

STOICHIOMETRIC LiNbO₃ SINGLE-CRYSTAL FIBERS FOR NONLINEAR OPTICAL APPLICATIONS

Y.S. LUH

Center for Materials Research, Stanford University, Stanford, California 94305-4045, USA

M.M. FEJER and R.L. BYER

Applied Physics Department, Stanford University, Stanford, California 94305-4090, USA

and

R.S. FEIGELSON

Center for Materials Research, Stanford University, Stanford, California 94305-4045, USA

A vapor transport equilibration technique has been used to improve the homogeneity and adjust the Li/Nb ratio in small LiNbO₃ single crystal rods and fibers grown by the laser heated pedestal growth method. When equilibrated with a Li-rich powder, containing a mixture of LiNbO₃ and Li₃NbO₄, crystals of stoichiometric composition can be obtained. This treatment was used to raise the phase-matching temperature of congruent LiNbO₃ for second harmonic generation of 1064 nm radiation from 4 to 238°C. The 238°C phase-matching temperature is above the annealing temperature for photorefractive damage. This property, along with the good optical homogeneity, should allow efficient conversion of CW laser sources. We also, for the first time, demonstrated the doubling of 954 nm radiation in a LiNbO₃ crystal.

1. Introduction

The large nonlinear optical coefficient and good physical properties of LiNbO₃ make it an attractive material for nonlinear optical applications. Unfortunately, LiNbO₃ crystals used in nonlinear optical devices at visible and near IR wavelengths have, in the past, suffered from two serious drawbacks. Spatial variations in the birefringence [1-3] make it impossible to phase-match at all points within a crystal at the same temperature. Only crystals grown from congruent melts have good optical quality and negligible variations in birefringence [3]. LiNbO₃ crystals irradiated with moderately intense laser radiation suffer photorefractive damage [4]. This photorefractive damage can be removed by thermal annealing [5,6] at temperatures from 110 to 180° depending on the purity of the crystal. These two drawbacks greatly reduce the usefulness of LiNbO₃ in nonlinear optical devices.

Byer et al. [7] reported the use of warm phase-matching LiNbO₃ for efficient second harmonic generation (SHG) of Nd:YAG laser radiation. They grew crystals from melts doped with 0.5 to 1 mol% of MgO to raise the phase-matching temperature (T_{pm}) to 120°C. Meanwhile, through careful preparation of the melt to reduce its iron impurity concentration, and post growth annealing in an oxygen atmosphere at 1000°C for 24 h, they lowered the damage annealing temperature from 180 to 110°C [7,8].

Several years ago Zhong et al. [9] reported reduced photorefractive damage in LiNbO₃ doped with 5 mol% MgO. Further work by Bryan and co-workers [10-13] confirmed this result and demonstrated that the improved performance is due to a hundredfold increase in the photoconductivity. More recently, Nightingale et al. [14] demonstrated at 53% conversion efficiency for SHG in 5 mol% Mg-doped congruent LiNbO₃ crystals. However, the variation of the refractive index

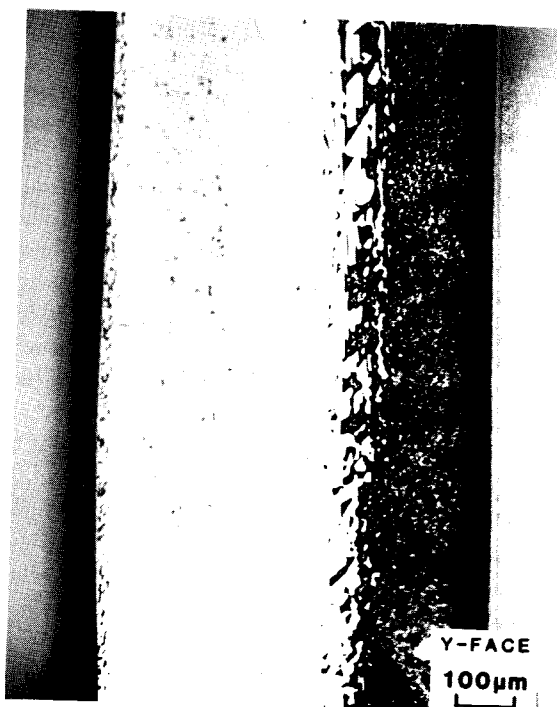


Fig. 1. Domain structure of an a -axis fiber grown with asymmetrical heating, showing shifted domain boundary.

