Vapor-transport equilibrated near-stoichiometric lithium tantalate for frequency-conversion applications

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Near-stoichiometric lithium tantalate (SLT) crystals were produced from congruent lithium tantalate by a vapor-transport equilibration process. Because of the resultant increase in photoconductivity and reduction in photogalvanism, the crystals showed no observable photorefractive damage at 514.5 nm up to the highest intensity used, 2 MW/cm^2. The crystals also exhibited low green-induced infrared absorption, a Curie temperature of 693 °C, and a coercive field of 80 V/mm. The SLT samples were periodically poled with an 8-μm-period grating, permitting first-order quasi-phase-matched second-harmonic generation of 532-nm radiation at 43 °C. A 17-mm-long sample generated 1.6 W of continuous-wave output power at 532 nm for 50 h. With 150-ns pulses at a 100-kHz repetition rate in the same sample, 5-W average-power, 532-nm radiation was generated for 1000 h. No damage to the crystal and no aging effects were observed during these experiments. © 2004 Optical Society of America

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Frequency conversion of light in periodically poled lithium niobate (LN) and periodically poled lithium tantalate (LT) has been widely demonstrated during the past decade. LT and LN crystals are typically grown with a congruently melting composition by the Czochralski method. This approach results in congruent crystals with the same chemical composition as the melt. The growth of these crystals has been well studied and routinely produces homogeneous optical-quality material. However, two materials issues have limited the performance of congruent periodically poled LN and periodically poled LT crystals for frequency conversion at room temperature that involves high intensities of visible light: photorefractive damage (PRD) and green-induced infrared absorption (GRIIRA).[1] In addition, the high coercive fields required for domain reversal complicate scaling to large apertures. Congruent 5-mol.% MgO:$LiNbO_3$ crystals show improved resistance to PRD,[2] but the coercive field needed for the poling process is greater than 5 kV/mm at room temperature. Recent publications on melt-grown near-stoichiometric MgO:$LiNbO_3$ crystals[1,3,4] and melt-grown near-stoichiometric LT and MgO:$LiTaO_3$ crystals show a remarkable decrease in coercive field, PRD, and GRIIRA.[5–7] Growth of near-stoichiometric LN and LT crystals is much more challenging than growth of congruent crystals. In this study near-stoichiometric lithium-tantalate (SLT) crystals were produced from congruent lithium tantalate (CLT) by vapor-transport equilibration (VTE),[8,9] a much simpler process. We report here on the fabrication process, measurements of transport properties related to PRD, and a successful 1000-h life test generating 5 W of 532-nm radiation at near room temperature.

CLT does not have the 1:1:3 molar ratio implied by the chemical formula $LiTaO_3$ but is instead 1.6% deficient in lithium. In a widely accepted defect model,[10] charge neutrality requires that, for every four lithium vacancies, there is one Ta^{4+} ion on a lithium site. This defect, known as a Ta^{4+} antisite, is associated with PRD and GRIIRA in CLT.[1] Growth of near-stoichiometric LT, with a greatly reduced tantalum antisite defect density, has been demonstrated elsewhere by the double crucible melt growth[5,6] and the potassium-flux growth[7] methods. These techniques require precise control of material flux rates and temperature and are quite challenging to implement. Nonetheless, SLT and SLN, with their decreased sensitivity to PRD and GRIIRA, may have significant applications in efficient, high-power frequency conversion at visible wavelengths.

Compared with melt-growth processes, VTE is a simple technique that transforms widely available CLT wafers into near-stoichiometric ones.[8,9] Congruent wafers are simply heated in a crucible with a prereacted two-phase powder containing more lithium than the 1:1:3 stoichiometric molar ratio. At high temperature there is a net transfer of lithium from the powder into the crystal through vapor transport and solid-state diffusion that continues until the crystal composition reaches the near-stoichiometric phase boundary. This equilibration method lends itself naturally to the production of homogeneous crystals. Moreover, the process does not require precise control of powder composition or temperature for achieving reproducible results.

In this study 5.08-cm wafers of optical-grade, z-cut, 1-mm-thick, undoped CLT from Yamaju Ceramics, were placed in a platinum crucible with a two-phase prereacted powder made from 70%(m) Li_2O and 30%(m) Ta_2O_5. The wafers were heated in nitrogen to 1360 °C for 100 h. The Curie temperature of the wafers after processing was 693 ± 3 °C, measured with differential thermal analysis. Since VTE takes place above this temperature, the vapor-transport-equilibrated near-stoichiometric lithium tantalate (VSLT) wafers were polydomain. They were then restored to a single-domain state with electric field poling at 185 °C and graphite contacts. This step

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was followed by air annealing at 620 °C for 10 h to eliminate the faint coloration that typically appears during the poling process.

