

Optical Properties of Lithium-Rich Lithium Niobate Fabricated by Vapor Transport Equilibration

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Abstract—Lithium-rich lithium niobate of excellent optical homogeneity can be fabricated by a vapor transport equilibration (VTE) technique. The high optical quality, uniformly birefringent crystals noncritically phase match for second harmonic generation of 1064 nm Nd:YAG radiation to 532 nm at 238°C. The refractive indexes and their temperature dependence have been measured to derive temperature-dependent Sellmeier equations which predict noncritical phase matching for wavelengths as short as 976 nm to generate blue at 488 nm at room temperature. The Sellmeier equations accurately predict experimental phase-matching temperatures over a wide temperature range.

LITHIUM niobate exists over a solid-solution range of 44–50 mole percent Li₂O. However, only crystals grown from melts of the congruent composition have good optical quality and uniform birefringence [1], [2]. Unfortunately, crystals of this composition suffer from photorefractive damage when used in nonlinear optical applications involving visible radiation, e.g., second-harmonic generation (SHG) of the 1064 nm output of a Nd:YAG laser [3]. While lithium-rich compositions have greater birefringence and hence higher phase-matching temperatures, they cannot be grown from the melt without birefringence variations that preclude application of such crystals to optical devices. Crystals grown from melts doped with several percent MgO have been used in such applications, as they are less susceptible to the photorefractive effect [4]. However, the useful length of MgO doped crystals is limited by birefringence variations caused by variations in the MgO concentrations [5]. Thus, there is a need for crystals that are optically homogeneous and that phase match above the annealing temperature for the photorefractive effect.

It has recently been shown that lithium niobate of compositions close to stoichiometric with excellent optical quality can be produced by a vapor phase transport equilibration (VTE) technique [6], [7]. The full-width at half-maximum intensity for SHG of 1064 nm in a 20 mm sample was shown to be 0.4 K, comparable to the width expected for a perfectly homogeneous crystal [7]. Phase matching for this interaction was observed at a tempera-

ture of 238°C, well above the 110°C annealing temperature [8] for the photorefractive effect. A conversion efficiency of 42 percent for SHG of 1064 nm was achieved in an 8 mm long sample using a Q-switched laser with pulse energies around 1 mJ [9].

In order to assess potential device applications of this material, it is necessary to obtain Sellmeier equations with temperature dependent parameters adequate for the prediction of phase-matching temperatures. In this paper we present the two sets of parameters required to completely characterize the temperature dependence of the indexes n_o and n_e . The Sellmeier equation used is of the form

$$n^2 = A_1 + \frac{A_2 + B_1 F}{\lambda^2 - (A_3 + B_2 F)^2} + B_3 F - A_4 \lambda^2. \quad (1)$$

The parameters A_1 through A_4 and B_1 through B_3 are constants depending on the material, λ is the vacuum wavelength in nm, n stands for either n_o or n_e , and the temperature dependence enters through the parameter F where $F = (T - T_0) / (T + T_0 + 546)$. T_0 is a reference temperature, in our case 24.5°C. All temperatures are measured in degrees centigrade. Sellmeier equations of this form have been given previously for lithium niobate crystals grown from stoichiometric melts (solid composition approximately 48.7 mole percent Li₂O [10]) and congruently grown crystals (approximately 48.4 percent Li₂O [10]) [11]–[13]. Note that literature values for the Li₂O content of these compositions vary by several tenths of a percent [1], [10]. Values given in this paper, taken from [10], are representative of current results.

The samples used in the present work were fabricated by heating to 1100°C in a closed crucible partially filled with a powdered mixture of LiNbO₃ and Li₃NbO₄. There is a net transfer of lithium from the powder into the crystal through a series path of vapor transport and solid-state diffusion that continues until the crystal composition reaches that of the phase boundary, approximately 49.9 mole percent Li₂O [10]. Material processed to this lithium-rich phase boundary is highly birefringent, exhibiting a phase-matching temperature of 238°C for second-harmonic generation (SHG) of 1064 nm radiation, compared to –8°C for the congruent composition [7], [2].