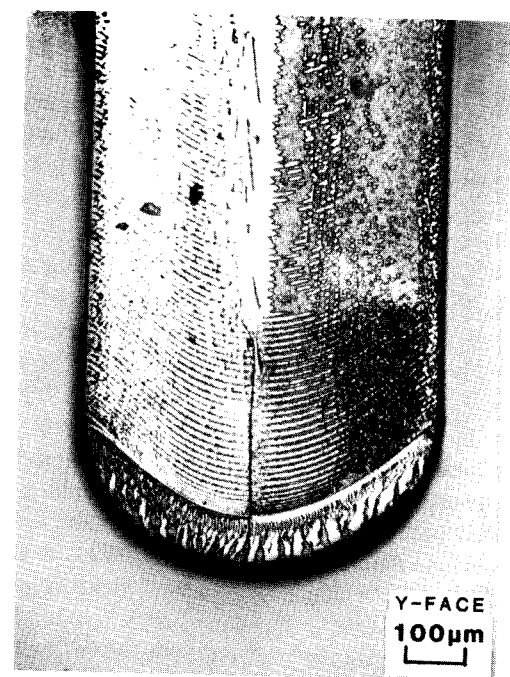


Fig. 2. Quasi-periodic domain structure of an a -axis fiber grown with asymmetrical heating and rotating seed during growth.

caused by a variation of the Mg concentration in the as-grown crystal still limited to useful phase-matchable length. The variation in Mg concentration results from a distribution coefficient of Mg in LiNbO_3 of 1.2 to 1.3 [15–17].

In this paper we report on the growth of LiNbO_3 single crystal fibers and a heat treatment procedure which produces both a uniform fiber composition and increased T_{pm} for SHG of 1064 nm to above the damage annealing temperature. We also report, for the first time, the SHG of 954 nm in LiNbO_3 to generate 477 nm blue radiation.

2. Fiber growth and ferroelectric domain structures

Single crystal optical fibers offer a combination of material properties and waveguide geometry that is not available in either glass fibers or bulk single crystals. Growth of single crystal fibers using the laser heated pedestal growth (LHPG) method has been an active research program at Stanford University since 1980 [18,19]. One of the most heavily investigated materials in this program is LiNbO_3 , which is potentially useful for applications in nonlinear fiber devices such as modulators, mixers, harmonic generators, and parametric oscillators.

Using the LHPG method, LiNbO_3 single crystal fibers have been routinely grown along both the c -axis and the a -axis with diameters ranging from 50 to 800 μm . Since optical applications of LiNbO_3 require single domain crystals, or crystals with well defined periodic domains for quasi-phase-matching [20–22], we studied the domain structure in the LiNbO_3 single crystal fibers. Recently we reported the ferroelectric domain structures in the as-grown fibers and proposed a model based on the thermoelectric effect to explain the observed results [23]. Unlike the multi-domain structure found in large crystals, fibers grown along the c -axis with diameters up to 800 μm were virtually single domain. a -Axis grown fibers showed a bi-domain configuration with a domain boundary along the a -axis and parallel to the c -face. By focusing through a single domain region, these a -axis fibers can be used in nonlinear optical applications without any poling procedure.

As predicted by the thermoelectric model [23], *a*-axis fibers with an uneven bi-domain structure as shown in fig. 1 have been grown recently. Fig. 2 shows the quasi-periodic domain structure in an *a*-axis fiber grown using asymmetrical heating and seed rotation during growth to introduce an alternating radial thermal gradient. Further studies might lead to techniques for the fabrication of *a*-axis fibers with completely single domain or well controlled periodic domain structures that are useful for quasi-phase-matching a variety of nonlinear optical interactions.

3. Fiber processing

LiNbO₃ fibers used for SHG measurements in this study were grown using source rods cut from a congruently grown Czochralski boule. As expected, the T_{pm} of these fibers for the noncritical SHG of 1064 nm radiation is near 4°C and the material suffers severe photorefractive damage unless T_{pm} is raised to above the damage annealing temperature.