After VTE, several experiments were performed to characterize the photorefractive properties of the VSLT. The dominant contribution to PRD in LN and LT is the space-charge field induced by the balance of photogalvanic and drift currents.[11] To examine this effect more carefully we considered a simplified (linear, one-dimensional) constitutive relation for charge transport in the crystal:

$$\mathbf{J} = \sigma\mathbf{E} + \kappa I\hat{\mathbf{z}}, \tag{1}$$

where $\mathbf{J}$ is the current density in the crystal, σ is the conductivity, $\mathbf{E}$ is the space-charge field in the medium, κI is the photogalvanic response to an optical intensity I, and $\hat{\mathbf{z}}$ is a unit vector along the ferroelectric axis. At steady state ($J = 0$) the electric field is proportional to the ratio of the photogalvanic response to the conductivity. At high intensity the conductivity is dominated by photoconductivity, which we take as linear in intensity, i.e., $\sigma_{\mathrm{ph}} = \beta I$. Thus, the steady-state electric field can be characterized by a saturated space-charge field, $E_{\mathrm{sc}}\hat{\mathbf{z}} \rightarrow -\kappa/\beta\hat{\mathbf{z}}$.[12] This saturated space-charge field is a measure of the field induced by the photogalvanic current and is typical of the largest fields encountered even in more realistic three-dimensional geometries. Since the photoinduced change in the refractive index is created through the electro-optic effect, compositions with smaller saturated space-charge fields will exhibit less PRD.

Reducing the lithium deficiency found in congruent crystals can decrease E_{SC} by increasing the photoconductivity. In the most basic model of conduction in these crystals, the conductivity is proportional to the carrier lifetime in the medium, which should be inversely proportional to the density of deep traps in the crystal. Assuming that this density is proportional to the nonstoichiometry in congruent crystals, one would expect the conductivity to increase and the sensitivity to photorefractive damage to decrease by orders of magnitude in near-stoichiometric crystals.

To compare the improvement in E_{SC} for the VSLT relative to unmodified CLT, we measured the photoconductive and photogalvanic currents for a given light intensity. The use of a focused laser beam is necessary to reach the optical intensities typical of frequency-conversion interactions. To avoid pyroelectric currents between conventional electrodes that result from heating by absorption of the focused pump we used a modified liquid-electrolyte electric field poling apparatus, focusing the laser through a quartz window to illuminate the sample (Fig. 1). A picoammeter was used to measure the photoconductive and photogalvanic currents. The saturated space-charge field is then the ratio of the photogalvanic current to the photoconductive current multiplied by the applied field. With 0.5 W of 514.5-nm radiation focused to a 35-μm spot ($1/e^2$ intensity half-width), CLT and VSLT samples exhibited photogalvanic currents of 2.2×10^{-12} and 1.2×10^{-12} A, respectively. Photoconductive currents of 0.35×10^{-12} A for CLT and 1.5×10^{-12} A for VSLT were measured with applied fields of 200 and 20 V/cm, respectively. These values corresponded to E_{SC} values of 1270 ± 300 V/cm for CLT and 16 ± 4 V/cm for VSLT, a 75-fold reduction. We verified that this reduction makes possible a substantial improvement in PRD resistance by focusing 9 W of 514.5-nm z-polarized radiation to a 12-μm spot in a VSLT sample, corresponding to an intensity of 2 MW/cm^2, the maximum intensity used. No beam distortion was observed. This test showed at least a 100-fold improvement in the PRD resistance of VSLT over CLT, consistent with the expectations set by the deep-trap model.

Another important defect-related process that prevents efficient, high-power frequency conversion in the visible is GRIIRA. Although the process responsible for GRIIRA is not well understood, the sensitivity to GRIIRA appears to correlate with $\mathrm{Ta}_{\mathrm{Li}}^{4+}$ density.[1] As with PRD, improvements in stoichiometry can be expected to similarly improve GRIIRA resistance compared with that of CLT.

Photothermal common-path interferometry,[13] which permits measurement of the changes in the IR absorption in the presence of 532-nm radiation at parts-in-10^6 levels, was used to measure GRIIRA in VSLT and CLT. Two z-polarized pump beams, at wavelengths of 532 and 1064 nm, were x propagated for these measurements. In CLT, infrared absorption increased by 33% with 532-nm radiation intensities of only 320 W/cm^2. In VSLT an increase of 10% in the infrared absorption required an intensity of 32 kW/cm^2. This 100-fold reduction in sensitivity is comparable to the reduction in saturated space charge.

