

Investigation of Sc³⁺ in LiNbO₃ single crystals

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The effect of trivalent Sc³⁺ doping in LiNbO₃ was studied and compared to Mg²⁺-doped LiNbO₃. The 1 to 3 mol% Sc-doped LiNbO₃ single crystals were grown by the Czochralski technique. The effect of scandium dopant concentration on the lattice parameters, Curie temperature and laser (515 nm) induced photorefractive damage was investigated.

1. INTRODUCTION

Since its discovery LiNbO₃ has been a well known and well studied ferroelectric material. It is characterized by a large spontaneous polarization, $P_S = 0.71 \text{ C}\cdot\text{m}^{-2}$, which gives rise to large linear and nonlinear optical coefficients. This has led to many applications in piezoelectric, surface acoustic wave, acousto-optic and electro-optic devices.

One area that LiNbO₃ could have an impact would be as a frequency doubler for infrared radiation, utilizing the large nonlinear d-coefficients, $d_{31} / Id_{36}^{\text{KDP}} = -12.3$ and $d_{31} / Id_{36}^{\text{KDP}} = -8.6$, to efficiently produce green light. [1]

This application is hampered by the easy susceptibility of LiNbO₃ to changes in its refractive indices. When laser radiation is incident on the crystal, the electro-optic coefficients couple to space charge-generated electric field. This is known as photorefractive or optical damage and it is especially dominant in the more energetic visible wavelength range.

Due to the high carrier conductivity in the illuminated region, the charge carriers accumulate at the periphery of this region forming, forming an electric field, E_j . From the equation:

$$\Delta\left(\frac{1}{n^2}\right)_i = \sum_j r_{ij}E_j \quad (1)$$

the induced changes in the refractive indices are determined by the linear electro-optic r-coefficients. In LiNbO₃ the r_{33} ($32 \times 10^{-12} \text{ m}\cdot\text{V}^{-1}$) is 3 times larger than the r_{31} ($10 \times 10^{-12} \text{ m}\cdot\text{V}^{-1}$) coefficient, therefore the observed birefringence, $\Delta n = n_e - n_o$, is primarily due to changes in n_e . [1]

1.1. Mg-DOPED LITHIUM NIOBATE

It has been reported that MgO doping up to 4.5 to 5.0 mol% drastically reduces the photorefractive damage. [2] The reduction in the damage level is reportedly two orders of magnitude below the undoped LiNbO₃.

Subsequent studies determined that in this concentration region there is a change in the defect structure which in turn influences the photoconductivity. [3] Other physical properties were also found to change at this MgO concentration. [4] At low MgO concentrations, the Curie temperature, T_C , increased, peaking in the 5-7 mol% range and again decreased in the high concentration range. This behavior has been attributed to a change in Mg site occupancy from the A-site to

the B-site, resulting in a maximum vacancy concentration corresponding to the peak in the Tc.

There has been a vast amount of work into dopant effects in LiNbO₃, where the largest interest has been in photorefractive applications, where a maximum change in birefringence is needed to efficiently produce holographic images in the crystal. This is possible with multi-valent transition metal cations, where the photon induced oxidation/reduction process serves as a source of excited state carriers/trapping sites. Since it is evident that the defect structure and dopant play an important role in determining the response to laser radiation, the effect a trivalent cation with one valence state has on LiNbO₃ may provide a basis for comparison to the divalent dopants to provide a better understanding of the dopant-defect-property relationship.

