

Preparation and characterization of off-congruent lithium niobate crystals

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Vapor transport equilibration was used to prepare lithium niobate crystals of a variety of controlled off-congruent compositions. Crystals were characterized through measurement of the ferroelectric Curie temperature T_c and measurement of the temperature for noncritical phase matching T_{PM} of second-harmonic generation from both 1.064- and 1.32- μm laser sources. Across the majority of the single-phase region, both T_c and T_{PM} were observed to vary nearly linearly with Li/Nb ratio. The variation in T_{PM} with Li/Nb ratio was observed to change direction within the single-phase region at some small but finite compositional interval away from the Li-rich phase boundary. Crystals equilibrated to the Li-rich phase boundary had excellent optical homogeneity. Preparation of Li-poor crystals was hampered by extremely slow lithium diffusivity and problems with second-phase precipitation.

I. BACKGROUND AND INTRODUCTION

Lithium niobate is well known as a technologically important single-crystal oxide material. Although commonly referred to as LiNbO_3 , the phase exists over a wide solid solution range, from compositions near the stoichiometric value to lithium-poor compositions as low as approximately 45 mol % Li_2O at 1200 °C. Figure 1 shows a previously reported phase diagram for lithium niobate.¹ Various workers have studied and refined its details.²⁻⁷

Almost all lithium niobate produced commercially is grown by the Czochralski technique and has a composition near the congruently melting value of roughly 48.4 mol % Li_2O .^{7,8} Due to segregation effects, production by a Czochralski process of crystals having a specified off-congruent composition is a difficult undertaking.

Vapor transport equilibration (VTE) is a technique first described by Holman⁴ for preparing uniform lithium niobate crystals of any desired composition within the solid solution phase field. In essence, VTE consists of annealing crystal samples in close proximity to a relatively much larger mass of lithium niobate powder of a desired composition. Given sufficient time at sufficiently high temperature, the Li/Nb ratio in the crystal equilibrates to that in the powder via a mechanism involving vapor transport and solid-state diffusion.

In the present work, we used VTE to prepare lithium niobate crystals of a variety of controlled off-congruent compositions. We characterized the crystals through measurement of the ferroelectric Curie temperature T_c and measurement of the temperature for noncritical phase matching T_{PM} of second-harmonic generation from both 1.064- and 1.32- μm laser sources.

Our aims were threefold. First, we intended to establish accurate standards for lithium niobate crystal composition measurement. Second, we intended to investigate the location of and any peculiarities associated with the phase boundary regions. Third, we hoped to study and refine VTE processing techniques for efficient preparation of off-

congruent crystals with attractive device application potential.

II. VTE PROCESSING

Starting crystals for VTE processing were fabricated from poled Czochralski-grown boules of congruent composition. Crystals were saw cut into z-oriented plates of various cross sections with thicknesses of 0.5, 1, and 2 mm.

In preparing single-phase powder charges for VTE, significant effort was directed toward specifying and controlling Li/Nb ratios. The starting chemicals were Li_2CO_3 and Nb_2O_5 . All chemical lots were screened through spark source mass spectrometry to ensure purity in excess of 99.99%. The moisture content of the starting chemicals was monitored through aliquot drying tests. The atomic weight of lithium in Li_2CO_3 was monitored through thermal ionization mass spectrometry. Considering all possible error sources, absolute accuracy in establishing a desired single-phase powder charge composition was determined to be ± 0.01 mol % Li_2O .

Two-phase powder charges were also prepared using Li_2CO_3 and Nb_2O_5 as starting chemicals. Powder ratios were chosen to establish net compositions of 65 mol % Li_2O and 40 mol % Li_2O , respectively, for the lithium-rich and lithium-poor two-phase mixtures.