It has been shown [24–26] that the Li/Nb ratio can be varied from 0.9 to 1.0 at 1100°C. This compositional variation can significantly affect material properties, such as T_{pm} for second harmonic generation, birefringence, and Curie temperature (T_c). The T_{pm} of the crystal increases as the Li concentration in the melt increases. Holman [27] used a vapor phase technique to study Li in- and out-diffusion in LiNbO₃ crystal and to fabricate planar waveguides. We adapted his technique to alter the Li/Nb ratio and improve the homogeneity in small diameter single crystal fibers. This technique involves annealing LiNbO₃ fibers in close proximity to a powder containing mixed lithium niobate phases. The mass of the powder considerably exceeded that of the fiber, fixing the chemical potentials of the system. The composition of the fiber is then altered as a result of preferential Li₂O transport between the fiber and the powder until the Li₂O chemical potential of the fiber reaches that of the powder. We called this process vapor transport equilibration (VTE). Two kinds of the powder can be formed: one is Li-rich powder, a mixture of

LiNbO₃ and Li₃NbO₄; the other is Li-poor powder, a mixture of LiNbO₃ and LiNb₃O₈. X-ray powder diffraction analysis was used to ensure that the powder contains proper phases after every usage.

The stoichiometric composition was achieved by annealing the as-grown fibers in a platinum crucible containing Li-rich powder. The crucible used has a dimension of 5 cm in both diameter and height which was filled with Li-rich powder up to 2/3 of its volume. The fiber was laid above the powder supported by two pieces of thin foil of platinum at both ends. The crucible was then heated in an oxygen rich atmosphere at 1100°C for a time that depended on fiber diameter, *d*.

Consider a cylinder with diameter *d*, initial uniform composition C_1 and surface concentration C_0 . The concentration, *C*, at center after diffusion time *t* is given by [28]

$$\frac{C - C_1}{C_0 - C_1} = 1 - \frac{4}{d} \sum_{n=1}^{\infty} \frac{\exp(-\alpha_n^2 D t)}{\alpha_n J_1(\frac{1}{2}\alpha_n d)}, \quad (1)$$

where *D* is the diffusion coefficient and α_n s are roots of

$$J_0(\frac{1}{2}\alpha_n d) = 0, \quad (2)$$

and J_0 and J_1 are Bessel functions of the first kind of zeroth and first order respectively. When the diffusion time, *t*, is equal to $d^2/3D$, the final composition difference, $C - C_0$, will be less than 0.1% that of the initial difference, $C_1 - C_0$. In the case of a LiNbO₃ fiber starting with the congruent composition, $C_0 - C_1$ is 1.5 mol% Li₂O and the final variation of the Li₂O in the fiber is less than 0.0015 mol% when $t \geq d^2/3D$. Increasing the diffusion time by 30% improves the homogeneity by one order of magnitude. Therefore, to ensure adequate time for the crystal to reach appropriate homogeneity, we chose $t \geq d^2/3D$ for all equilibration processes. Given the lower bound of the diffusion coefficient for Li in LiNbO₃ [27,29], $D = 3600 \mu\text{m}^2/\text{h}$ at 1100°C, the typical time we used to equilibrate a 350 μm diameter fiber was 30–40 h. The temperature dependence of the diffusion coefficient leads to a rapid increase in the diffusion time at lower temperatures.

Although Svaasand et al. [24] and Holman [27]

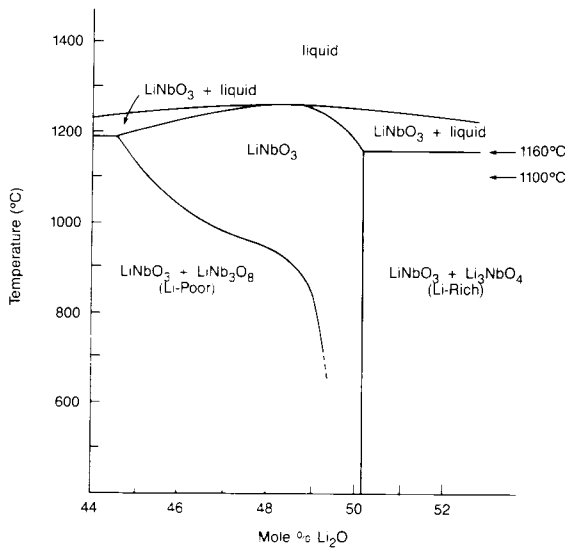


Fig. 3. Phase diagram of Li₂O–Nb₂O₅ pseudo-binary system in the existence regime of LiNbO₃ (after Svaasand et al. [24]).

