Journal of Crystal Growth 352 (2012) 59–62

Contents lists available at SciVerse ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Laser heated pedestal growth of potassium lithium niobate for UV generation

Gisele Maxwell [a,*], Alan Petersen [b], Dylan Dalton [a], Bennett Ponting [a]

[a] Shasta Crystals Inc., 5206 Industrial Way, Anderson, CA 96007, USA
[b] Newport Spectra-Physics, 3635 Peterson Way, Santa Clara, CA 95054, USA

ARTICLE INFO

Available online 23 January 2012

Keywords:
A1. Solid solutions
A2. Laser heated pedestal growth
B1. Niobates
B2. Nonlinear optic materials
B3. Solid state lasers

ABSTRACT

Potassium lithium niobate (KLN) is a nonlinear optical material with a high nonlinearity. It has the potential to improve the performance and reduce the cost of blue and UV lasers. KLN crystals are not commercially viable because growth by traditional techniques is not possible. In an effort to develop commercially viable KLN, single crystals of the material were grown by the laser heated pedestal growth method (LHPG) with compositions of $x=0.02$, 0.06 and 0.2 following $K_3Li_{2-x}Nb_{5+x}O_{15+2x}$. Noncritical phase matching at 20 °C for previously unreported compositions of $x=0.02$ and 0.06 was measured at 795 nm and 805 nm, respectively. Overall, the results suggest that single crystal KLN can be used for SHG into the UV region of the spectrum and can be developed into a commercially viable nonlinear optical material.

1. Introduction

Economically viable blue and UV lasers have potential applications ranging from scientific research and instrumentation to neuroscience, DNA sequencing, commercial printing and display devices. However, the blue and UV regions of the electromagnetic spectrum have been challenging regions for laser generation. Using the second harmonic generation (SHG) properties of nonlinear crystals in combination with IR lasers would be a promising cost-effective approach if commercially viable nonlinear crystals with the required properties where available. Potassium lithium niobate (KLN) is a strong candidate to realize these potential applications. It has a high non-linear optical coefficient of 12 pm/V [1], a transparency range of 0.35 to 5 μm and a damage threshold of 0.6×10^{-12} W/m^2 in CW regime. Additionally, it does not exhibit photochromic damage (gray tracking) [2] and it is non-hygroscopic.

However, traditional melt growth of KLN is complicated because it is not congruently melting [2,3], as seen in Fig. 1. With traditional growth methods the composition of the grown crystal continuously changes following the solidus line from the starting composition down to a composition with phase separation of the solid solution and Li_3NbO_4. This is perhaps the biggest disadvantage of KLN, but it leads to one of its greatest assets. KLN forms a solid solution along the 30 mol% K_2O isopleth which can be used to compositionally tune the wavelength of SHG. The KLN solid solution follows $K_3Li_{2-x}Nb_{5+x}O_{15+2x}$. The noncritical phase matching (NCPM) shifts to shorter wavelengths for decreasing x. Though there is still discussion over the exact nature of the phase diagram [4,5]. Additionally, the composition space below $x=0.1$ has not been reported [6]. The Sellmeier coefficients indicate noncritical phase matching of 762 nm for $x=0$ at room temperature (795 nm for $x=0.06$) [6,7].

To overcome the growth complications of KLN we have employed the laser heated pedestal growth (LHPG) method to grow KLN single crystals with compositions ranging from $x=0.2$ down to $x=0.02$. LHPG has two advantages that enable the technique to be used for the growth of KLN: 1) high thermal gradients and 2) the composition of the melt is continuously updated with new material by the feed rod. With high thermal gradients kinetic forces, rather than thermodynamic forces, dominated the growth process. Essentially, the crystal is quenched through the liquid–solid solution phase preventing segregation. Additionally, because the composition of the melt is continuously updated, segregation of one constituent into the melt is not thermodynamically favorable.

In this work we report on LHPG growth of KLN down to compositions of $x=0.02$, a region of the phase diagram that has not previously been reported.

2. Procedure

2.1. Crystal growth

Three batches of powders with x values of 0.02, 0.06 and 0.2 were mixed following $K_3Li_{2-x}Nb_{5+x}O_{15+2x}$ from 99.999% pure Li_2CO_3 and Nb_2O_5 and 99.998% pure K_2CO_3 source materials.

* Corresponding author. Tel.: +1 530 378 0395.
E-mail address: gisele.maxwell@gmail.com (G. Maxwell).

0022-0248/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2012.01.022

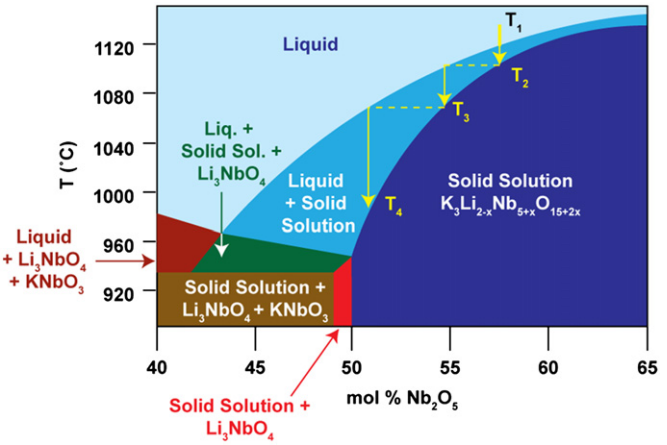

Fig. 1. KLN phased diagram for the 30 mol% K_2O isopleth and 40 to 65 mol% Nb_2O_5. The region from 50 to 65 mol% Nb_2O_5 forms a solid solution.

