

# Periodically poled vapor transport equilibrated lithium niobate for visible light generation

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## ABSTRACT

The ability to achieve high quality periodic poling in lithium niobate (LN) has allowed quasi-phase-matching to be used for second-order nonlinear optics, leading to experimental demonstration of efficient optical frequency generation throughout its wide transparency range (0.35-4.5  $\mu\text{m}$ ). Applications of congruent lithium niobate involving visible or ultraviolet wavelengths are limited to low power or high temperature operation due to the effects of photorefractive damage (PRD) and green-induced infrared absorption (GRIIRA). The standard methods of suppressing PRD include doping with 5 mol-% MgO or ZnO and varying crystal stoichiometry. More recent methods employ a combination of lower doping level and near-stoichiometric composition. We use vapor transport equilibration (VTE) and significantly lower MgO doping (<0.5% in the melt) to obtain near-stoichiometric PRD-resistant crystals with improved parameters for periodic poling compared to the commercially available 5% MgO-doped congruent crystals. An efficient process for periodic poling at room temperature using baked photoresist as a patterned dielectric on one crystal surface with LiCl-solution electrodes was developed for periods as short as 8.3 microns for 0.5% and 7 microns for 0.3% MgO-doped VTE:LN. The quality of periodic poling improves as the MgO concentration is lowered. Stable second harmonic generation of 1.3-W continuous-wave 532-nm radiation was observed near room temperature (43 degrees Celsius, as determined by the phase matching condition) with no sign of degradation in a 1.5-cm long crystal of 0.3-% MgO-doped VTE:LN periodically poled with a period of 7.06 microns.

**Keywords:** Nonlinear materials, lithium niobate, stoichiometric, VTE, photorefractive damage, periodic poling, SHG

## 1. INTRODUCTION

Ferroelectric materials such as lithium niobate (LN) and lithium tantalate (LT) play an important role in nonlinear optics. The ability to spatially modulate their second-order nonlinear coefficient via periodic poling allows their use for efficient second-order nonlinear mixing via quasi-phase-matching (QPM). In addition, they have large nonlinear optical coefficients, and their transparency range extends from the UV to the mid-infrared. Applications in the visible of the commonly grown and commercially available congruent lithium niobate (CLN) and lithium tantalate (CLT) are limited by photorefractive damage (PRD) and green-induced infrared absorption (GRIIRA).<sup>1</sup>

The two existing solutions for the PRD and GRIIRA problems in LN and LT are doping and stoichiometry control. In the first one, congruent crystals are doped with 5 mol-% or more MgO, ZnO or another appropriate oxide, leading to a decrease of PRD by nearly 3 orders of magnitude.<sup>2,3</sup> MgO-doped CLN (MgO:CLN) is commercially available with good optical quality. Generation of intermediate and high-power orange<sup>4</sup>, green<sup>5</sup>, blue<sup>6</sup> and UV<sup>7,8</sup> light by frequency doubling has been demonstrated recently using periodically-poled MgO:CLN. Compared to non-doped CLN, however, it has some disadvantages: it is harder to grow because of the high doping level; achieving high quality periodic poling is significantly more complicated; in regard to integrated-optics applications, annealed (APE) and reverse (RPE) proton exchanged waveguides in MgO:CLN are characterized by three times smaller conversion efficiency for second harmonic generation (SHG) due to details of the proton diffusion properties.

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The second approach to solving the PRD and GRIIRA problems is to use a combination of light or no doping and near-stoichiometric crystal composition. Near-stoichiometric LN (SLN) and LT (SLT) grown using the double crucible Czochralski growth<sup>9,10</sup> (DCG) method and the top seeded solution growth method<sup>1,11,12,13,14</sup> (TSSG) have become commercially available, (SLN usually doped with 1% MgO to improve their resistance to PRD and GRIIRA). Up to 4.4 W of green was recently generated in a periodically-poled SLT crystal<sup>15</sup>. In DCG- or TSSG- grown near-stoichiometric lithium niobate, only low-power (~ 1 mW or less) visible light generation has been demonstrated so far<sup>16</sup>. Although DCG and TSSG SLN with 1% MgO are easier to periodically pole than 5% MgO:CLN and promising for the development of more efficient PRD-resistant APE and RPE waveguides, they are even harder to grow.

