Influence of composition of MgO-doped lithium niobate on phase-matching temperature for frequency doubling in the visible

W. M. Young and R. S. Feigelson
Department of Materials Science and Engineering, Stanford University, Stanford, California 94305

D. H. Jundt and M. M. Fejer
Department of Applied Physics, Stanford University, Stanford, California 94305

The dependence of the phase-matching temperature for second harmonic generation (SHG) of 1064-nm radiation on Li/Nb and Li/Mg ratios in MgO-doped lithium niobate crystals was investigated. Crystals studied were grown from melts with 0, 1, 2, and 5 mol % MgO and were equilibrated to different Li contents through a vapor-phase-transport process. Crystals with no MgO doping, equilibrated to the Li-rich phase boundary, had the highest phase-matching temperature. At room temperature (25.5 °C), this material phase-matched for SHG of 978.4-nm radiation to generate blue light.

Lithium niobate is well known as a crystal with large nonlinear susceptibilities and high optical quality useful for a variety of frequency conversion applications.[1,2] Commercially available crystals of the congruently melting composition can be used for phase-matched second harmonic generation (SHG) of fundamental wavelengths as short as 1.078 μm at room temperature,[3] but are of limited utility at these temperatures because of optically induced refractive index variations ("photorefractive damage") that cause severe beam distortions. The photorefractive effect has been shown to decrease markedly at temperatures exceeding 120–170 °C,[4] so techniques for raising the phase-matching temperature of lithium niobate are of considerable practical importance. Since the birefringence of lithium niobate decreases with temperature, composition modifications that increase the room temperature birefringence increase the phase-matching temperature at a particular wavelength. Since the dispersion increases at short wavelengths, such highly birefringent crystals also allow phase-matching of shorter wavelengths at a given temperature. Both the addition of Mg to lithium niobate[5–8] and increasing the Li/Nb ratio in lithium niobate[9,10] have been shown to increase the birefringence and hence the phase-matching temperatures for SHG in the visible. Mg:lithium niobate, which has the additional advantage of a higher photoconductivity that further reduces the photorefractive effect,[6] has been used to efficiently double the 1.06-μm output of a cw Nd:YAG laser.[11] In order to extend such devices to shorter wavelengths or higher phase-matching temperatures, it is interesting to search for compositions with even higher birefringence.

Earlier work has shown that lithium niobate exists over a range of compositions of $x = 46$ mol % to $x = 50$ mol %,[12] where x is defined as the molar percentage of Li$_2$O in xLi$_2$O + $(1 - x)$Nb$_2$O$_5$ = Li$_{2x}$Nb$_{2(1 - x)}$O$_3$. In this formula and throughout the reminder of this paper we do not attempt to account for the defects necessary for charge balance.[13] Crystals have been grown with Mg doping of y mol %, with $0 < y < 9\%$, where y is related to the melt composition by $(\text{MgO})_y{:}(\text{Li}_{2x}\text{Nb}_{2(1 - x)}\text{O}_3)_{1 - y}$. The birefringence is a strong function of both x and y as mentioned above. We have used the phase-matching temperature for noncritical SHG of 1.064-μm radiation as a convenient indicator of crystal birefringence, with a higher temperature indicating higher room-temperature birefringence. The phase-matching temperature of $y = 0$ LiNbO$_3$ increases monotonically with x, reaching a maximum of 236 °C for crystals with the phase-boundary composition.[14,15] Crystals grown from melts with $x = 50$ mol % and y varying between 0 and 5 mol % show the highest phase-matching temperature (120 °C) for $y = 3$ mol % MgO, while crystals grown from a melt with $y = 5$ mol % show a phase-matching temperature increasing with x for melt compositions in the range $47.6 < x < 51.5$ mol %.[6] These results suggested to us that a combination of MgO doping and an increase in Li content might produce crystals with an even higher phase-matching temperature. In this communication, we report on experiments conducted to find the composition yielding the highest 1.064-μm phase-matching temperature.

Since it is difficult to grow high-quality lithium niobate crystals of other than the congruently melting composition, we used a vapor transport equilibration technique (VTE)[14,16] to control the Li/Nb ratio of the crystals. The samples were heated in a covered crucible partially filled with Li$_{2x}$Nb$_{2(1 - x)}$O$_3$ powder of the desired x composition. 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 is in thermodynamic equilibrium with the Li$_2$O vapor pressure determined by the Li content of the powder. The MgO concentration of the crystals does not change during the VTE process due to the low mobility of Mg ions in the crystal and the much lower MgO vapor pressure as compared to the Li$_2$O vapor pressure. We note here that the presence of magnesium in the crystals might affect the vapor pressure of Li$_2$O. If this is the case, the Li content of the equilibrated MgO-doped LiNbO$_3$ crystals will be different from the Li content of the powder. However, the Li content for crystals of fixed MgO doping still will be a

monotonic function of the well-controlled Li content of the powder. The method is adequate to study trends in phase-matching temperatures.