Both single- and two-phase powders were mixed, reacted, milled, and then rereacted to ensure compositional homogeneity. A number of configurations were explored for the VTE processing itself. Most commonly, 750 g of reacted powder were loaded into a cylindrical platinum crucible 95 mm high by 135 mm in diameter. The lithium niobate crystals, with a total mass of 1–2 g, were supported parallel to and slightly above the powder surface on platinum pins driven into the powder. A platinum lid 100 mm in diameter was set over the top of the crystals, supported along its outer edges by a ridge of powder.

The processing temperature was 1100 ± 0.5 °C for all the VTE, determined using a calibrated thermocouple in-

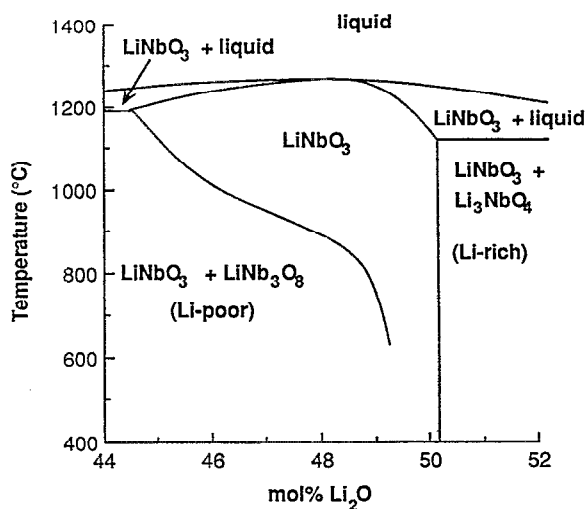


FIG. 1. Approximate phase diagram for lithium niobate (after Ref. 1).

serted into the bulk of a powder charge. Processing times varied depending on crystal thickness and powder composition. In general, thicker crystals and lower lithium concentrations required longer processing times for a given degree of compositional uniformity. Required processing times were observed to vary with roughly the square of the crystal thickness, indicative of diffusion-controlled process kinetics. For the most commonly used crystal thickness of 0.5 mm, exclusive of beginning and ending thermal ramps, a minimum processing time of 60 h was used for powder compositions at the Li-rich phase boundary while a maximum of 400 h was used for powder compositions at the Li-poor boundary. A parallel study of the observed dramatic variation of Li diffusivity with Li/Nb ratio will be reported separately.⁹

For VTE processing involving single-phase or lithium-rich two-phase powders, specimens and powders were cooled together to room temperature over a 24-h period. For VTE involving lithium-poor two-phase powders, such 24-h cooling resulted in the formation of bulk inclusions in the crystals, probably second-phase precipitates. Inclusions were avoided by removing crucibles containing crystals and powder from the 1100 °C furnace resulting in cooling to room temperature within 60 min.

III. CHARACTERIZATION TECHNIQUES

T_c measurements were performed by a standard dielectric technique.¹⁰ On cycling the temperature of a sample, a dielectric anomaly such as a ferroelectric phase transition was indicated by a sharp peak in the phase difference between sample and reference arms of an ac impedance bridge circuit. Crystal samples were prepared by saw cutting the processed z plates to cross-sectional dimensions of roughly 4 mm (x) by 6 mm (y), then painting the z faces with a thin coat of platinum paste. Measured T_c values were determined to be independent of ac frequency over a range from less than 10 kHz to greater than 1 MHz. Most

of the T_c measurements were performed using a 1-V peak-to-peak signal at 300 kHz, as this frequency yielded the sharpest phase difference peaks. The phase difference peaking effect was strong enough to enable a furnace ramp rate during cycling of 1 °C/min. Following an initial 90-min furnace ramp from room temperature to a temperature near T_c , thermal cycles spanned roughly 10 °C peak to peak and were each carried out in roughly 20 min. Temperature cycling was carried out under computer control. Similar phase difference peaks were detected on heating and cooling. No thermal hysteresis was observed.

The use of multiple measurement thermocouples positioned against either face of an adjustable sample holder allowed tuning the system for a given sample size to achieve sample placement in the thermal center of the furnace, thereby minimizing thermal gradient effects and maximizing temperature measurement accuracy. The absolute accuracy of a T_c measurement was determined to be ± 0.3 °C. The reproducibility of a given measurement was ± 0.1 °C. Two identical apparatuses were employed in the work, both yielding equivalent measurements.