The vapor transport equilibration (VTE) method<sup>17</sup> allows conversion of wafers of easy-to-grow commercially available CLN (CLT) to stoichiometric or near-stoichiometric ones. The crystalline wafers are enclosed together with lithium rich two-phase LN (LT) powder at high temperature to allow equilibration via vapor-phase transport of Li<sub>2</sub>O from the powder to the crystal and solid-state diffusion. The process self-terminates when the crystal composition reaches the phase boundary of the single phase region, which is very close to the stoichiometric ratio of 50:50 Li:Nb(Ta). VTE naturally lends itself to the fabrication of homogenous near-stoichiometric crystals and does not require precise control of powder composition or temperature to achieve reproducible results. VTE has been demonstrated to produce PRD-resistant SLT.<sup>18</sup> A VTE-SLT sample was periodically poled with a period of 8  $\mu\text{m}$  and used in SHG of 5 W of 532-nm green light for 1000 hours at a QPM temperature of 43 °C without any observed damage or efficiency degradation.<sup>18</sup> The GRIIRA effect was shown to be 100 times smaller than in CLT.

Second harmonic generation of 532-nm green light in periodically poled lightly-MgO-doped VTE-SLN has been reported<sup>19</sup> at a power level (120  $\mu\text{W}$ ) too low to attest for significant resistance to PRD. More recently, Chen et al<sup>20</sup> demonstrated SHG of 43 mW of 400-nm violet light by third-order quasi-phase matching in periodically poled 1.8 mol-% MgO-doped VTE SLN with a period of 7.8  $\mu\text{m}$ . PRD-resistant 1% MgO-doped SLN fabricated by VTE<sup>21</sup> was also demonstrated. Our recent studies of VTE on 1 and 5% MgO:LN revealed the appearance of light scattering defects in the crystal toward the end of the VTE process. We solved that problem by developing PRD-resistant VTE- MgO:SLN with lower doping (0.3 and 0.5 mol%)<sup>22</sup>. Scattering defects were never observed in 0.3- % and could be suppressed in 0.5- % MgO:SLN by proper design of the VTE process. The PRD-resistance of the above compositions was confirmed by measuring the space-charge field caused by high-intensity green radiation, as well as by beam-fanning experiments. The GRIIRA resistance of a PRD-resistant 0.3-% MgO:SLN sample was tested via common-path photothermal interferometry. No observable GRIIRA effect was generated by a 0.5-W, 80- $\mu\text{m}$  diameter green beam at 514 nm. Periodic poling with periods as short as 8-10  $\mu\text{m}$  was also reported in the same work, reaching the range of periods (4-12  $\mu\text{m}$ ) necessary for SHG of visible light. Lower doping concentration correlated with better quality of periodic poling.

In this paper we describe further advances in short-pitch periodic poling of 0.3- and 0.5- mol% VTE-MgO:SLN that allowed high-quality poling at periods of 9.6 and 8.3  $\mu\text{m}$  appropriate for SHG of 589- and 560-nm yellow-orange and yellow-green radiation, respectively. In addition, poling at a period of 7  $\mu\text{m}$  period is described. It allowed the fabrication of a sample for SHG of 532-nm green radiation. Using a 10-W CW Nd:YAG laser at 1.064  $\mu\text{m}$ , stable room-temperature SHG of 1.3 W of green was obtained.