1.2. Sc-DOPED LITHIUM NIOBATE

Scandium was selected because the cationic radius is very similar to Mg²⁺ and from the distribution coefficient, the affinity of the LiNbO₃ structure for Sc and Mg are about equal, Table 1. Work into scandium doped LiNbO₃ was first reported in 1966, where the as-grown domain structure was studied. [5] Later the Li₂O-Nb₂O₅-Sc₂O₃ phase diagram was investigated. [6] Recently, scandium was found to reduce the photorefractive damage in LiNbO₃, leading to studies into the concentration effects on the optical and physical properties. [7]

2. EXPERIMENTAL

The Sc-doped LiNbO₃ crystals were grown by the Czochralski technique and pulled from congruent (Li/Nb = 0.941) melts doped with 1

Table 1.
LiNbO₃ Dopant Cations

Cation	Valence	Ionic Radii* (nm)	Keff**
Li	1+	7.4	—
Nb	5+	6.4	—
Mg	2+	7.2	1.3
Sc	3+	7.3	1.2
Ti	4+	6.05	0.7-0.9

* From Ref. 11

** From Ref. 1

to 3 mol% Sc added in their oxide forms. The crystals, 2.5 cm in diameter and 5 - 6 cm in length, were inclusion-free, water-clear and transparent. The measured distribution coefficient of 1.3 was close to the reported value of 1.2. [1] Samples were taken from subgrain boundary-free area of the crystal, as determined by X-ray topography. Growth striations and inhomogeneities were not observed in both Schlieren and polarized microscopy techniques.

The lattice parameters were calculated from a least squares fit of 32 high two-theta peaks, using a silicon internal standard. The Curie temperature, was measured using differential thermal analysis. The experimental procedure was the same as described in the literature. [8] Chemical analysis was performed using X-ray fluorescence to measure the scandium concentration and inductively coupled plasma technique was used to measure the iron concentration, which was less than 1 ppm in all crystals. Powdered samples for lattice parameter and Curie temperature measurements were taken from the same area in the crystal as that used for compositional analysis.

3. RESULTS AND DISCUSSION

The lattice parameters as a function of scandium concentration were found to be in good agreement with the literature and generally followed the same trends as $\text{Mg}:\text{LiNbO}_3$, Figure 1. The effect of the increasing dopant concentration was to smoothly and gradually increased the size of the unit cell, with a predominant basal plane expansion. As previously pointed out in the literature, this result is not unexpected since the cation sizes of the dopant and the host are approximately the same.

The T_C of the $\text{Sc}:\text{LiNbO}_3$ exhibited the same general behavior as $\text{Mg}:\text{LiNbO}_3$, but the magnitude of the T_C elevation was smaller, and the peak in the T_C occurred at a much lower Sc concentration, Figure 2. Due to the similarity of the two dopants in terms of size, the T_C elevation may also indicate Sc occupation on the A-site in the low scandium region and joint occupation of the A and B-sites in the high scandium region. Previously reported ESR results indicated that Fe^{3+} occupies the A-site and therefore based on size and valence, it is reasonable to assume that the Sc cation would occupy the A-site in low concentrations. [10]

The photorefractive damage caused by 515 nm radiation from an argon ion laser was measured using the Senarmont compensator method, using a HeNe (633 nm) laser as the probe beam. In Figure 3, the 1 mol% $\text{Sc}:\text{LiNbO}_3$ displayed the lowest level of damage. The damage level increased as the scandium concentration increased above the 1 mol% level. This is a departure from the behavior observed in $\text{Mg}:\text{LiNbO}_3$. The minimal damage level in $\text{MgO}:\text{LiNbO}_3$ reportedly occurs near 5 mol% Mg. A comparable damage level was observed to occur in $\text{Sc}:\text{LiNbO}_3$ at the 2 mol% Sc level.

The cause of this behavior is not clearly understood. It has been proposed that an

