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Optical Characterizations of $LiNbO_3$ Single Crystals Doped with MgO/TiO_2*

You-Song Kim
Research Institute of Industrial Science & Technology
Pohang Institute of Science & Technology

ABSTRACT

The applicability of $LiNbO_3$ as a substrate for fabrication of Ti-indiffused waveguide electro-optic devices is limited. Ti diffuses comparatively solwly in congruently melting $LiNbO_3$; the Curie temperature of this material is too low to permit diffusion temperatures much above 1100 °C without the necessity of re-poling the crystal. Both of these difficulties could be eliminated by incorporating certain dopants in $LiNbO_3$.

Crystals of $LiNbO_3$ doped with Ti and Mg were grown and evaluated. The electroptic coefficients and birefringence of doped crystals were measured at λ=.6328 and 1.32 μm. Curie temperatures were measured. The Curie temperature of both undoped and Ti-doped $LiNbO_3$ was 1130 °C ; that for Mg-doped $LiNbO_3$ was 30° higher. From these data, a composition for the crystals was estimated. Thermogravimetric data confirmed this estimate and showed that the composition of Mg : $LiNbO_3$ was 49.3±0.2mole% Li_2O ; the composition of the undoped and Ti : $LiNbO_3$ samples was 48.6±0.2mole%. Diffusion of Ti into both Mg-doped and Ti-doped $LiNbO_3$ crystals was studied as a function of Li/NbO_3 ratio and temperature.

1. INTRODUCTION

The technology for preparation of single-mode optical waveguides by in-diffusion of Ti into congruently melting $LiNbO_3$ is well established [1]. There are certain limitations to the use of this material, however. The Curie temperature of this composition is too low to permit diffusions much above 1100 °C wihtout the necessity for repoling the crystal. Diffusion of Ti into this material is slow. In addition, $LiNbO_3$ has a small realizable($\triangle$n) under the influence of an applied electric field [2]. To circumvent some of these porblems, we attempted to alter the properties of $LiNbO_3$ through the use of dopants.

The literature of $LiNbO_3$ is replete with studies of dopants in $LiNbO_3$. Certain of these dopants ard known to have strong effects on the properties of $LiNbO_3$. Doping of $LiNbO_3$ with MgO significantly alters the phase-matching temperature for second harmonic generation [3] and slightly reduces both ne and no [4].

*Based upon the work performed at AT & T Bell Labs.

The effect on ne and no upon addition of Ti to such a doped crystal must also be determined in order to use the Ti-doped crystal for the fabrication of Ti-diffused waveguides.

The results of a study of Mg and Ti dopants in $LiNbO_3$ are described. Information obtained on Ti diffusion properties, ferroelectric transition temperatures, electro-optic properties and birefringence of these doped materials is discussed.

2. SAMPLE PREPARATION

All crystals were grown along the z-axis and were approximately 19㎜ to 25㎜ diameter by several centimeters in length. From these, discs(2.0cm dia.×1㎜) or plates(1.0cm×2.0cm×1㎜) were machined and polished to provide samples for this study. The crystals grown included : 1) an undoped crystal of $LiNbO_3$ grown from a congruent melt, 2) a sample of $LiNbO_3$ doped with Ti in the range of 3.0mole%, and 3) a sample of $LiNbO_3$ doped with Mg in the range of 10mole%.

3. EVALUATIONS

The crystals were examined for physical quality and defects. Optical properties examined included the room temperature birefringence, and measurement of the electro-optic properties at the wavelengths of 0.6328μm and 1.32μm.

The interferograms and the birefringence pattern of the crystals revealed that both physical and optical quality were good and suggested that the crystals were chemically homegeneous.

The measured birefringence and electro-optic coefficients of the crystals are as follows :

Birefringence($\triangle$n) at 25°C

Crystal	λ=0.6328μm	λ=1.32μm
Undoped $LiNbO_3$	0.0837	0.0622
Mg : $LiNbO_3$	0.0861	0.0691
Ti : $LiNbO_3$	0.0804	0.0635

Electro-optic Coefficients(10^{-12}m/v)

Crystal		λ=0.6328μm	λ=1.32μm
Undoped $LiNbO_3$	r_{13}	11.0±0.5	10.3±1.0
	r_{33}	36.7±0.5	34.1±1.0
Mg : $LiNbO_3$	r_{13}	11.2±0.5	9.7±1.0
	r_{33}	36.0±0.5	34.0±1.0
Ti : $LiNbO_3$	r_{13}	10.7±0.5	9.3±1.0
	r_{33}	36.6±0.5	33.6±1.0

The measured values of the birefringence of the undoped crystals are comparable to those measured on commercially grown crystals of the nominal congruently melting composition. It is evident that the birefringence of the Mg-doped crystal is higher. The electro-optic coefficients(r_{13} & r_{33}) of the crystals, important to electro-optic device design, are measured here at 1.32μm for the first time.