Index of refraction measurements were obtained by the minimum deviation prism technique, using a lithium-rich crystal fabricated into a prism of apex angle 36.6° with 1 × 10 mm optical faces. The optic axis was aligned with

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the axis of the prism to better than 0.5° . The uncertainties in the index of refraction measurements are dominated by the errors in aligning the axis of the thin prism to the rotation axis of the goniometer. Table I shows the measured ordinary and extraordinary indexes of refraction for lithium-rich lithium niobate at room temperature.

The temperature dependence of the indexes was measured using the same prism by recording the change in the deflection angle for temperatures up to 300°C . Fig. 1 shows the measured changes in refractive index for two wavelengths, 325 and 1064 nm, together with a parabolic least square fit of the form

$$n(25^\circ\text{C} + \Delta T) - n(25^\circ\text{C}) = X\Delta T + 0.5Y(\Delta T)^2 \quad (2)$$

where n is the refractive index, ΔT is the temperature above 25°C , and X and Y are the resulting parameters of the fit. Taking the derivative of (2) with respect to the temperature, the temperature derivative of the index of refraction is

$$\frac{dn}{dT}(25^\circ\text{C} + \Delta T) = X + Y\Delta T. \quad (3)$$

The parameters X and Y for the four wavelengths for which the temperature dependence was measured are shown in Table II.

A nonlinear least-squares routine (Levenberg-Marquardt method [14]) was used that simultaneously optimized the 14 parameters for the Sellmeier equations for n_o and n_e . The input consisted of the refractive index data from Table I, and dn/dT values evaluated at 50, 150, and 250°C using the coefficients from Table II. To improve the accuracy of the infrared indexes and the birefringence, two additional data points were included in the fit: the phase-matching angle for SHG of 1064 nm radiation at 22°C , 22.55° , and the signal wavelength, 575.5 nm, for parametric fluorescence with a 476.5 nm pump at 444°C . Table III shows the parameters for the temperature dependent Sellmeier equations for n_o and n_e for lithium-rich lithium niobate.

To test the validity of the predictions based on the parameters given in Table III, several phase-matching temperatures were experimentally determined. In addition, the temperature dependence of the signal wavelength for optical parametric fluorescence was determined for pump wavelengths 514.5, 488.0, and 476.5 nm [15]. The agreement of the prediction with the experimental data for the parametric fluorescence, shown in Fig. 2, is better than 6 K for all points and 3.6 K on average. The temperatures measured for SHG with the pump-wavelengths 954, 1064, and 1318 nm were -62.5 , 238, and 520°C , respectively, as shown in Fig. 3. While the SHG for 1064 nm is in very good agreement, the predicted phase-matching temperatures for 954 and 1318 nm are off by -23 and -11 K, respectively, suggesting that the form assumed for the temperature dependence of the indexes is inadequate for

TABLE I
MEASURED INDEXES OF REFRACTION FOR VAPOR TRANSPORT EQUILIBRATED LITHIUM NIOBATE AT ROOM TEMPERATURE

Wavelength (nm)	n_e	n_o
1064	2.1440 ± 0.0005	2.2339 ± 0.0005
632.8	2.1890 ± 0.0004	2.2878 ± 0.0005
514.5	2.2270 ± 0.0004	2.3334 ± 0.0004
501.7	2.2329 ± 0.0004	2.3405 ± 0.0004
496.5	2.2352 ± 0.0005	2.3437 ± 0.0004
488.0	2.2398 ± 0.0004	2.3495 ± 0.0004
476.5	2.2465 ± 0.0004	2.3573 ± 0.0005
472.7	2.2489 ± 0.0005	2.3604 ± 0.0005
465.8	2.2530 ± 0.0004	2.3658 ± 0.0004
457.9	2.2584 ± 0.0004	2.3719 ± 0.0004
454.5	2.2608 ± 0.0004	2.3751 ± 0.0005
325.0	2.467 ± 0.0005	2.636 ± 0.002