## 2. FABRICATION OF THE PERIODICALLY-POLED VTE-SLN CRYSTALS

The MgO:SLN was fabricated by performing VTE on CLN substrates with 0.3 and 0.5 mol-% MgO, as described in ref. 22. The equilibration of the samples and wafers used in the experiments with periodic poling was performed in the lithium-rich powder at temperatures in the range 1090 to 1050 °C. Activation energy of 2.8 eV was assumed during conversion of the equilibration time at a given temperature to equivalent time at 1050 °C. The 0.5-% samples were equilibrated for ~350 hours at 1050 °C, while the 0.3-% samples were equilibrated for ~700 hours at 1050 °C. The thickness of the samples prior to equilibration was ~0.52 mm. After the equilibration, the samples were polished on both sides. The final thickness of the samples was reduced to ~0.3 mm, to facilitate the short-pitch periodic poling.

Some information relevant to the domain inversion process was determined without using a periodic pattern. The coercive field was measured for 0.3-% VTE-MgO:SLN by taking hysteresis loops. A triangular voltage waveform with a period of 500 s was applied to the crystal using LiCl liquid electrodes. The estimated coercive field for several samples was in the range between 2 and 2.4 kV/mm. Similar loops for a sample of 5-% MgO:CLN demonstrated a coercive field ranging between 7.4 kV/mm during the first loop and 5.3 kV/mm during the second and third loops. Important information about the kinetics of domain inversion was obtained by measuring the rate of domain wall

movement as a function of applied electric field. We used the method employed by Nakamura et al<sup>23</sup>. The data on domain wall velocity versus applied field is represented by the 'x' symbols on Figure 1. The black line is the corresponding dependence for 5 mol-% MgO:CLN determined in ref. 23. The circles represent a few points measured for groups of domains that merged during application of the domain-inversion voltage. In general, the merging of domains allows for a significant increase of domain wall velocity by as much as 2 orders of magnitude. In order to avoid domain merging, special care had to be taken in choosing the length of the voltage pulse for electric fields above 2.5 kV/mm.

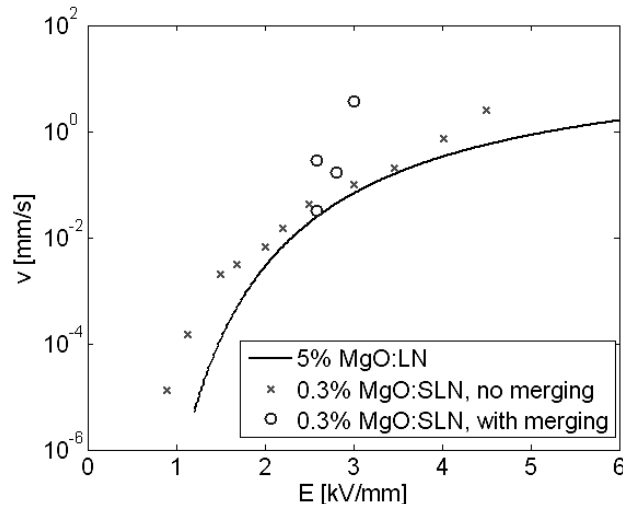
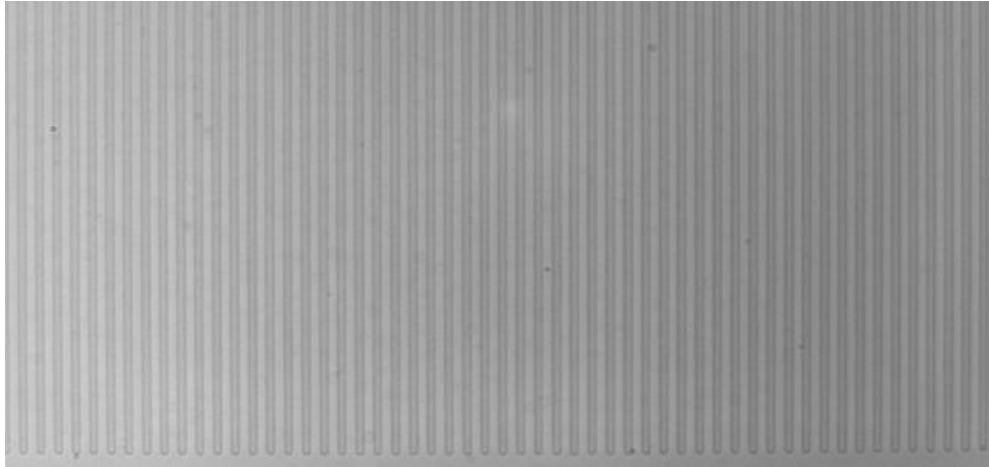


