

# Nonlinear Optical Properties of Congruent and Li-Compensated $\text{LiNbO}_3$ Crystals

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We carried out a comparative study of the optical properties of congruent and lithium-compensated  $\text{LiNbO}_3$  crystals. The vapor transport equilibration(VTE) method was applied to a thin congruent crystal to obtain the latter sample. Among several signatures of Li-compensation in the bulk material, we observed changes in the UV absorption edge and the Raman linewidth of the  $A_1(z)$  mode. Nonlinear optical properties such as second harmonic generation (SHG) and photorefractivity have been comparatively studied. The SHG phase matching wavelength had a significant shift after VTE. A tunable SHG experiment proved to be a sensitive method for probing a small change in the Li-composition.

## I. INTRODUCTION

Lithium niobate (LN) is one of the most widely used nonlinear optical crystals for electro-optic modulators and frequency conversion devices. Extensive research activities in both ferroelectric physics and optics in LN have given birth to periodically poled LN (PPLN) which has opened a new application era in nonlinear optics since a quasi phase-matching (QPM) configuration has been realized in this material in a controllable manner [1,2]. In most nonlinear frequency conversion cases, PPLN has a polarization reversal period of  $4 \mu\text{m} \sim 30 \mu\text{m}$ . Although there are several methods for reversing polarization in this scale, electric field poling at room temperature is accepted as the most reliable one to date [2]. Using this method, recent works demonstrated that LN-family crystals are good candidates for coherent light generation from the mid-IR up to the blue spectral region [3-5]. Nevertheless, the high coercive field ( $\sim 22 \text{ kV/mm}$ ) in commercially available LN crystals has limited the aperture size of PPLN in nonlinear optical applications. The largest thickness reported so far is 1 mm [6], although 0.5 mm is a commonly used thickness.

It has been verified experimentally that the large coercive field originates from the stoichiometric defects in congruently grown LN crystals (CLN) [7] in which a certain amount of Li-deficiency is formed according

to the phase diagram [8]. Thus, large LN crystals, which are uniform in terms of composition and optical properties, are most easily obtained in the congruent composition. The congruent melting composition ratio,  $[\text{Li}_2\text{O}]/[\text{Nb}_2\text{O}_5]$ , was found to be  $0.942 \sim 0.946$  [9], in agreement with the Li vacancy model of Lerner *et al.* [8], who suggested that an excess of Nb atoms might occupy the Li positions with the creation of appropriate numbers of Li-vacancies for charge neutrality. In this model, no Nb-vacancy is assumed, and only one fifth of the missing Li sites are occupied by Nb ions while the others exist as Li-vacancies. Although the Li-vacancy model can explain some important aspects of CLN [10], the defect model still needs experimental verification. The situation is similar for  $\text{LiTaO}_3$  (LT).

Although the ease of crystal growth is one of the main reasons CLN and congruent LT (CLT) are the most widely used in industry, significant research efforts have been focused on fabricating stoichiometric crystals, which will reduce the coercive field, facilitating periodic poling of thicker crystals [7,11]. As a result, it has recently been reported that the coercive field has been significantly reduced in stoichiometric LT (SLT) grown with excess  $\text{Li}_2\text{O}$ , by adopting double crucibles in a Czochralski-growth furnace [11,12]. As an application in nonlinear optics, a 2-mm-thick SLT was successfully poled with a coercive field of just  $1.7 \text{ kV/mm}$ , compared to  $21 \text{ kV/mm}$  in CLT, and was used in an optical parametric oscillator(OPO) [13]. The large aperture offered

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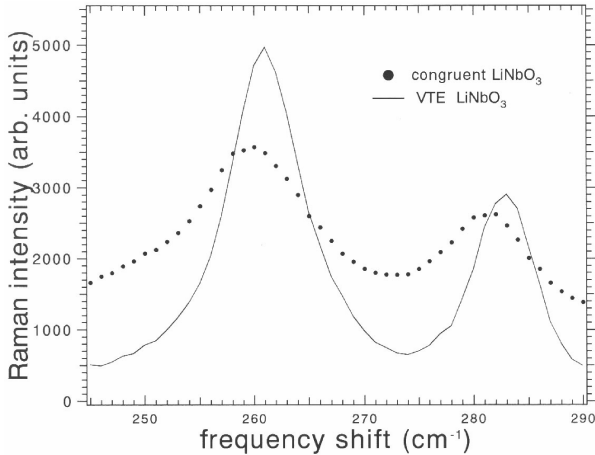


Fig. 1. Raman spectra of  $A_1(z)$  modes in CLN and VLN.

superior flexibility in cavity applications of periodically poled crystals. A significant decrease in the coercive field was also observed in near-stoichiometric LN grown by the same method [7].

