric crystal, 1195°C, shows good agreement with other author's report [4, 7, 8]. Curie temperature has a linear relationship with  $[Li]/[Nb]$  ratio, if the resulting data is pwt a following equation showing relationship between the Curie temperature and  $[Li]/[Nb]$  ratio reported by Gallagher *et al.* [9],

$$T_c = 9095.2 - 369.05C + 4.228C^2$$

where  $C$  is mol% of  $Li_2O$

the resulting crystal composition is 49.7 mol%  $Li_2O$ .

Curie temperature of  $MgO$  doped crystal increased up to 1220°C, which might be due to  $Mg$  ions in

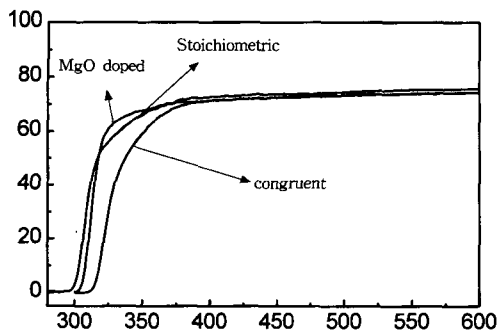


Fig. 4. optical transmittance in UV/VIS light range.

$\text{LiNbO}_3$  taking part in reducing cations vacancies in  $\text{LiNbO}_3$ , while also reducing cations vibration by thermal effect.

Figure 4 is the optical transmittance in the UV/VIS/IR light range. About 10 nm blue shifts ( $\sim 300$  nm) of absorption edge in UV/VIS light range were observed in stoichiometric and MgO doped samples. A unifying explanation of the observed changes can be given assuming that Mg replaces  $V_{\text{Li}}$  (vacancy in Li site) and  $\text{Nb}_{\text{Li}}$  (Nb ion in Li site). Congruent composition of  $\text{LiNbO}_3$  is away from the stoichiometric composition. thus non-stoichiometric  $\text{LiNbO}_3$  contains a high concentration of  $V_{\text{Li}}$  and  $\text{Nb}_{\text{Li}}$ . Replacement of  $\text{Nb}_{\text{Li}}$  by Mg then causes the decrease of intrinsic defects and shifts the properties of  $\text{LiNbO}_3$  to the direction of a higher  $[\text{Li}]/[\text{Nb}]$  ratio, as observed. From the Curie temperature results shown above, the features of crystal with high  $[\text{Li}]/[\text{Nb}]$  ratio are similar to those in crystal with lower  $[\text{Li}]/[\text{Nb}]$  but higher  $[\text{Mg}]$ .

Usually  $\text{LiNbO}_3$  crystals grown in air contain small amounts of hydrogen. This hydroxyl ion content give rise to an O-H absorption at about  $3500 \text{ cm}^{-1}$ . Due to the fact that  $\text{H}^+$  ions weakly bond with  $\text{O}^{2-}$  in  $\text{LiNbO}_3$ , OH spectrum is very sensitive to the variation of the ion surroundings. Figure 5 shows O-H absorption peaks in the near infrared light range. In case of MgO doped sample, absorption band large shifted to a shorter wavelength of 2828 nm. This brings us to assume that the new defect

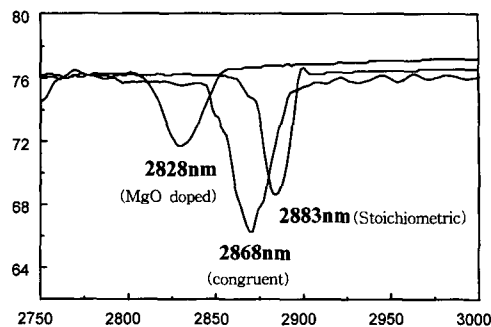


Fig. 5. O-H absorption peak in near infrared light range.

structure was generated from highly doped  $\text{Mg}^{2+}$ . It is considered that doped Mg replaces  $\text{Nb}_{\text{Li}}$  and some portion of Mg occupy the Nb site. then Mg addition probably forms  $(\text{Mg}_{\text{Nb}})^3$ , which weakens the bonding strength between cations and their surrounded oxygens. Otherwise, it causes the strong O-H bonding strength and shifts OH absorption band to a short wavelength.

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