An accurate determination of crystal composition through use of the Curie point measurement was made on several samples of the three $LiNbO_3$ crystals by using a sensitive DTA system and a calibration curve established previously [5]. The measured values of the phase transition temperatures(accurate within ±2°C) and the estimated compositions of the three crystals were determined to be :

Crystal	Measured Tc(C)	Calculated Li_2O(mole%)
1. Undoped	1130°±2	48.65±0.5
2. Ti-doped	1130°±2	48.65±0.5
3. Mg-doped	1160°±2	49.50±0.5

The Curie temperature of the Mg−doped crystal is approximately 30° higher than that of the other crystals, consistent with previously reported data.

The Mg and Ti contents of the doped boules were determined by electron probe microanalysis(EPMA), using pure metal Mg and Ti as standards. The Mg−doped crystals contained 10.7+0.10 mole% MgO. The Ti−doped samples contained 2.9+0.10 mole% TiO_2.

Selected discs of both doped boules were equilibrated to the Li_2O−rich or Li_2O−deficient phase boundaries of $LiNbO_3$ at 1050°C. This was done by the vapor phase equilibration method(VPEq) [6]. A crystal was suspended from a recording electrobalance into a suitable two−phase crucible of either $LiNbO_3$ and $LiNb_3O_8$ as a sink of Li_2O or Li_3NbO_4 and $LiNbO_3$ as a source of Li_2O.

The weight gain or loss data accumulated by thermogravimetric analysis(TGA) on these crystals, reported fully elsewhere [7], confirm that the composition of the as−received Mg−doped $LiNbO_3$ is higher in Li_2O than either the undoped or the Ti−doped crystals, agreeing with the Curie temperature measurements. The Curie point versus composition calibration curve is therefore valid for Mg : $LiNbO_3$ and Ti : $LiNbO_3$ crystals doped to the levels used in this study.

The Ti diffusion properties of three compositions(as prepared by VPEq) of both types of doped crystals were studied at three temperatures. The Ti diffusivities for both types of doped crystals are higher than for corresponding undoped samples at the same temperature and composition [7]. Activation energies(E_A) determined from Arrhenius plots of the Ti diffusivity are lower than those calculated for undoped material [7], as given in the table below :

Sample	Composition (Mole% Li_2O)	Activation Energy (eV)
Undoped $LiNbO_3$	50.0	2.25
Undoped $LiNbO_3$	48.6	2.27
Undoped $LiNbO_3$	48.3	1.97
Undoped $LiNbO_3$	48.1	1.67
Mg : $LiNbO_3$	50.0	1.58
Mg : $LiNbO_3$	49.5	1.42
Mg : $LiNbO_3$	48.4	1.37(2temperatures only)
Ti : $LiNbO_3$	50.0	1.88
Ti : $LiNbO_3$	48.6	1.96
Ti : $LiNbO_3$	48.3	2.26(2 points only)

The EA for Ti diffusion in to Mg : $LiNbO_3$ is significantly lower than for either undoped $LiNbO_3$ or Ti : $LiNbO_3$.

4. CONCLUSIONS

The Mg−doped samples hold promise as substrates for optical waveguide fabrication. They have a higher Curie temperature than undoped $LiNbO_3$ and exhibit a higher Ti diffusivity(and lower activation energy). Thus deeper Ti diffused waveguides are easily obtained without the necessity for repoling or special diffusion treatment. The electro−optic coefficients of this material are comparable to those of congruent $LiNbO_3$. The doped crystals, both Ti and Mg, can be successfully heat−treated by VPEq to any desired composition in the single phase field of $LiNbO_3$. This process will also homogenize the crystals and improve the electro−optic coefficients in a non−uniform crystal.

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