Figure 1. Domain wall velocity as a function of the applied electric field for different compositions of MgO:LiNbO<sub>3</sub>

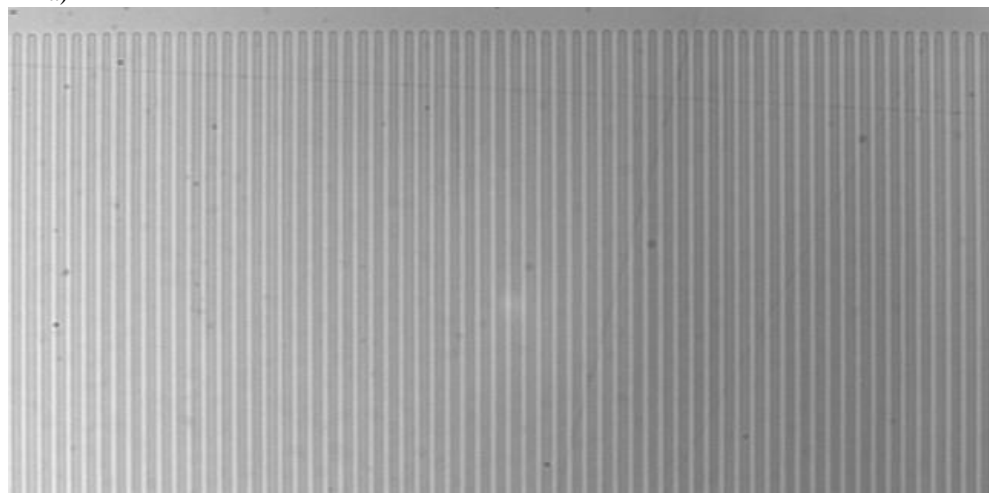
The coercive field in MgO:LiNbO<sub>3</sub> is determined primarily by the field necessary for achieving nucleation of domains with inverted polarization. Therefore, achieving nucleation for periodic poling requires that the electric field near the periodic electrodes be at least as large as the coercive field. As can be seen from fig. 1, the domain wall velocity is appreciable for both 0.3-% and 5-% MgO:LiNbO<sub>3</sub> at electric fields significantly smaller than their respective coercive fields of 2 and 5-7 kV/mm, respectively. This poses serious difficulty in obtaining good periodic patterns for MgO:LiNbO<sub>3</sub>. In non-doped LiNbO<sub>3</sub>, the field necessary for nucleation is only a few percent larger than the field necessary for domain-wall movement (ref. 23). Intuitively, it could be expected that lower doping levels would allow easier periodic poling. This is in fact experimentally observed (ref. 22).

For periodic poling, single-step photolithography was carried out using Shipley 1818 photoresist. The photoresist was spun at a slow rate in order to form as thick a layer as possible. After the pattern was lithographically transferred onto the photoresist, a hard bake followed (temperature ranging between 130 and 170 °C, lower temperature requiring longer bake time). After the hard bake, the thickness of the photoresist was ~3.5 μm. The hard-baked resist on the +z side of the wafer was used as an insulator during the electric-field poling process. The trenches in the photoresist were contacts for a liquid-electrolyte electrode consisting of saturated solution of LiCl. A series of short (~0.1-ms) high-voltage pulses (~ 1.9 kV/mm for 0.3-% and ~2.4 kV/mm for 0.5-% MgO:SLN) was applied for poling until the appropriate amount of charge was delivered. The fringe fields near the electrode edges<sup>24</sup> allowed local enhancement of the electric field adequate for domain nucleation. The polarization inversion was allowed to penetrate throughout the substrate thickness. Thinner substrates exhibited significantly better quality of periodic poling than thicker substrates.

