Laser Heated Pedestal Growth of Potassium Lithium Niobate for
UV Generation

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ABSTRACT

Potassium lithium niobate (KLN), a nonlinear optical material with high nonlinearity and other desirable
properties, has the potential to improve the performance and reduce the cost of blue and UV lasers. KLN crystals
have not entered the commercial mainstream because it is impossible to grow them reproducibly by conventional
techniques. We have developed a proprietary process based on the laser heated pedestal growth (LHPG) technique
that eliminates technical barriers to manufacturing KLN crystals.

This paper describes the LHPG method of KLN crystal growth including improvements in crystal uniformity and
transparency, and our latest harmonic generation results in the UV.

1. INTRODUCTION

Potassium Lithium Niobate is an attractive ferroelectric crystal for nonlinear optical applications. Laser
manufacturers could improve the performance and reduce the cost of blue and UV lasers by incorporating potassium
lithium niobate (KLN) as a frequency doubling crystal in their systems. KLN has a number of highly desirable
optical properties:

- KLN crystals offer very high non-linear optical coefficients which should transfer into very high
  conversion efficiency;

- KLN crystals show no photochromic damage;

- KLN crystals are non-hygroscopic;

- KLN crystals with the formula k3Li2... can be compositionally adjusted over the range 0<x<0.3 allowing
  noncritical phase matching at a wavelength between 760 and 970 nm and second harmonic generation from
  380 to 485 nm.

Table 1: Characteristics of Three Commercially Available Frequency Doubling Crystals compared with KLN

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Potassium Lithium Niobate (KLN) crystals have not entered the commercial mainstream because it is difficult to
grow them reproducibly with the required performance and cost by conventional methods such as Czochralski or top
seeded solution growth. We are using the Laser Heated Pedestal Growth

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technique that eliminates the technical barriers to growing potassium lithium niobate crystals for UV generation. Under proper conditions the ultimate crystal composition is defined by the starting material and a very rapid liquid to solid transition. We have grown such crystals and our method and initial results are reported here.

2. EXPERIMENTAL PROCEDURES

1. Crystal Growth - The starting materials were made by using 99.998% k2CO3, 99.999% Li2CO3 and 99.999% Nb2O5. The chemicals were thoroughly mixed by grinding them in an agate mortar and then a SPEX mixer. This mixture was then pressed into pellets and then reacted in air at 900 degrees Celsius for hours. After reaction the pellets were ground to powders, pressed into pellets again and sintered at 900 degrees Celsius for hours. Each pellet was then cut into ceramic rods of 1.5 mm square with length of 25 mm. The ceramic rods are used as feedstock in the LHPG system. The seed is made of a single crystal oriented along the x axis. Crystals using precursor rods consisting of k2OLi2O and Nb2O5 in proportions corresponding to x = 0.2 and x = 0.06 were grown with a pull rate of mm/hour, a feed rate of mm/hour and watts of laser power. After growth the crystals were annealed at 350 degrees Celsius for eight hours.

2. Absorption Measurements - Transmission measurements were performed by using a Spectrophotometer containing two identical slits in the reference and the sample planes. Each slit was slightly smaller than the cross section of the crystals when viewed from the side. The sample was put over the slit in the sample position after the zero procedure on the instrument was run. Despite the small size of our samples, this allowed us to monitor the difference in UV edge for each crystal composition.

3. Harmonic Generation - Second harmonic generation was measured by focusing a tunable 1.5 watt CW Ti Sapphire laser along the length of the crystals. The Ti sapphire wavelength was measured using an optical spectrum analyzer. The generated harmonic beam was separated from the fundamental using a dichroic mirror and a filter.

3. RESULTS and DISCUSSION

1. Crystal Growth - Several KLN crystals of composition corresponding to x= 0.2 and x=0.06 were grown using our LHPG setup with length approximately 20mm with a diameter of 1 mm (figure 1). Under the microscope the crystals appeared clear, transparent and exempt from fractures, bubbles and inclusions. Figure 2 shows the cross section of a mounted and polished crystal grown in the (100) direction. Growth rates for both compositions varied between mm/hour. Changes in growth rates did not affect the visual quality of the crystals upon inspection. However, for any chosen growth rate the temperature gradients during growth had to be carefully controlled. Several experiments yielded cracked crystals when temperature gradients were too high, and with gradients too low the crystals would grow polycrystalline. Growth rates and temperature gradients were chosen in light of the nature of KLN. Figure 3 shows an isoplethic cross-section of the ternary phase diagram for KLN, assuming the concentration of potassium is 30 mol %. In growth by the Czochralski or top seeded solution growth the liquid cools from the original temperature (t1) to the solidification temperature (T2) and begins to crystallize. At T2, the crystal has a higher niobium concentration than the liquid surrounding it. That liquid solidifies at a lower temperature (T3) than the original liquid. The crystal continues to grow as the temperature drops to T3. But at T3, the liquid surrounding the crystal has an even lower niobium concentration and an even lower solidification temperature (T4) etc. The composition of the crystal changes continuously as it grows. Before the crystal grows to a technologically useful length, the material reaches the lower left quadrant of its phase diagram, which contains only regions where
KLN cannot form at all. The small KLN crystals that grow are likely to crack because of their compositional inhomogeneity. There problems occur in the Czochralski technique because the crystal grows so slowly (about 200 microns per hour) that thermodynamic factors, rather than kinetic factors, dominate the growth process. Laser Heated Pedestal Growth is a better technique for growing KLN because the crystal grows so fast (up to 5 cm/hour) that kinetics rather than thermodynamics govern the growth process. In this case the melt and the crystal maintain the same composition and the composition remains the same throughout the volume of the crystal. Therefore, our choice of growth parameters was based on a compromise between crystal quality, crystal homogeneity and crystal compositional uniformity.

2. Absorption Measurements - The UV absorption edges of the two crystal compositions $x=0.2$ and $x=0.06$ are compared in Figure 4. Transmission spectra were measured transversed to the growth dimension and not corrected for reflection or other insertion losses. Consistent with previous reports the UV edge shifts to shorter wavelengths with higher Li fraction (smaller $x$). The same phenomenon is observed in Lithium Niobate and Lithium tantalate where the UV edge shifts to shorter wavelengths as composition shifts from congruency to stoichiometry.

3. Harmonic Generation - Figure 5 shows the non-critical phase matching wavelength as a function of composition. For $x=0.06$ published Sellmeier coefficients indicate the non-critical phase matching wavelength should be about 795 nm. However, our experiment with a 3 mm long sample showed no well-defined non-critical phase matching wavelength. Instead second harmonic generation was observed over the range of 770 - 935 nm with a broad maximum of approximately 835 nm. This result can be attributed to slight compositional variations and/or strain within the cross section of the crystal. This can be explained by the following:

1) the non critical phase matching wavelength is rather sensitive to crystal composition and there is some uncertainty regarding the shape of the KLN phase diagram near the stoichiometry;

2) the growth rates are too slow;

3) the annealing procedure is not appropriate;

4) the temperature gradients are not high enough to maintain the polarization of the crystal in one direction;

5) we need to compensate for potassium and lithium evaporation from the melt zone by adjusting the temperature of the melt.

When viewed through the polished ends the samples exhibit some optical distortion which could be an indication of a multi-domain structure or strain. When we substitute a 1.7 watt 5 pico-second 80 megahertz mode locked Ti sapphire laser as the excitation source we observe second harmonic generation over a similar wavelength range. Using a 5 mm long crystal we measure about 1 percent harmonic conversion at 820 nm. During all these experiments no optical damage was observed in any of the samples.

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