Journal of Korean Association of Crystal Growth
Vol. 5, No. 2 (1995) 94-99

Second harmonic generation (SHG) properties of potassium lithium niobate crystals grown by μ-PD method

Dae-Ho Yoon and Tsuguo Fukuda*
Department of Materials Science and Technology, Faculty of Engineering, Iwate University, Morioka 020, Japan
**Institute for Materials Research, Tohoku University, Sendai 980, Japan*

μ-PD법에 의해 육성한 KLN단결정의 제2고조파 발생 (SHG) 특성

윤대호, 福田承生*
岩手대학 공학부 재료물성공학과, 盛岡 020, 일본
*東北대학 금속재료연구소, 仙台 980, 일본

Abstract Potassium lithium niobate (KLN) crystals, grown by the micro pulling down (μ-PD) method, have been considered on the interchange between incongruent melt composition and second harmonic generation (SHG) properties because of the sensitive interaction. Correlation between the composition of crystals and the wavelength of SHG applications from ultra-violet to green region was found. Also, the μ-PD KLN crystals showed a homogeneity of noncritical phase matching and an excellent SHG property which is converted to blue laser light with half wavelength by the red irradiation.

요 약 μ-PD법에 의해 육성한 KLN 단결정은 적색 레이저를 이용한 제2고조파 발생 (SHG) 특성 평가에 의해 noncritical phase-matching(NCPM) 파장의 균일성과 우수한 온도 특성을 갖고 있음을 확인하였다. 또한 융액의 조성을 변화시키면서 성장된 결정의 NCPM 파장 측정에 의해 조성과 SHG 특성 사이에는 민감한 상호관계가 있음을 알 수 있었다. 이로부터 원료의 조성제어를 통한 μ-PD KLN은 청색에서 녹색파장에 걸치는 넓은 범위에서의

선택적인 SHG 응용이 기대된다.

The recent developments of nonlinear optical materials are important steps toward applications in the field of blue and green second harmonic generation (SHG). The growth of tungsten bronze crystals such as $Sr_{0.6}Ba_{0.4}Nb_2O_6$, $Ba_2NaNb_5O_{15}$, $K_3Li_2Nb_{5-x}Ta_xO_{15}$, and $K_3Li_2Nb_5O_{15}$ has been of considerable interest for many years [1-3] because of the unique advantages of bronze crystals which possess extraordinary large transverse and longitudinal electro-optic coefficients. However, growth of these crystals is of extreme difficulty because of problems, such as sample cracking during the transition from the paraelectric to the ferroelectric phase.

Potassium lithium niobate, $K_3Li_{2-x}Nb_{5+x}O_{15+2x}$ (KLN), has been recognized as a potentially useful material for nonlinear optical applications [4,5], both because it is remarkably stable under intense laser radiation, and because of its large electro-optical and nonlinear optical coefficients. Recently, significant advances in efficient compact diode-pumped solid state laser sources have been realized with this material [6]. However, KLN is difficult to grow due to the formation of cracks and the composition change by the conventional crystal growth methods [7,8]. Even though KLN has the sensitive interaction between the chemical composition and the nonlinear optical properties [9], few reports have been studied this correlationship.

We have investigated the growth of micro single crystals by the micro-pulling down (μ-PD) method from an incongruent melt [10,11]. Very successful second harmonic generation (SHG) of blue light has been also obtained in KLN crystals [11]. However, nonlinear optical properties which is influenced by compositional variations are not described. This paper is focused on the SHG properties of μ-PD KLN crystals, which are related to composition and compositional homogeneity, with consideration of the consequences of an incongruent melt.

The 30 % K_2O section of the phase diagram for the K_2O-Li_2O-Nb_2O_5 system [9], extending between 40 % and 63 % Nb_2O_5, is shown in Fig. 1. From the phase diagram of KLN can be seen, one of the main problems is composition changes along the growth axis, which is caused to crack, during growth because of the segregation phenomenon along the solidus line.

To investigate the growth of crack-free KLN single crystals with homogeneous compositions, we have applied by μ-PD method. The starting compositions have been used between $-0.6 \leqq x \leqq 0.5$ (in $K_3Li_{2-x}Nb_{5+x}O_{15+2x}$), scaled before sintering. The μ-PD method for small diameter crystal growth is characterized by extruding thin single crystals from a micro nozzle at the bottom of a crucible. Using the micro nozzle at the crucible bottom, crystals with constant diameter similar to that of the capil-

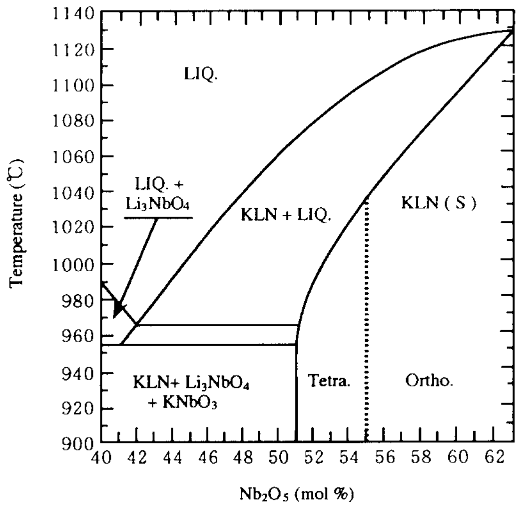

Fig. 1. The 30 mol% K_2O section of the phase diagram of the K_2O-Li_2O-Nb_2O_5 system.

lary can be easily produced.