All T_c measurement values for processed crystals were cross checked through T_c measurements of corresponding powder charge samples. T_c measurements on powder samples were performed by packing roughly 0.5 g of powder between the sample holder plates of the T_c measurement apparatus. The associated phase difference peaks were broader than for crystal samples, necessitating 15 °C peak-to-peak, 30-min thermal cycles, and reducing absolute measurement accuracy to ± 0.6 °C and reproducibility to ± 0.2 °C.

T_{PM} measurements were performed using a pulsed Nd:YAG laser operating at 1.064 μm and a cw Nd:YAG laser operating on several lines close to 1.32 μm . Output at 532 and 660 nm was detected with a silicon photodiode. A gated integrator was used to measure the signal from the pulsed laser, and a lock-in amplifier detected the optically chopped signal from the cw laser. Samples were prepared by saw cutting, most commonly to dimensions of 4 mm (x) by 6 mm (y) by 0.5 mm (z), then polishing the y faces to typical optical specifications. Orientation accuracy of the y faces was within 30 arcmin. The samples were placed in an oven or a cryostat and the temperature was scanned at rates less than 1 °C/min to observe the phase-matching tuning curve. The sample temperature was measured using a type-K thermocouple in direct contact with the sample. Absolute accuracy of a T_{PM} measurement ranged from ± 0.6 to ± 4 °C, depending on the full width at half-maximum (FWHM) of the phase-matching peak.

IV. RESULTS

A. Single-phase region

The single-phase VTE experiments were significant primarily as establishing standards for lithium niobate crystal composition measurement. VTE processing generally yielded uncracked crystals with slightly roughened surfaces but no visible inclusions. When necessary, roughened surfaces were easily polished by standard techniques.

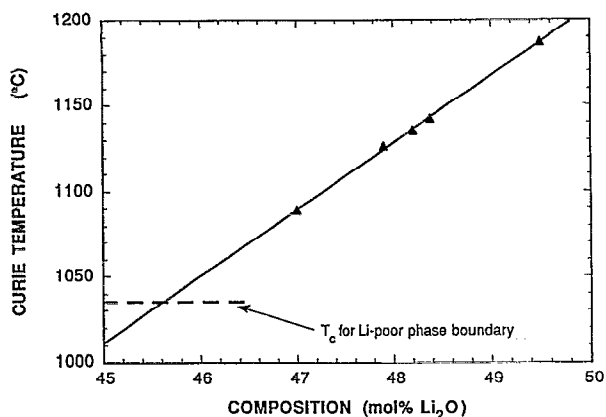


FIG. 2. Ferroelectric Curie temperature vs lithium niobate composition.

Figure 2 shows the dependence of T_c on crystal composition based on measurements of five compositions across the single-phase field. A least-squares linear fit of the data yielded the following equations:

$$T_c = -746.73 + 39.064 [\text{Li}], \quad (1a)$$

$$[\text{Li}] = 19.149 + 2.557 \times 10^{-2} T_c \quad (1b)$$

with T_c in $^{\circ}\text{C}$ and $[\text{Li}]$ representing crystal composition in mol % Li_2O . As previously reported, for Li/Nb ratios greater than roughly 49.8 mol % Li_2O , the ferroelectric phase is stable to the melting point. The observed linearity in the composition dependence of T_c for lithium niobate has previously been reported by a number of authors.^{3,5} Recent work by Grabmaier, Wersing, and Koestler,¹¹ however, reports a very nonlinear dependence. The reason for this discrepancy is not clear.

