SINGLE CRYSTAL GROWTH OF OPTIC-GRADE $LiNbO_3$ USING A FLOATING ZONE TECHNIQUE

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ABSTRACT

The effect of dopant and stoichiometry on the optical properties of $LiNbO_3$ were studied. We prepared three samples, which are undoped, MgO doped $LiNbO_3$ 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].

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 Czocralski technique in 1965. $LiNbO_3$ possesses a high Curie temperaure(1210℃). It has high mechanical quality factor(Q_m) and low acoustic losses, and has turned out to be excellent material for high-frequency tranducer and SAW devices. Recently single crystals of $LiNbO_3$ has been targeted as a expected useful materials for electro-optic devices. Bulk crystals used for optical use will be required higher quality to prevent optical damage than SAW materials.

However, photorefractive effect remains as a problem for the usage of lights in visible region. In order to suppress the photorefraction, doping of MgO in

$LiNbO_3$ has been mainly studied(Bryan et al.; Furukawa et al.; Wen et al.). Bryan et al. reported that doping of MgO more than 4.5mol% to the 48.6mol% Li_2O of congruent melt composition is efficient for the suppression. On the other hand, it is well known that $LiNbO_3$ shows a large variation in the [Li]/[Nb] ratio, i.e., the solid solution range is from 45 to 51 mol% Li_2O. However, the effect of nonstoichiometry on the defect structure of $LiNbO_3$ is still under investigation, and the [Li]/[Nb] ratio of $LiNbO_3$ is not agreed upon.[2] 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 optical properties of $LiNbO_3$

EXPERIMENTAL PROCEDURES

The anisotropy of thermal expansion along the c-axis and a-axis in $LiNbO_3$[3] making the crystal easy to be cracked during cooling, was stabilized by a heat reservoir using alumina tube.[4](fig. 1) The starting materials were high purity (99.99wt%)Li_2CO_3, Nb_2O_5, MgO. The growth rate was 3mm/hr and the rotation rate for both the c-axis seed and the feed rod was 30rpm in opposite directions. Growth was accomplished in argon and annealing treatment was done in air at 1000℃ for 20h after growth. For the growth of a near-stoichiometric $LiNbO_3$ crystal, the crystal growth was carried out in Li-rich melt(58.5mol%Li_2O) by Czochralski method. The pulling rate was kept below 1mm/hr in order to suppress compositional changes throughout the crystal. Nb contents in the resulting crystal was measured by EPMA using pure Nb_2O_5 as a standard sample. Undoped, 5mol%MgO doped crystals with congruent composition and stoichiometric crystal were cut and polished and analyzed by FT-IR and spectrophotometer. The value of dielectric constant was measured in a frequency range of 100kHz with increasing temperature by HP 4194A impedance/gain-phase analyser.

RESULTS AND DISCUSSIONS

The resulting crystals were 27mm in length and 6-7mm in diameter. Undoped crystal was colorless, clear and transparent, while 5mol%MgO doped crystal was slightly milky color. The EPMA result showed that the composition of the grown crystal was near stoichiometric and the compositional change between top and middle part of the crystal was under 0.5mol%. Fig. 2 shows 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 within experimental error. Fig. 3 shows the measured dielectric constant with increasing temperature. At specific temperature, dielectric constant value increased abrubtly. Phase transition from ferroelectric to paraelectric occurs at this temperature. The Curie temperature of stoichiometric sample and MgO doped sample were much higher than undoped congruent sample. Fig. 4 is optical transmittance in UV/VIS/IR light range. About 10nm blue shifts of absorption edge in UV/VIS light range were observed in stoichiometric and MgO doped samples. The features of crystals with high [Li]/[Nb] ratio are similar to those in crystals with lower [Li]/[Nb] but higher [Mg]. A unifying explanation of the observed changes can be given assuming that Mg replaces Nb_{Li}. As shown above non-stoichiometric $LiNbO_3$ contains a high concentration of Nb_{Li}. Replacement of Nb_{Li} by Mg then causes the decrease of intrinsic defects and shifts the properties of $LiNbO_3$ to the direction of a higher [Li]/[Nb] ratio, as observed. In near infrared light range, O-H absorption band is observed in grown $LiNbO_3$ crystals. In case of MgO doped sample, absorption band shifted a short wavelength to 2828nm. It is considered that threshold effect by Mg addition propbably forms $(Mg_{Nb})^{3-}$, which causes the strong O-H bonding strength.