both reported a vertical Li-rich phase boundary, recent work by O'Bryan et al. [30] showed that at temperatures exceeding 1060 °C the Li-rich phase boundary moves toward lower Li concentrations and is lower than the stoichiometric composition. Because of the strong dependence of T_{pm} on the crystal composition, we can accurately determine the exact shape of the Li-rich phase boundary by correlating T_{pm} with VTE processing at different temperatures.

A similar annealing process with Li-poor powder can be used to lower the Li/Nb ratio in the fiber. However, due to the curved phase boundary of LiNbO₃ at the Li-poor side, as shown in fig. 3, the composition of the fiber after annealing will be a strong function of the annealing temperature. Thus, to achieve a particular Li/Nb ratio with uniform composition in the fiber by equilibrating with Li-poor powder, both the temperature and the time of annealing have to be adjusted. Identical process can also be used to alter the composition of small rods or thin plates of LiNbO₃.

4. SHG phase-matching temperature measurements

a-Axis LiNbO₃ fibers are properly oriented for noncritically phase-matched SHG. Since 1100 °C is lower than the T_c of congruent LiNbO₃ and the T_c increases with the Li/Nb ratio [31], equilibration of the fiber at 1100 °C with Li-rich powder will not alter the domain structure. This has been confirmed by chemical etching to reveal the domain structure after VTE. Therefore poling is not necessary after VTE.

After VTE using Li-rich powder, the T_{pm} for SHG of 1064 nm radiation in the fiber was raised from 4 °C (congruent material) to 238 °C. This temperature, which is above the annealing temper-

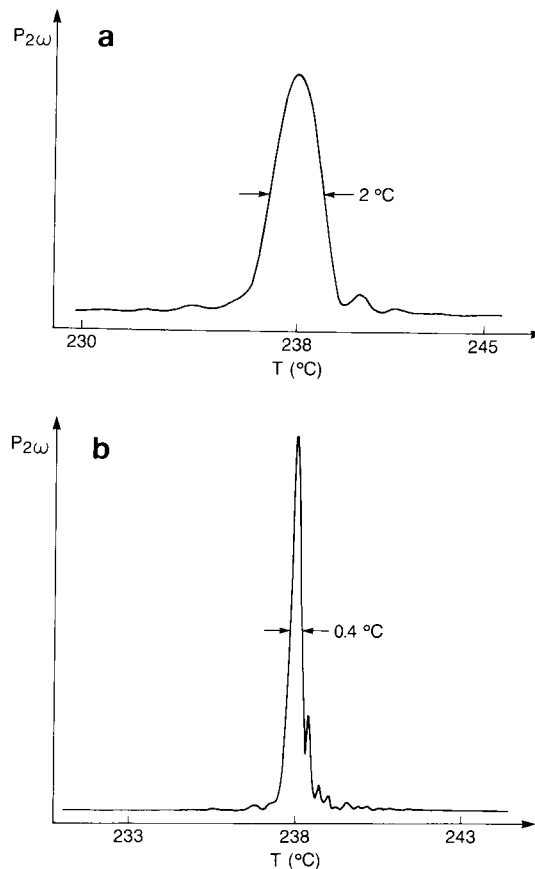


Fig. 4. Power at 532 nm generated by noncritical SHG of 1064 nm radiation from a Nd:YAG laser in stoichiometric LiNbO₃: (a) 4 mm long *a*-axis fiber, 0.35 mm in diameter, annealed for 38 h; (b) 20 mm × 0.7 mm × 0.7 mm *a*-axis rod, annealed for 67 h.