Figure 3 shows the measured dependence on crystal composition of T_{PM} for 1.064- and 1.32- μm frequency doubling. Ignoring the data point at 49.95 mol % Li_2O to be discussed in the next section, for 1.064- μm doubling, a least-squares fit of the data yielded the following equations:

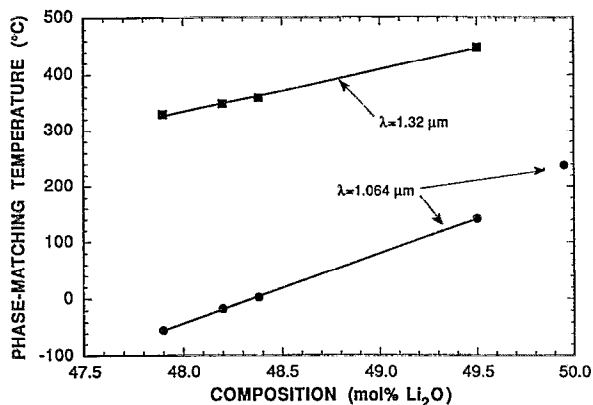


FIG. 3. Phase-matching temperature for noncritical frequency doubling of 1.064- and 1.32- μm laser vs lithium niobate composition.

$$T_{\text{PM}} = -5927.8 + 122.61 [\text{Li}], \quad (2a)$$

$$[\text{Li}] = 48.345 + 8.1543 \times 10^{-3} T_{\text{PM}}, \quad (2b)$$

with T_{PM} in $^{\circ}\text{C}$ and $[\text{Li}]$ representing crystal composition in mol % Li_2O . The analogous equations for 1.32- μm doubling follow:

$$T_{\text{PM}} = -3285.9 + 75.409 [\text{Li}], \quad (3a)$$

$$[\text{Li}] = 43.588 + 1.3225 \times 10^{-2} T_{\text{PM}}. \quad (3b)$$

The observed linearity in the composition dependence of T_{PM} across the majority of the lithium niobate single-phase field is consistent with previous reports from several authors.^{12,13} Again, one recent report¹⁴ suggests a strongly nonlinear dependence.

The quality of the observed phase-matching peaks varied widely with sample composition. For compositions near the starting congruent composition, FWHM values were measured to be roughly 1.7°C for a 6-mm path length, in close agreement with theoretical predictions based on the dispersion data in Ref. 15. The phase-matching peaks of samples of other compositions were broader than predicted by factors between 2 and 5, indicating inhomogeneities in refractive index. Attempts at visual observation of such inhomogeneities were unsuccessful, limited by the fact that none of the single-phase VTE samples were greater than 0.5 mm in thickness.

B. Lithium-rich phase boundary region

VTE processing to the lithium-rich phase boundary composition generally yielded uncracked crystals with no evidence of second-phase precipitation in the crystal bulk. As-processed crystals typically had surfaces that were rougher than those found on crystals processed in single-phase powders, however, these rougher surfaces were likewise found to be easily polished. Careful visual inspection of most of the thicker samples fabricated for T_{PM} measurement, however, revealed refractive index variations. These variations, observable through a sample's polished optical end faces, appeared to be confined to a nearly planar region parallel to and midway between the sample's large faces. In samples with such inhomogeneities, reproducible T_{PM} measurement generally required directing the fundamental laser beam along a path offset from this central plane.

With the ferroelectric phase stable to the melting point, and T_{PM} for 1.32- μm frequency doubling greater than 450°C , characterization of samples equilibrated to compositions in the region of the Li-rich phase boundary was limited to measurement of T_{PM} for 1.064- μm frequency doubling. Samples equilibrated at 1100°C in two-phase powder to the Li-rich phase boundary were measured to have a 1.064- μm frequency doubling T_{PM} value of $233.7 \pm 0.6^{\circ}\text{C}$. The discrepancy between this value and the 238°C value reported previously^{16,17} is likely due to uncertainty in the previous value or a difference in VTE processing temperature.