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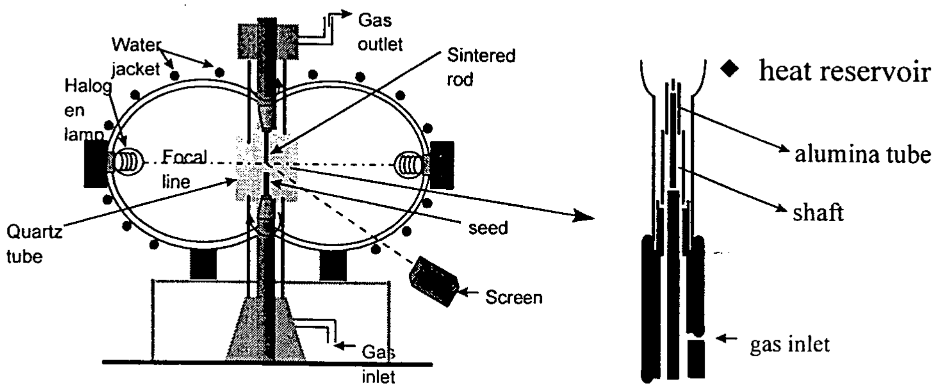

Fig. 1. Schematic illustration of the features of floating zone apparutus and heat reservoir

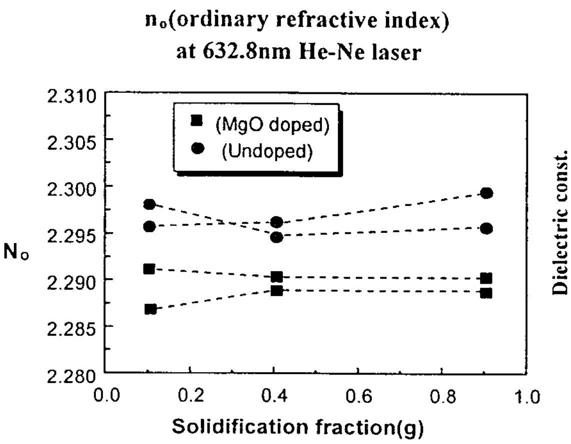

Fig. 2. The ordinary refractive indices of grown crystals along the solidification fraction

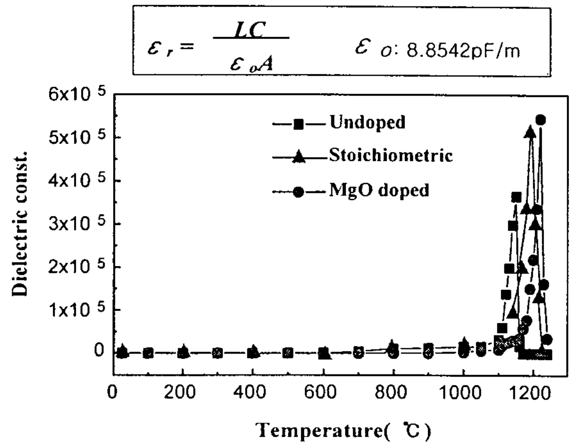

Fig. 3. The dielectric constant of grown crystals with increasing temperature

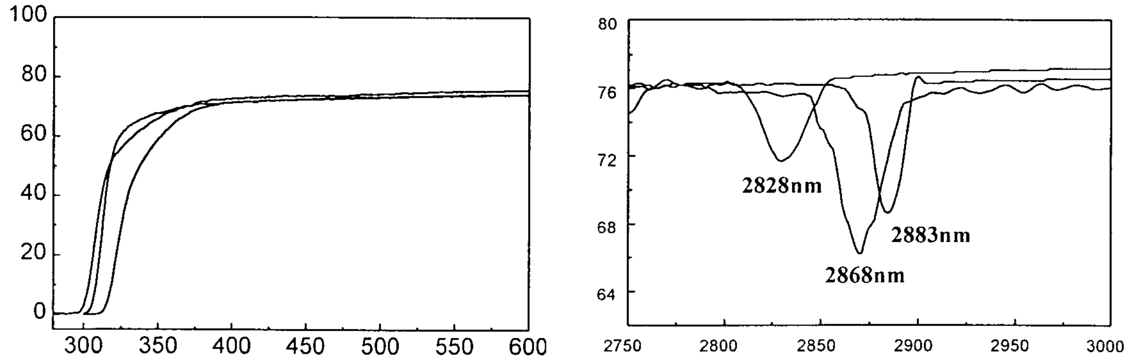

Fig. 4. optical transmttance in UV/VIS/IR light range