However, it should be noted that it is still not easy to obtain a large SLT or stoichiometric LN(SLN) crystal (*e.g.*, 3" in diameter) by using the Czochralski-growth method. Thus, it will be meaningful to study post-processing methods on the widely available CLN to compensate for the Li-deficiency in the crystal. In this work, we performed vapor transport equilibration (VTE) on CLN crystals [14] and comparatively studied the linear and the nonlinear optical properties of CLN and VTE-LN(VLN). As signatures of Li-compensation to the CLN crystal, we observed a shift in the UV-absorption edge, as well as a narrowing in the Raman spectrum of  $A_1(z)$  mode after VTE. We performed a wavelength-tunable second harmonic generation (SHG) experiment and observed a significant shift in the phase matching wavelength. The photorefractive beam fanning effect was also quantified for both samples, indicating that VTE had increased photorefractivity.

## II. EXPERIMENTS AND RESULTS

We used a 1-mm-thick  $z$ -plate wafer of CLN made by Crystal Technology, Inc. For VTE, it was placed in an oven with a Li-rich environment, which contained a mixture of  $\text{Li}_3\text{Nb}_2\text{O}_4$  and  $\text{LiNbO}_3$  powders (Li : Nb = 60 : 40, in molar ratio), and the oven was maintained at 1000 °C for 130 hours. After VTE, the sample was annealed at 800 °C. The  $x$ -faces of both the CLN and the VLN crystals were cut and polished as entrance and exit planes for the laser beam, resulting in a size of 5.5 mm  $\times$  5.0 mm  $\times$  1.0 mm along the  $x$ ,  $y$ , and  $z$  direction, respectively.

First, optical absorption spectra were measured for both CLN and VLN in the visible-UV region, by us-

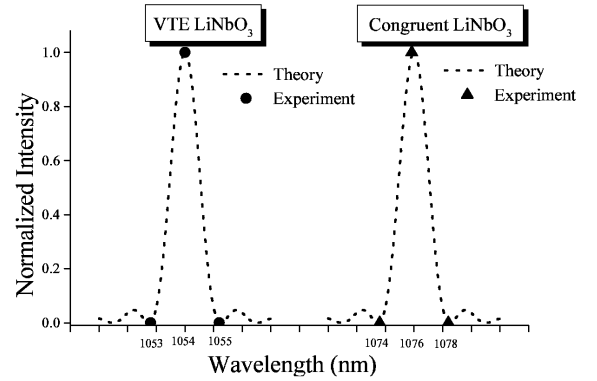


Fig. 2. SHG intensity versus input fundamental wavelength. Theoretical curves were obtained in the low fundamental depletion approximation.

ing a Cary 5E UV-VIS-NIR spectrophotometer (Varian Co.). We used unpolarized light propagating along the  $z$ -axis (that is, the optic axis) of the crystals. Here, we define the absorption edge as the photon energy (or wavelength) of the incident light where the absorption coefficient reaches a value of  $20 \text{ cm}^{-1}$ . For VLN, the absorption edge was measured to be 3.95 eV (wavelength,  $\lambda = 315 \text{ nm}$ ), as compared to 3.89 eV ( $\lambda = 319 \text{ nm}$ ) for CLN, which is consistent with the results in the Refs. 15 and 16. One of the direct consequences of the VTE effect is that the Li-deficiencies have been compensated for. The absorption edge shift to higher photon energy can be explained by a reduction of the inter-gap states as the stoichiometric defects decrease due to the compensation by lithium. From the above values, it can be inferred that the material composition ratio [Li]/[Nb] in the crystal changed from 0.945 (CLN) to 0.969 (VLN) [16].

As another piece of evidence for defect reduction, we measured the Raman spectra of both crystals at 90 K. Each sample was excited through the  $x$ -plane by using a cw Ar-ion laser ( $\lambda = 515.4 \text{ nm}$ , Coherent Inc., Innova 70). An incident power of 50 mW was used in our Raman scattering experiment. The back-scattered Raman emission from the crystal was collected by a lens, and the frequency shift with respect to the incident light was measured with a triple-grating spectrometer (Jobin Yvon T64000) [17,18]. The temperature of the crystal in the cryostat was controlled within  $\pm 0.3 \text{ K}$ . At 90 K, the frequency shifts of the  $A_1(z)$  optical modes were found to be at  $260 \text{ cm}^{-1}$  and  $282 \text{ cm}^{-1}$ . The Raman spectra markedly showed the composition dependence, as shown in Fig. 1. The linewidth of each Raman resonance for VLN was sharper than for CLN, which confirmed the VTE effect. This narrowing of the linewidths can be explained consistently by a reduction of the nonstoichiometric defects, which results in less scattering of phonons by defects in the crystal lattice [17,18].