In contrast to the majority of single-phase VTE samples, the phase-match curves displayed a well-defined sinc² characteristic with central peak FWHM values of 1.0 and

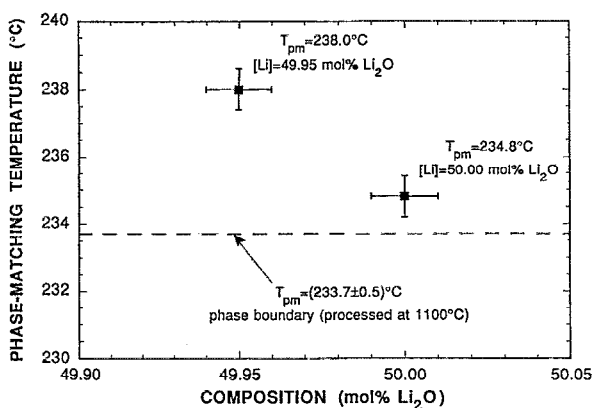


FIG. 4. Phase-matching temperature for 1.064- μm noncritical frequency doubling vs lithium niobate composition in the region of the Li-rich phase boundary.

0.6 °C for 6- and 10-mm path lengths, respectively, in agreement with theoretical calculations based on the data in Ref. 15. Additional 1.064- μm frequency doubling experiments corroborated the high optical quality of these lithium-rich phase boundary specimens.¹⁸ A similarly fabricated sample 15 mm in length was measured to display a FWHM value of 0.4 °C, also in close agreement with theory. The FWHM for a sample 25 mm in length was beyond measurement resolution, less than 0.3 °C.

Extrapolation to 233.7 ° of the data represented by Eq. (2b) suggests a Li-rich phase boundary composition of 50.25 mol % Li₂O at 1100 °C. However, additional VTE experiments involving single-phase compositions in the vicinity of the phase boundary produced results in conflict with such simple extrapolation. Figure 4 illustrates the findings.

At 1100 °C, there appears to exist in the single-phase field a range of Li/Nb ratios with corresponding T_{PM} values in excess of the 233.7 °C value measured for the phase boundary composition. Although the differences in T_{PM} are small, the differences are greater than the associated measurement uncertainty and they are reproducible. In confirming the validity of the data represented in Fig. 4, VTE processing of both 50.00 mol % Li₂O and the two-phase mixture was in one instance carried out simultaneously using two crucibles in the same furnace. Corresponding measurement samples were then held side by side in the T_{PM} measurement apparatus and then reversed in confirming the measured T_{PM} difference.

It thus appears that $dT_{\text{PM}}/d[\text{Li}]$ changes sign within the single-phase region at some small but finite compositional interval away from the Li-rich phase boundary. A physical explanation for such behavior is not obvious, although it is notable that similar peaks in the composition dependence of T_{PM} have recently been reported for lithium niobate crystals doped with magnesium.¹⁹ Linear extrapolation from the measured T_{PM} values for 49.95 and 50.00 mol % Li₂O to a phase boundary T_{PM} of 233.7 °C suggests a phase boundary composition at 1100 °C of 50.02 mol % Li₂O.

These observations conflict with the previous report by O'Bryan and co-workers⁷ of phase boundary compositions at 1060, 1100, and 1150 °C of 49.96, 49.89, and 49.81 mol % Li₂O, respectively. The discrepancy is larger than can be accounted for by the uncertainty in either our composition specification or our measured T_{PM} differentials. There is insufficient information in Ref. 7 to assess the relevant uncertainty values in that work. It would be illuminating to map in more detail the composition dependence of T_{PM} in the vicinity of the Li-rich phase boundary and also to measure T_{PM} for phase boundary VTE specimens processed at a variety of temperatures.

C. Lithium-poor phase boundary region

As mentioned above, VTE to the lithium-poor phase boundary required relatively long processing times, roughly 400 h for 0.5-mm plates. Also already noted, avoidance of the formation of bulk inclusions in the cooling crystals required relatively high cooling rates, from 1100 °C to room temperature in less than 60 min. The typical surface condition of the as-processed crystals was intermediate between those associated with single-phase and lithium-rich two-phase VTE. Again, standard polishing was adequate to remove the roughness.