The 1-mm-thick VSLT crystals were periodically poled by well-developed electric field poling techniques.[14] Periodic electrodes were photolithographically patterned on the $+z$ face of the crystal, and an electric field was applied via a liquid electrolyte. The coercive fields of these crystals were found to be as low as 80 V/mm, corresponding to a 200-fold decrease compared with CLT.

Tests of nonlinear optical performance were performed with a 17-mm-long, 8-μm-period VSLT crystal designed for second-harmonic generation (SHG) of 532-nm radiation near room temperature. Shown as the inset in Fig. 2, the domain pattern was made

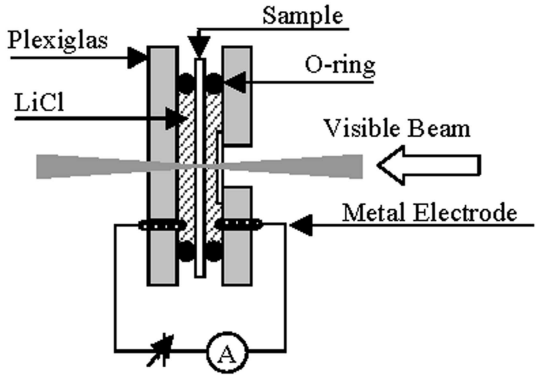

Fig. 1. Fixture for the measurements of the photogalvanic and photoconductive currents.

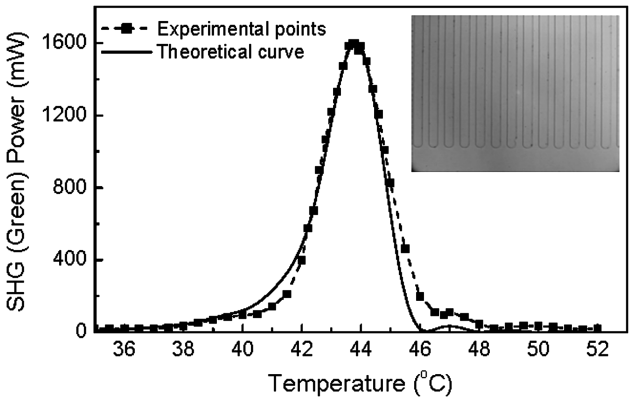

Fig. 2. Temperature tuning curve for SHG of 1.064-μm radiation in a 17-mm-long, 8-μm-period VSLT. The dependence is not a simple sinc^2 because of the near-confocal focusing of the pump beam. The close agreement between theory and experiment indicates the optical homogeneity of the VSLT crystal. Inset, 8-μm-period quasi-phase-matched grating made visible by etching in hydrofluoric acid.

visible by etching in hydrofluoric acid. When 18 W of single-frequency 1064-nm continuous-wave (cw) radiation was focused into the crystal, 1.6 W of 532-nm radiation was produced at a temperature of 43 °C, correspondingly to a normalized efficiency of 0.3%/W cm, compared with a theoretical value of approximately 1%/W cm, with the difference being consistent with the nonideal duty cycle of the quasi-phase-matched grating. Figure 2 shows experimental and theoretical tuning curves for the second-harmonic power as a function of temperature. The near-ideal tuning behavior indicates homogeneity of the refractive index of the crystal over the 17-mm length of the sample. To explore long-term aging effects we measured the second-harmonic power over a 1000-h interval, using a pulsed 1064-nm pump laser that delivers 150-ns pulses at a repetition rate of 100 kHz with an average power of 14 W. With 5 W of second-harmonic generation for 1000 h, the efficiency did not change measurably, indicating that the sample was stable for the duration of the test.

We have reported first-order, multiwatt, quasi-phase-matched SHG of 532-nm radiation in a periodically poled VSLT crystal. The tested crystal generated 1.6 W of cw green light and 5-W average power at a repetition rate of 100 kHz for 1000 h at an operating temperature of 43 °C. No damage to the crystal and no aging effects were observed during the experiments. VSLT crystals show high photoconductivity, a reduced saturated space-charge field, and no PRD at the maximum intensity used (2 MW/cm^2). These crystals also show improved resistance to GRIIRA, a Curie temperature of 693 °C, and what are to our knowledge the lowest reported coercive fields of 80 V/mm. VSLT appears to be suitable for efficient, high-power frequency conversion in the visible and infrared at near room temperature. With such low coercive fields it may be possible to pole thicker substrates and (or) achieve poling of rotated-cut materials for larger-area apertures for scaling to even higher powers and pulse energy.

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