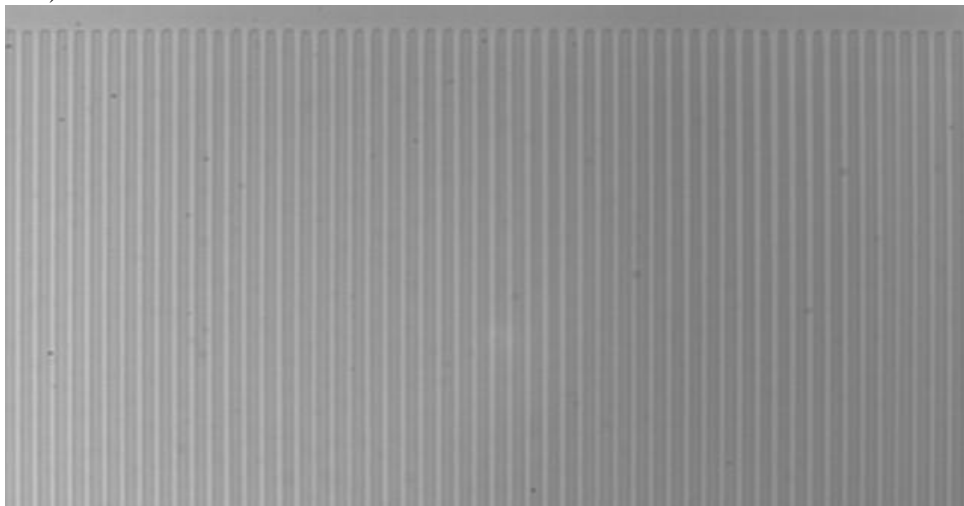
Figure 2 shows periodic poling of 0.28-mm thick MgO:SLN at periods appropriate of yellow-light generation. The periodic pattern has been revealed by etching in 50-% hydrofluoric acid. With our poling method, although during the poling process the undesirable merging of domains would normally originate near the side opposite to the periodic electrodes, at the end the two sides of the crystal have very similar patterns. The pattern on the opposite side of the electrodes is shown in the images. A 0.3-% crystal with a period of 9.6 μm for room-temperature first-order SHG of 589 nm light is displayed on fig.2 a), while a period of 8.3 μm for SHG of 560-nm yellow-green light in a different region of the same crystal is shown on fig. 2 b). Figure 2 c) contains an image of a 0.5-% crystal poled at 9.7 μm. The duty cycle is near 50 % in fig. 2 a), while it is between 60 and 70% in fig. 2 b) and c). The periodic poling is of excellent quality without any defects in the pattern.



a)



b)



c)

Figure 2. Periodic poling of 0.3- and 0.5- MgO:SLN.  
a) 0.3-%, period=9.6  $\mu\text{m}$ ; b) 0.3-%, period=8.22  $\mu\text{m}$ ; c) 0.5-%, period=9.7  $\mu\text{m}$ .

Periodic poling of a 0.33-mm thick 0.3-% MgO:SLN at a period of 7  $\mu\text{m}$  is shown on Figure 3. The three images in the figure represent different locations along two patterned stripes, one of which was used in the experiments on SHG of 532-nm green light described in the following section. The poling pattern is of variable quality, but non-the-less allowed the generation of more than 1.3 W of green power.