The powders were mixed by grinding in an agate mortar and subsequent agate-ball milling. The milled powders were pressed into 1 in diameter pellets and reacted in air at 900 °C for 24 h. The reacted pellets were ground and milled. The reacted powders were again pressed into 1 in diameter pellets and sintered at 900 °C for 8 h. The pellets were cut into ceramic rods 1.5 mm square by 25 mm long.

The ceramic rods were used as feed-stock in laser heated pedestal growth (LHPG) of the single crystal KLN. Single crystal seeds oriented along *x*-axis were employed to initiate growth. Growth rates ranged from 20 to 40 mm/h with a feed rate of 9 mm/h and 13 W of laser power. The crystals were subsequently annealed for 8 h at 350 °C.

2.2. Characterization

Transmission measurements were made using a spectrophotometer (Perkin Elmer Lambda 900). The entrance and emission slits were set equal to one another and smaller than the diameter of the crystals. The instrument was zeroed before each sample measurement.

Second harmonic generation for crystals with $x=0.06$ was measured by focusing a tunable 1.5 W CW Ti sapphire (SP3900 from Spectra Physics) laser along the length of the crystals. The Ti sapphire wavelength was measured using an optical spectrum analyzer. The generated second harmonic beam was distinguished from the fundamental beam using a dichroic mirror and filter.

Second harmonic generation for crystals with $x=0.02$ was measured by focusing an 808 nm 200 mW CW diode laser from CrystaLaser along the length of the crystals. The generated second harmonic beam was distinguished from the fundamental beam using a bandpass filter. Intensity of the generated and fundamental beams were detected with photo diodes. Measurement data was recorded and conversion efficiency was calculated using Matlab.

3. Results and discussion

3.1. Crystal growth

KLN crystals with compositions corresponding to $x=0.02$, 0.06 and 0.2 where grown along the *x*-axis to lengths around 20 mm. The morphologies of the grown crystals (Fig. 2a) were inspected via optical microscopy. The crystals were clear, transparent and free of fractures, bubbles and inclusions. The cross-section of a polished crystal is shown in Fig. 2b. The visual quality of the crystals did not vary over the range of growth rates attempted (20–40 mm/h). However, regardless of the growth rate, the temperature gradients had to be carefully controlled. Excessive temperature gradients led to cracked crystals and gradients too low caused the growth to turn polycrystalline. The specific growth rates and temperature gradients where chosen in light of the nature of the KLN phase diagram for 30 mol% K_2O.

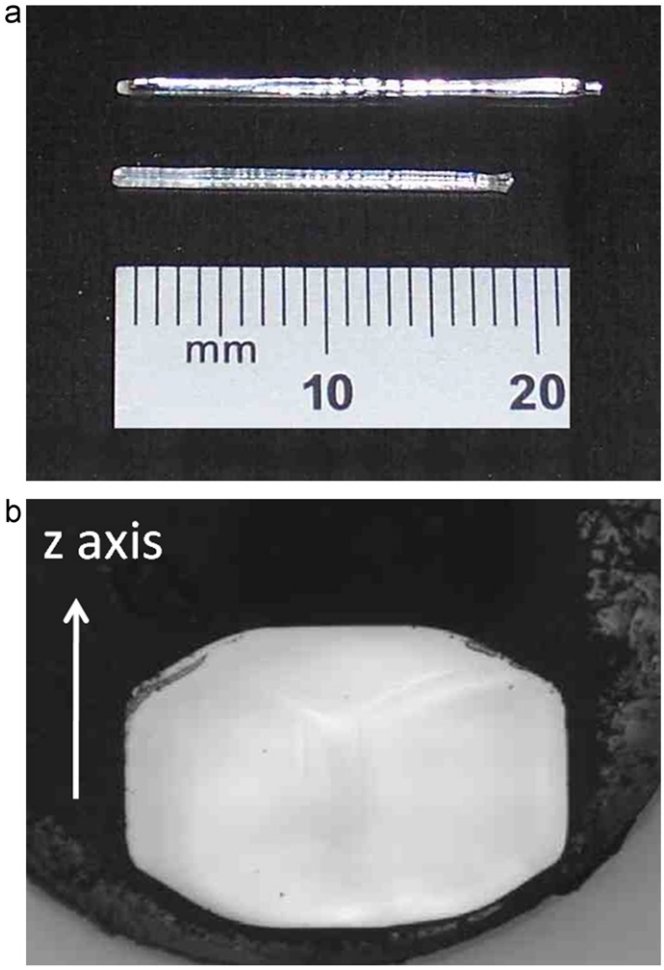

Fig. 2. (a) Selected KLN crystals grown along the *x*-axis and (b) a polished cross-section with the *z*-axis labeled.

3.2. Transmission

Transmission measurements for KLN crystals with *x* values of 0.06 and 0.2 are shown in Fig. 3. As the value of *x* is decreased (decreasing Nb and increasing Li) the UV edge shifts to shorter wavelengths, which is consistent with previous reports [8]. This is a promising trend as the SHG moves to shorter wavelengths so does the UV absorption edge, which suggests that the crystal will not absorb the generated light and will exhibit efficient SHG. The observed UV shift follows similar shifts observed in lithium niobate and lithium tantalate where the UV edge shifts to shorter wavelengths as the composition shifts from congruency to stoichiometry.

3.3. Second harmonic generation

SHG results for $x=0.02$ and 0.06 are shown in Figs. 4 and 5, respectfully. For $x=0.02$, two SHG peaks were observed, a primary