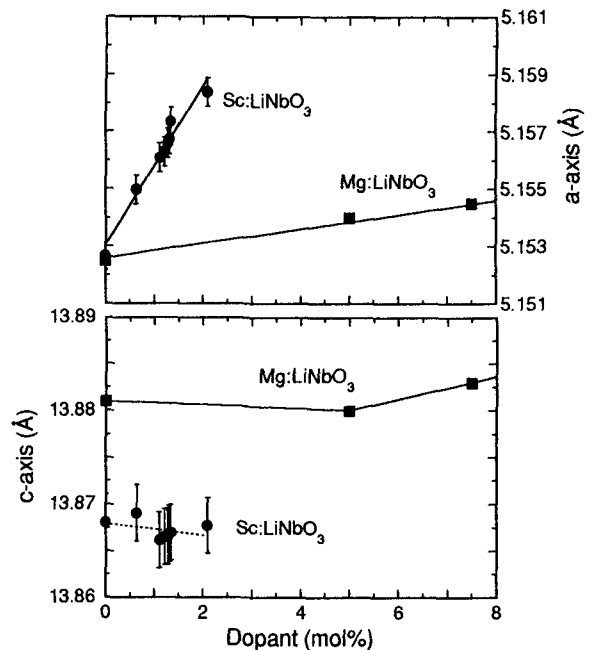


Figure 1. Lattice parameters as a function of Sc concentration. $\text{Mg}:\text{LiNbO}_3$ data was taken from Ref. 12.

increase in vacancy concentration and decrease in photorefractive damage are related. The vacancies may serve as trapping sites for mobile carriers and by increasing the trapping site concentration the carrier mobility is decreased, resulting in a weaker electric field. [2] If it is assumed that the maximum in the T_C is due to a maximum in the vacancy concentration, which has been shown to occur, then the observed behavior in $\text{Mg}:\text{LiNbO}_3$ does seem to agree with the vacancy model. [4] This also seems to be the case for the $\text{Sc}:\text{LiNbO}_3$, where the maximum T_C does occur at 1.2 mol% Sc and the minimum damage level occurred at 1 mol% Sc. The difference in the dopant concentration indicates that the Sc cation is more efficient in producing cation vacancies than the Mg cation. The higher valence could create two vacancies for each Sc cation if the Sc occupies the A-site. Whether

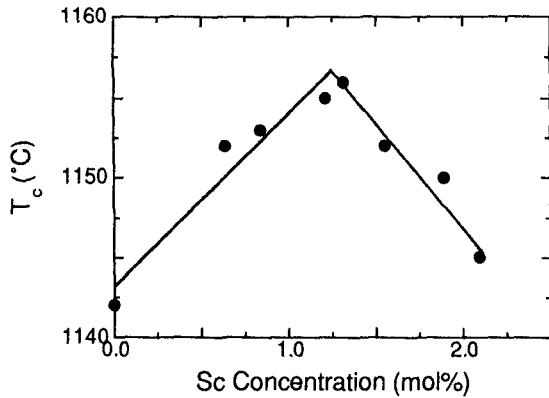


Figure 2. Curie temperature as a function of Sc concentration

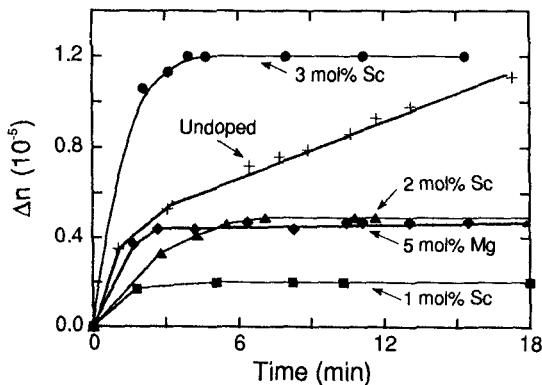


Figure 3. Photorefractive damage induced by argon ion laser (515 nm, 7 W/cm) of several Sc:LiNbO₃ single crystals. 633 nm HeNe laser was used as a probe beam.

the lower damage level is a direct consequence of the high vacancy concentration is still not known. More work into trivalent and divalent dopants should shed more light on the relationship between the vacancy concentration and photoconductivity.

4. CONCLUSIONS

Sc₂O₃ and MgO doping of LiNbO₃ was found to have qualitatively similar physical effects on the lattice parameters, T_c and photorefractive damage level as a function of dopant concentration. The effect of dopant valence was attributed to differences observed in the concentration dependence of the measured properties.

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