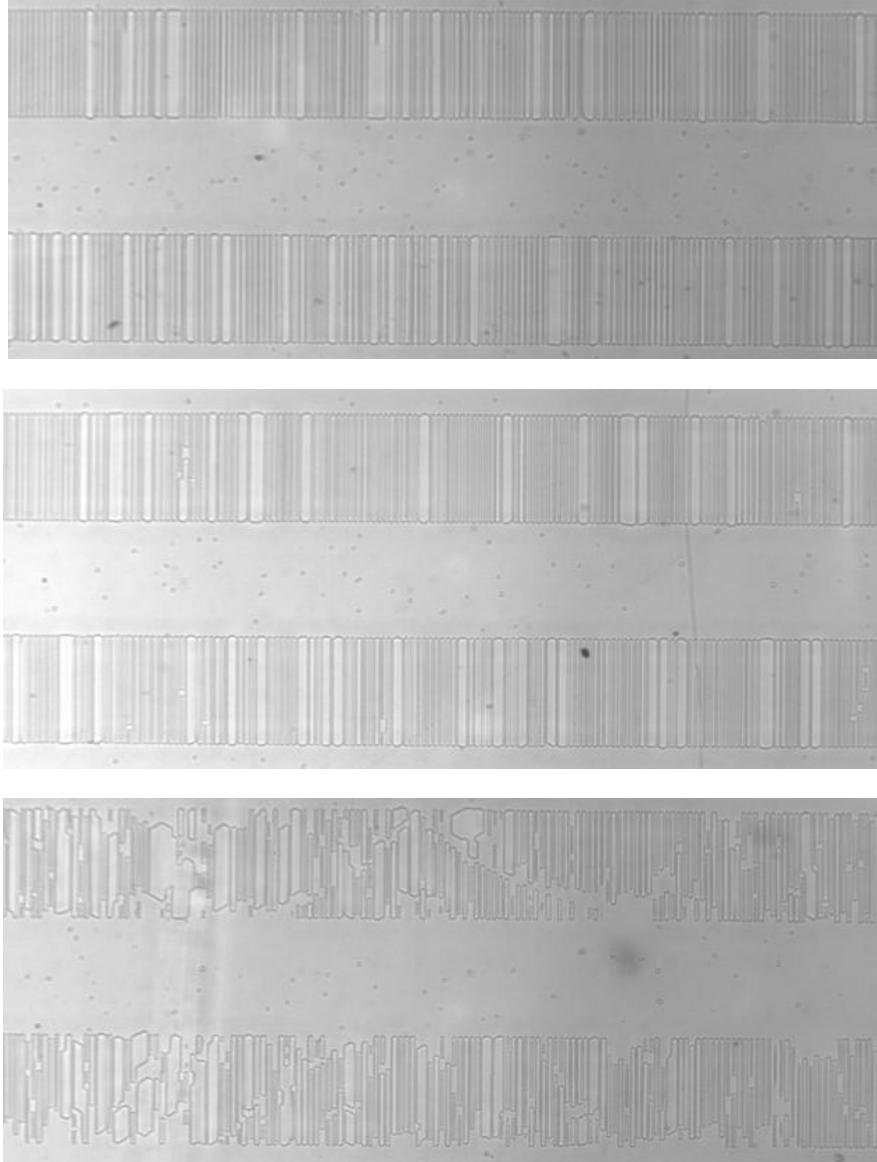


Figure 3. Periodic poling of three different regions along the patterned stripes used in the SHG of 1.3 W of green in 0.3-% MgO:SLN. The sample thickness is 0.33 mm. The period is 7  $\mu\text{m}$ .

Domain inversion of much better quality at a period of 7  $\mu\text{m}$  was obtained on small-area poling of a 0.28-mm thick substrate (fig. 4). We are working to extend poling of such quality to longer samples so that high-efficiency SHG of 532-nm green light can be demonstrated in 0.3-% MgO:SLN.