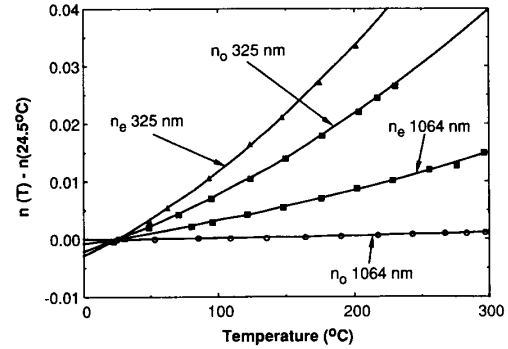


Fig. 1. Change of refractive index with temperature for two wavelengths. The reference temperature is 25°C . The solid line represents the result from a parabolic approximation.

TABLE II
PARAMETERS FOR THE REFRACTIVE INDEX CHANGE WITH TEMPERATURE OBTAINED BY TAKING THE DERIVATIVE OF THE PARABOLIC APPROXIMATION OF FIG. 1

Wavelength (nm)	$X n_e$ (10^{-6}K^{-1})	$Y n_e$ (10^{-8}K^{-2})	$X n_o$ (10^{-6}K^{-1})	$Y n_o$ (10^{-8}K^{-2})
1064	38.5	11.5	1.41	2.14
632.8	43.1	20.2	5.22	4.74
454.5	62.2	22.2	19.3	6.64
325.0	129	71.3	87.1	41.9

$\frac{dn}{dT}(25^\circ\text{C} + \Delta T) = X + Y\Delta T$

TABLE III
PARAMETERS FOR THE TEMPERATURE-DEPENDENT SELLMIEIER EQUATION

Parameter	n_e	n_o
A_1	4.546 ± 0.007	4.913 ± 0.006
A_2	$(9.17 \pm 0.16) \times 10^{-4}$	$(1.163 \pm 0.013) \times 10^{-5}$
A_3	$(2.148 \pm 0.025) \times 10^{-2}$	$(2.201 \pm 0.015) \times 10^{-2}$
A_4	$(3.03 \pm 0.59) \times 10^{-8}$	$(2.73 \pm 0.44) \times 10^{-8}$
B_1	$(1.93 \pm 0.55) \times 10^{-2}$	$(9.4 \pm 2.9) \times 10^{-3}$
B_2	$(5.3 \pm 0.77) \times 10^{-5}$	$(3.98 \pm 0.30) \times 10^{-5}$
B_3	$(2.72 \pm 0.15) \times 10^{-7}$	$(1.6 \pm 0.72) \times 10^{-8}$

$n^2 = A_1 + \frac{A_2 + B_1 F}{\lambda^2 - (A_3 + B_2 F)} + B_3 F \cdot A_4 \lambda^2$ λ given in nm
 $F = (T - 24.5)(T + 570.5)$ T given in $^\circ\text{C}$

temperatures much below 0°C or higher than 400°C . The experimental data presented here for SHG with a pump wavelength of 1064 nm agrees well with previously pub-

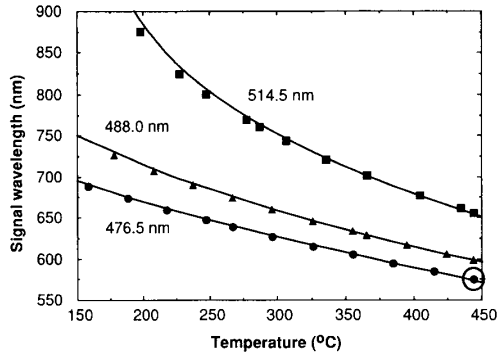


Fig. 2. Signal wavelength of optical parametric fluorescence for three different pump wavelengths. The solid lines are calculated using the Sellmeier parameters of Table III. The encircled data point at 444°C was used to improve the accuracy of the parameters, as described in the text.