As a nonlinear optical experiment, we observed the SHG from the CLN and the VLN crystals at room tem-

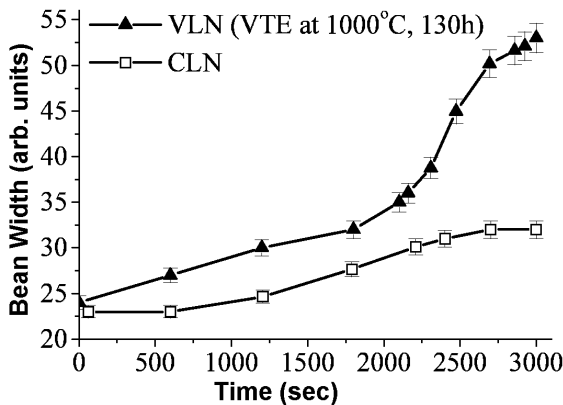


Fig. 3. Far-field beam width along the  $z$ -axis versus exposure time

perature with a variable fundamental input wavelength. The light source was a b-barium borate-based OPO pumped by the third harmonic ( $\lambda = 355$  nm) of a Q-switched Nd:YAG laser (Spectron, model TO BS7192). This source provided optical pulses of 7 ns operating at 10 Hz, over a wide wavelength tuning range from 420 nm to 2100 nm. We adopted a noncritical type-I phase-matching configuration utilizing  $d_{31}$  of the LN crystal; that is, the  $y$ -polarized OPO beam was focused on one of the  $x$ -faces of the sample, generating a second harmonic wave polarized along the  $z$ -axis. The SHG of CLN was found to be phase-matched at a fundamental wavelength of 1076 nm, while that of VLN was at 1054 nm, as shown in Fig. 2. Obviously, the shift in the phase-matching wavelength resulted from the fact that the ordinary and the extraordinary indices of refraction ( $n_o$  and  $n_e$ , respectively) had different dependences on the chemical composition. Indeed, it has recently been verified in a series of LN crystals with varying compositions that  $n_o$  increases somewhat as it approaches stoichiometry, while  $n_e$  decreases even more rapidly at the same temperature and wavelength [19,20]. It should be noted that an appreciable shift in the SHG phase-matching wavelength results from a small change in the composition in our samples. In addition, the phase matching wavelength is rather distinctly identified, providing an accurate means of evaluating the chemical composition, in contrast to experiments on the absorption edge and Raman spectral width.

We also investigated the change in the photorefractivity due to VTE by observing the laser beam fanning phenomenon through the crystals. A cw Ar-ion laser ( $\lambda = 488$  nm, Spectra-Physics Co., BeamLok model 2580) beam, polarized along the  $z$ -axis of the crystal, was incident on one of the  $x$ -faces and propagated along the  $x$ -axis of the crystal. A power of 30 mW was focused on a spot with a diameter of 0.32 mm. We monitored the far-field pattern of the transmitted beam at 30 cm from the sample by using a video camera during an exposure time of 50 minutes. The transmitted beam was fanned

along the  $z$ -axis with some distortion with exposure time. Figure 3 illustrates the temporal behavior of the beam width along the  $z$ -axis. We observed that it spread out faster and that the saturated beam width was larger in VLN than in CLN, indicating that the photorefractivity was enhanced when approaching stoichiometry. This result is in agreement with that by Kitamura *et al.*, who explained it by an increase in the photovoltaic effect and a decrease in the photoconductivity[20].

### III. CONCLUSION

In conclusion, we could successfully compensate for the Li-deficiency in congruent LiNbO<sub>3</sub> crystal by using the vapor transport equilibration method. We could confirm it by observing the absorption edge shift and the spectral narrowing in the Raman peaks. It is worth noting that the SHG phase matching wavelength was well defined and showed a large shift with even a small change in the composition, which provided an easy and accurate means of probing small composition changes. We also observed an increase in the photorefractivity, which needs to be avoided in high-intensity applications. Although our vapor transport equilibration could not make crystals close enough to a stoichiometric crystal in the present experiment, we are working on making more stoichiometric lithium-niobate crystals by adjusting processing parameters, such as raw material composition, processing temperature, and time, in VTE.

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