Lithium niobate crystals with $y = 1$ and 2 mol % (in melt) were grown at Stanford for previous research.[5] The Mg compositions given in this paper refer consistently to the melt rather than the solid. The solid compositions may be estimated from the distribution coefficient of Mg in lithium niobate which is thought to be around 1.3.[17] Crystals with $y = 5$ mol % were obtained from Crystal Technology Inc.[18] All samples were cut to dimensions $6 \times 3.8 \times 0.5$ mm^3 with the c axis aligned with the thin direction, and then equilibrated with powders of various Li/Nb ratios to obtain a series of x and y values. Lithium niobate powders with $x = 48.6$, 49, and 49.95 mol % were obtained from Crystal Technology. Powder with $x = 49.6$ mol % was fabricated by mixing powders of $x = 49$ and $x = 49.95$ mol % and annealing the mixture for 20 h at 1100 °C in a covered alumina crucible. A crystal with $y = 0$ equilibrated to the composition of the $x = 49.6$ mol % powder had a phase-matching temperature of 173 °C for doubling 1.064-μm radiation, in agreement with the results of similar work,[19] indicating that powder of the desired composition was generated by this procedure. Powder consisting of two phases (LiNbO$_3$ and Li$_3$NbO$_4$) was prepared from a mixture of Puratronic grade 99.999% Li$_2$CO$_3$ and 99.9999% Nb$_2$O$_5$.[20] The powder was reacted at 550 °C for 1 h, followed by two sequences of mixing and annealing. Each annealing procedure lasted 24 h at 1100 °C.

Crystals with $y = 1$, 2, and 5 mol % were equilibrated to each powder composition by heating to 1100 °C for 53 h in a covered alumina crucible which was partially filled with powder. In each run, a congruent, undoped crystal of the same dimensions was placed in the crucible to serve as a monitor for the process.

1.06-μm radiation for the SHG measurements was generated with a Nd:YAG laser operated in a long-pulse mode. The temperature was measured with a type-K thermocouple cemented to a copper block attached to the sample. The uncertainty in the measured temperature typically was 1 K. The phase-matching temperatures of the undoped monitor samples all agreed with previous results.[19]

Figure 1 shows the phase-matching temperature versus powder composition x for SHG of 1.064-μm radiation for crystals with $y = 0$, 1, 2, and 5 mol % MgO. The solid curves depict results from this study, and the dashed lines show the results of Refs. 19 and 6. Using the calibration curve for converting the melt into solid composition (Fig. 5 in Ref. 8), the stoichiometric lithium:niobium melt of the curve (Fig. 8, Ref. 6) has been converted to crystal composition 48.94% (x).[21] The highest phase-matching temperature, 236 °C, was obtained with $y = 0$ and x equilibrated to the Li-rich phase boundary.[14] Contrary to our expectations, it was not possible to find a higher phase-matching temperature than that of undoped Li-rich lithium niobate. As the MgO doping is increased, the maximum phase-matching temperature decreases, and occurs at monotonically lower Li content. In 5 mol % MgO-doped lithium niobate, the crystal equilibrated in powder with
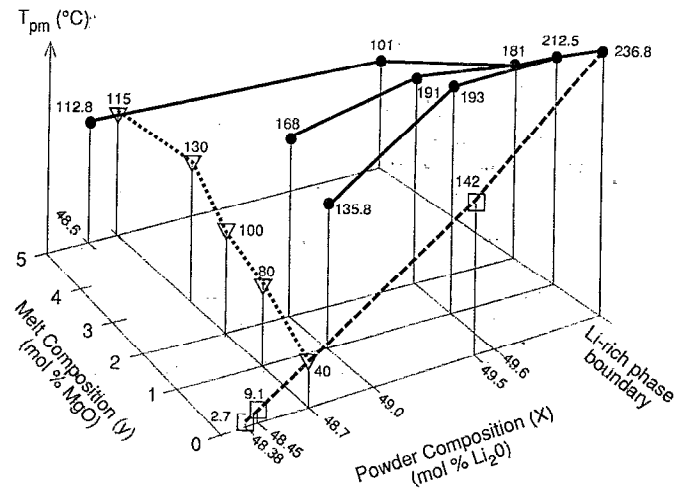

FIG. 1. Phase-matching temperature for doubling 1.064-μm radiation vs MgO doping in melt and Li$_2$O powder composition. (Solid lines: results from this study; dashed lines: results from Refs. 6 and 19.)

$x = 0.486$ has a higher phase-matching temperature (112.8 °C) than does the crystal close to the lithium-rich phase boundary composition (101 °C).

The optical quality of the crystals depended on the processing conditions. As was seen in previous experiments, crystals with $y = 0$ equilibrated to the Li-rich phase boundary had excellent optical quality.[14,15] Crystals equilibrated to other compositions were of lower quality (as judged by the width of the phase-matching peak), especially the Li-rich $y = 5$ mol % crystal, which also had visible scattering centers. It is possible that the high doping level facilitates precipitation of a second phase leading to inhomogeneities in the optical properties.

We established that the material with the highest phase-matching temperature for doubling 1.064-μm radiation in the investigated composition range is undoped LiNbO$_3$ equilibrated to the Li-rich phase boundary. Measurements with a Ti-sapphire laser show a phase-matching wavelength of 978.4 nm for these crystals at 25.5 °C, in good agreement with predictions from the Sellmeier equations (977.2 nm).[15] These results suggest applications to room-temperature sources of blue radiation, but better understanding of the photorefractive effects are necessary to ascertain the practicality of such devices.

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[21] The melt/solid calibration curve of Fig. 5 in Ref. 8 is for lithium niobate without MgO doping. The presence of Mg in the melt may modify somewhat the distribution coefficient for Li from that curve in Ref. 8, but in the absence of other information we use this value.

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