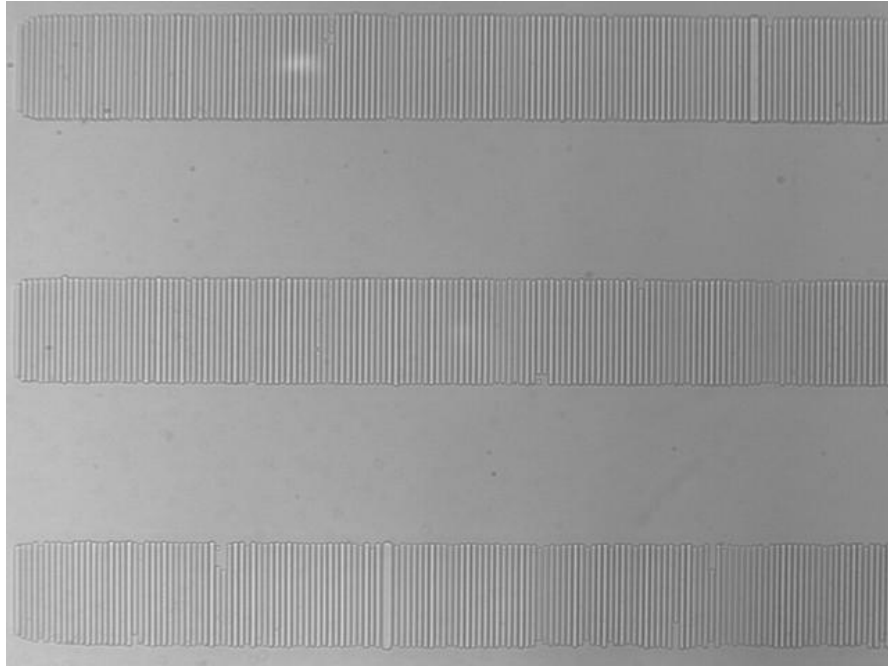


Figure 4. Good-quality periodic poling of 0.3-% MgO:SLN. The sample thickness is 0.28 mm. The period is 7  $\mu\text{m}$ .

At present, domain reversal with this simple method allows periodic poling at periods of about 7  $\mu\text{m}$  for 0.3-% MgO:SLN and 8.3  $\mu\text{m}$  for 0.5-% MgO:SLN with quality adequate for useful frequency conversion.

### 3. SHG OF HIGH-POWER CW GREEN IN 0.3-% DOPED VTE- SLN

The 1.5-cm long sample with periodic poling shown on Figure 3 was used in SHG of 532-nm green light. To avoid absorption due to chemical reduction caused by the VTE and the periodic poling processes, the crystal was annealed for 22 hours at 340  $^{\circ}\text{C}$  in air. After polishing the input and output faces, the device was mounted in an aluminum oven for temperature control. A thermo-electric cooler was used to stabilize the crystal temperature with a precision better than 0.1  $^{\circ}\text{C}$ . A 10-W continuous-wave Nd:YAG laser at 1064 nm was used as a pump. The crystal had no anti-reflection coatings, so a maximum of 8.6 W of pump power was available for SHG after the input facet. Near-optimum focusing for the 1.5-cm length was used. SHG output of  $1.12 \pm 0.02$  W was obtained at a phase-matching temperature of 43  $^{\circ}\text{C}$ , indicating that 1.3 W of green was generated inside the crystal. The small SHG power fluctuation was due to fluctuation of the pump laser. The green output power was stable and limited by the available pump power and the device efficiency determined by the quality of the periodic pattern. No signs of crystal degradation or instability were observed. The experiment was ceased after an hour of stable operation due to availability of the pump laser. Higher power green generation should be possible with a more powerful pump. The normalized SHG efficiency should be increased more than a factor of two by using high-quality periodic poling (as shown in Figure 4).

### 4. CONCLUSION

Low-doping level MgO:SLN resistant to photorefractive damage and GRIIRA was fabricated by vapor-transport equilibration. Periodic poling of good quality was obtained at periods appropriate for second harmonic generation of light in the green and yellow portion of the visible spectrum. Stable generation of 1.3 W of continuous-wave 532-nm green was demonstrated.

We are continuing our efforts on the generation of CW green light in VTE-SLN and expect to demonstrate significantly higher power at 532 nm in the near future.

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