Table 1
Phase-matching temperature for noncritical second harmonic generation in stoichiometric LiNbO₃

Wavelength (nm)	T_{pm} (°C)
1132	355
1064	238
1054	219
1047	204
954	-37

ature for photorefractive damage, is the highest T_{pm} reported to date for the SHG of 1064 nm radiation in LiNbO₃. Since diffusion tends to smooth out any concentration gradients, we expect good optical homogeneity in crystals treated with VTE. This supposition is verified by the phase-matching curves for SHG of 1064 nm radiation shown in fig. 4a and fig. 4b. The full width at half maximum (FWHM) of these peaks are consistent with those calculated from the length of the samples and the temperature derivative of the birefringence.

Phase-matching temperatures in the stoichiometric crystal at other wavelengths are shown in table 1. We have doubled 954 nm radiation to 477 nm at $T_{pm} = -37^\circ\text{C}$, the shortest wavelength reported to date for phase-matched SHG in LiNbO₃. Fig. 5 shows the temperature tuning curve for the SHG of 954 nm in a 1.7 mm long sample. The 954 nm radiation used in this experiment was generated using a hydrogen Raman shifter pumped by 532 nm radiation from a Nd:YAG laser equipped with a harmonic generator.

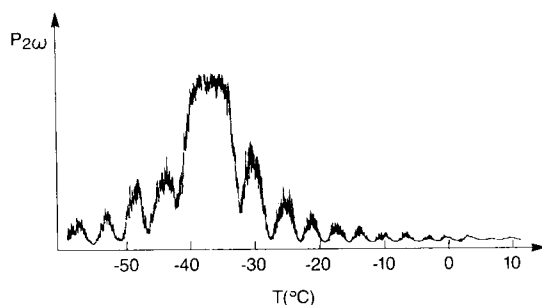


Fig. 5. Power at 477 nm generated by noncritical SHG of 954 nm radiation in an 1.7 mm long stoichiometric LiNbO₃ crystal.

5. Summary

Progress in LiNbO₃ fiber growth and control of domain structures using the thermoelectric model are reported. The VTE can be used to improve the homogeneity and adjust the Li/Nb ratio in small LiNbO₃ single crystal rods and fibers grown by the LHPG method. When equilibrated with a Li-rich LiNbO₃ powder, crystals of stoichiometric composition are obtained. By this treatment, the T_{pm} of LiNbO₃ for second harmonic generation of 1064 nm radiation is raised from 4°C (congruent material) to 238°C. The 238°C phase-matching temperature is above the annealing temperature for photorefractive damage. This property, along with the good optical homogeneity, should allow efficient conversion of CW laser sources. We also, for the first time, demonstrated the doubling of 954 nm radiation to generate 477 nm blue light in the LiNbO₃ crystal.

The phase-matching temperature for the 946 nm line of Nd:YAG will be measured. Progress in utilizing stoichiometric material in device applications along with further materials characterization, including photorefractive damage and SHG conversion efficiency will be reported.

Acknowledgments

The authors would like to express their appreciation to Dr. Eric Gustafson, Greg Magel, Dieter Jundt, T.Y. Fan, and Y.X. Fan for their assistance in phase-matching temperature measurements and helpful discussions. This work was supported by the NSF-MRL program through the Center for Materials Research at Stanford University.

References

- [1] J.E. Midwinter, Appl. Phys. Letters 1 (1967) 128.
- [2] F.R. Nash, G.D. Boyd, M. Sargent III and P.M. Bridenbaugh, J. Appl. Phys. 41 (1970) 2564.
- [3] R.L. Byer, J.F. Young and R.S. Feigelson, J. Appl. Phys. 41 (1970) 2320.
- [4] A. Ashkin, G.D. Boyd, J.M. Dziedzic, R.G. Smith, A.A. Ballman, J.J. Levinstein and K. Nassau, Appl. Phys. Letters 9 (1966) 72.