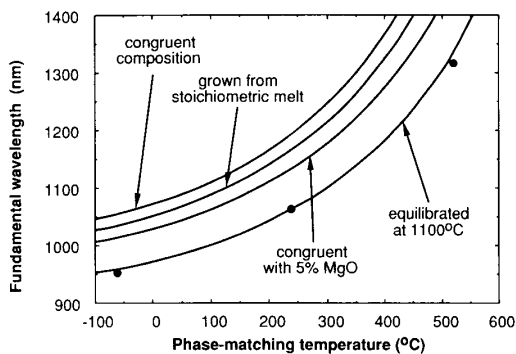


Fig. 3. Comparison of predicted phase-matching conditions for different crystal compositions. Circles depict experimental data points for equilibrated LiNbO_3 .

lished data [7]. However, the phase-matching temperature we observed for SHG of 954 nm was 25.5 K lower than reported in [7]. The reason for the discrepancy is not clear, but may be due to the use of material from different boules, or differences in processing conditions.

Fig. 3 compares the range of wavelengths that phase-match noncritically for SHG for different types of lithium niobate crystals. The curves for the crystals grown from stoichiometric and congruent melts were calculated using the parameters from [11] and [13]. For the material doped with 5 percent magnesium oxide, we used the parameters from [16]. The graph clearly shows that much shorter wavelengths can be phase matched with the vapor transport equilibrated material than with the other compositions. For example, SHG of 976 nm to generate blue radiation at 488 nm phase matches at room temperature for lithium-rich lithium niobate.

The lithium-rich phase boundary at high temperatures is not vertical, but moves toward lower Li_2O concentrations with increasing temperature [10]. For device fabrication, it is important to know the change in phase-matching temperature for small variations in the processing temperature. It is shown in [10], that for temperatures be-

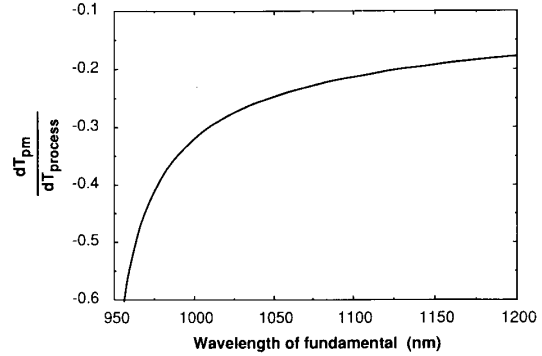


Fig. 4. Sensitivity of the phase-matching temperature T_{pm} to changes in the vapor transport equilibration temperature $T_{process}$.

tween 1060 and 1150°C, the molar percentage of Li_2O depends linearly on the processing temperature, with a slope of -1.7×10^{-3} mole percent/K. A change in the processing temperature thus leads to a slightly different Li_2O concentration which shifts the phase-matching temperatures for nonlinear interactions. To estimate the sensitivity of the phase-matching temperature to processing conditions, we assume that the coefficients of the Sellmeier equation may be linearly interpolated between those for congruent material [12] and those from Table III for the lithium-rich material. Fig. 4 shows the sensitivity of the temperature for noncritical phase matching to a change in processing temperature, calculated under this assumption. For example, an increase in processing temperature by 10 K leads to a decrease of the phase-matching temperature for SHG of 1064 nm by 2.3 K.

To summarize, we measured the temperature dependence of the refractive indexes of vapor transport equilibrated lithium-rich lithium niobate and calculated the coefficients for temperature-dependent Sellmeier equations for the ordinary and extraordinary indexes of refraction. The phase-matching temperatures for a wide range of interactions can be predicted to within a few kelvins in the temperature range 0 to 400°C. The equilibrated samples have excellent optical homogeneity and allow for noncritical phase matching for wavelengths as short as 488 nm at room temperature. Interpolation between the Sellmeier coefficients for lithium-rich and congruent lithium niobate allows estimation of the phase-matching temperatures for other compositions of lithium niobate that can be produced by the VTE technique. We are currently studying phase-matching temperatures of samples with different Li_2O concentrations in order to produce crystals useful for other interactions, and to develop composition dependent Sellmeier parameters.

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Dieter H. Jundt, photograph and biography not available at the time of publication.

Martin M. Fejer, photograph and biography not available at the time of publication.

Robert L. Byer (M'75-SM'83-F'87), for a photograph and biography, see this issue, p. 157.