T_c for crystals equilibrated to the lithium-poor phase boundary was measured to be 1035 ± 0.3 °C. An equivalent T_c value was measured directly on Li-poor two-phase powders. Extrapolation to 1035 °C of the data represented by Eq. (1b) suggests a Li-poor phase boundary composition of roughly 45.6 mol % Li₂O. This value may be compared with the 45.3-mol % Li₂O value reported by Svaasand *et al.*¹ In contrast to the lithium-rich case, no evidence was observed of anomalous physical property behavior in the vicinity of the phase boundary.

With a T_c value below 1100 °C, the ferroelectric domain character of the crystals equilibrated to the Li-poor phase boundary was necessarily established on cooling. Polishing, etching, and microscopy of as-processed crystals using standard techniques revealed a disordered mix of both domain orientations with an average domain width of roughly 40 μm . Correspondingly, all attempts to determine unambiguous phase-match peaks for noncritical frequency doubling were unsuccessful.

A variety of attempts to pole the material by reheating the processed crystals above T_c were unsuccessful as well. Simple air quenching of reheated crystals from 1100 °C at rates as high as 200 °C/min in hope of exploiting a natural thermoelectric poling field resulted in domain structures not observably different from the originals. Direct application of dc poling voltages in several different configurations resulted in the formation of bulk inclusions to an extent that rendered even 0.5-mm plates visually opaque. Cooling rates as high as 200 °C/min were ineffective at avoiding such precipitation.

V. DISCUSSION AND OUTLOOK

The techniques and data reported above for the single-phase region VTE experiments should be useful as estab-

lishing definitive standards for measurement of lithium niobate crystal composition. They should be further useful in enabling unambiguous measurements of composition-dependent lithium niobate physical properties. Historically, such measurements have been limited largely by uncertainties and nonuniformities in the composition of measurement specimens. Experimental studies are currently in progress using VTE-processed crystals in confirming or refining data on the compositional dependence of refractive index, surface-acoustic-wave velocity, and acoustic attenuation in lithium niobate.

Crystals prepared through VTE processing to the Li-rich phase boundary have already been successfully applied in a number of technologically significant nonlinear optical device demonstrations, including cw 1.064- μm frequency doubling with efficiencies approaching 70% and 532-nm power levels exceeding 1.5 W.²⁰ The relatively high T_{PM} of the Li-rich crystals offers the important benefit of avoidance of photorefractive damage effects. Further, preliminary evidence indicates accelerated photorefractive response time in Li-rich compositions, suggesting potential applications in photorefractive storage, particularly using transition metal-doped starting crystals.

Volume scale-up of VTE processing to the Li-rich phase boundary appears to be viable. In additional experiments, all standard commercial lithium niobate substrate orientations (x , y , z and 128° rotated off y in the y - z plane) were successfully processed in diameters up to 80 mm and thicknesses up to 3 mm. It is not certain whether the observed planar refractive index inhomogeneities may be eliminated by improvements in VTE processing or, if not, to what extent they will pose a problem for device applications.

The anomalous $dT_{\text{PM}}/d[\text{Li}]$ behavior warrants further investigation. It suggests the possibility of a qualitative change in the point-defect incorporation mechanism in moving toward the extreme Li-rich end of the single-phase field.

With a predicted T_{PM} of roughly 150 $^\circ\text{C}$ for 1.32- μm noncritical frequency doubling, important applications also exist for crystals prepared through VTE processing to the Li-poor phase boundary. Due to problems with uncontrollable domain multiplicity, however, VTE in the vicinity of the Li-poor phase boundary remains in large measure an unsolved technical challenge. For a VTE processing tem-

perature of 1100 $^\circ\text{C}$, such domain multiplicity problems may be expected for all composition values less than roughly 47.3 mol % Li_2O . Lower processing temperatures might be explored in attempting to preserve the single-domain character of the starting crystals, however, this would necessitate even longer processing times.

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