- [5] A.M. Glass, G.E. Peterson and P.M. Bridenbaugh, Optical index damage in electrooptic crystals, in: *Laser Induced Damage in Optical Materials, 1972* (NBS Special Publication 372), Eds. A.J. Glass and A.H. Guenther (NBS, Washington, DC, 1972) p. 15.
- [6] Y.K. part, R.S. Feigelson, W.L. Kway and R.L. Byer, *Optics News* 6 (1980) 36.
- [7] R.L. Byer, Y.K. Park, R.S. Feigelson and W.L. Kway, *Appl. Phys. Letters* 39 (1981) 17.
- [8] G.E. Peterson, A.M. Glass and T.J. Negran, *Appl. Phys. Letters* 19 (1971) 130.
- [9] G.-G. Zhong, J. Jian and Z.-K. Wu, in: *Proc. 11th Intern. Quantum Electronic Conf., IEEE Cat. No. 80 CH 1561-0*, June 1980, p. 631.
- [10] D.A. Bryan, R. Gerson and H.E. Tomaschke, *Appl. Phys. Letters* 44 (1984) 847.
- [11] K.L. Sweeney, L.E. Halliburton, D.A. Bryan, R.R. Rice, R. Gerson and H.E. Tomaschke, *Appl. Phys. Letters* 45 (1984) 805.
- [12] D.A. Bryan, R.R. Rice, R. Gerson, H.E. Tomaschke, K.L. Sweeney and L.E. Halliburton, *Opt. Eng.* 24 (1985) 138.
- [13] K.L. Sweeney, L.E. Halliburton, D.A. Bryan, R.R. Rice, R. Gerson and H.E. Tomaschke, *J. Appl. Phys.* 57 (1985) 1036.
- [14] J.L. Nightingale, W.J. Silva, G.E. Reade, A. Rybicki, W.J. Kozlovsky and R.L. Byer, in: *Proc. SPIE, Vol. 681, Laser and Nonlinear Optical Materials* (1986) p. 20.
- [15] K. Nassau, in: *Ferroelectricity, Proc. Symp. on Ferroelectricity*, Ed. E.F. Weller (Elsevier, New York, 1967) p. 259.
- [16] B.C. Grabmaier and F. Otto, in: *Proc. SPIE, Vol. 651, Integrated Optical Circuit Engineering III* (1986) p. 1.
- [17] B.C. Grabmaier and F. Otto, *J. Crystal Growth* 79 (1986) 682.
- [18] R.S. Feigelson, *J. Crystal Growth* 79 (1986) 669.
- [19] M.M. Fejer, J.L. Nightingale, G.A. Magel and R.L. Byer, *Rev. Sci. Instr.* 55 (1984) 1791.
- [20] D. Feng, N.-B. Ming, J.-F. Hong, Y.-S. Yang, J.-S. Zhu, Z. Yang and Y.-N. Wang, *Appl. Phys. Letters* 37 (1980) 607.
- [21] Y.-H. Xue, N.-B. Ming, J.-S. Zhu and D. Feng, *Chinese Phys.* 4 (1985) 554.
- [22] A. Feisst and P. Koidl, *Appl. Phys. Letters* 49 (1985) 1125.
- [23] Y.S. Luh, R.S. Feigelson, M.M. Fejer and R.L. Byer, *J. Crystal Growth* 78 (1986) 135.
- [24] L.O. Svaasand, M. Eriksrud, G. Nakken and A.P. Grande, *J. Crystal Growth* 22 (1974) 230.
- [25] H. Fay, W.J. Alford and H.M. Dess, *Appl. Phys. Letters* 12 (1968) 89.
- [26] J.B. Bergman, A. Ashkin, A.A. Ballman, J.M. Dziedzic, H.J. Levinstein and R.G. Smith, *Appl. Phys. Letters* 12 (1968) 92.
- [27] R.L. Holman, Novel uses of gravimetry in the processing of crystalline ceramics, in: *Processing of Crystalline Ceramics* (Materials Science Research, Vol. 11), Eds. H. Palmour III, R.F. Davis and T.M. Hare (Plenum, New York, 1978) p. 343.
- [28] J. Crank, *The Mathematics of Diffusion* (Clarendon, Oxford, 1975).
- [29] J.R. Carruther, I.P. Kaminow and L.W. Stulz, *Appl. Opt.* 13 (1974) 2333.
- [30] H.M. O'Bryan, P.K. Gallagher and C.D. Brandle, *J. Am. Ceram. Soc.* 68 (1985) 493.
- [31] J.R. Carruthers, G.E. Peterson and M. Grasso, *J. Appl. Phys.* 42 (1971) 1846.