Crack-free KLN crystals have been grown through the micro nozzle at the crucible bottom to form a micro single crystal (rod shape) with a cross section not more than 1 mm in diameter and a length of 150 mm. The habit of such KLN crystals is near to a linear needle, suitable for intensification of laser beams.

There is a close relation between the SHG properties and the composition of KLN crystals. Also, the homogeneity of crystal composition has a direct influence on the optical quality. The a-oriented KLN single crystals are properly oriented for noncritically phase-matched SHG [9]. The noncritical phase matching wavelength was measured by a Ti doped sapphire laser for these compositions. Radiation between 790 nm and 900 nm was generated from the Ti doped sapphire laser, with a power output of about 300 mW. The experimental arrangement is detailed in Fig. 2.

At first we used 1 mm long segments, cut from a-oriented KLN crystals, grown from melt compositions between x = -0.6 and x = 0.5 (according to $K_3Li_{2-x}Nb_{5+x}O_{15+2x}$) with optically polished 500 × 300 μm^2 front planes. Blue SHG of μ-PD KLN crystals was observed, however, we found that the SHG characteristics depend on the starting melt compositions of the grown crystals.

Table 1 presents the correlation between melts composotion and phase matched wevelength. The phase matched wavelength in-

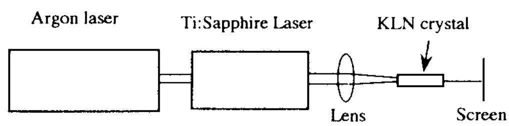

Fig. 2. Experimental arrangement for blue SHG measurement using a tunable Ti doped sapphire laser.

Table 1
Dependence of phase matched wavelength on melt composition

Melt composition (K_2O: Li_2O: Nb_2O_5)	Noncritical phase matched wavelength (nm)
30 : 17 : 53	> 900
30 : 20 : 50	≈ 880
30 : 23 : 47	≈ 820
30 : 25 : 45	≈ 815
30 : 26 : 44	≈ 817

creased as the Nb content in the melts increased. However, SHG was not detected at $x \geqq 0.3$ because of the spectral detection limit of the apparatus. This indicates that crystals grown by the μ - PD method from different melt compositions are able to control the noncritical phase matching wavelengths.

We also investigated the homogeneity of samples/segments prepared from a_1 - oriented crystals using the method of noncritical phase matching with a tunable Ti doped sapphire laser. Samples were prepared with lengths of 10 mm, taken from the middle part of a grown crystal (about 50 mm in length), and irradiated at the surface (a_2 plane) perpendicular to the growth axis. Figure 3 shows the phase matched wavelength along the crystal length for μ - PD KLN crystals grown from melt compositions of $x = -0.6$ and $x = -0.3$. The wavelength variations are ± 3 nm and ± 2 nm, respectively.

We estimate that wavelength variations in

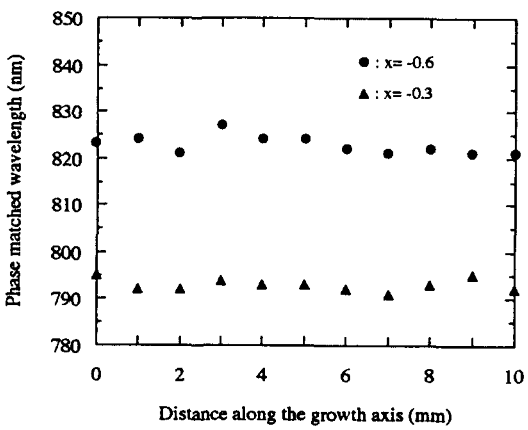

Fig. 3. Noncritical phase matched wavelength along the crystal length.

KLN are above ± 20 nm within the solidified fraction $g \leqq 0.1$, because of composition changes along the growth axis of 2 mol% in this region for a conventional growth method [12]. In μ - PD crystals, compositional homogeneity results in a nearly constant phase matched SHG wavelength along growth direction.

These results provide the dependence of the most appropriate composition for SHG applications from ultra-violet to green region and the developments of future growth technologies for a new material having improved composition homogeneity from incongruent melt compositions. It is considered that a change of composition in KLN crystals can affect the electro-optical and nonlinear optical properties because of the considerable change of the birefrigence with variation of the Nb content. However, the SHG wavelength in μ - PD KLN crystals is not always proportional to the Nb content of the melt composition. For example, two crystals grown from the melt compositions of $x = -0.6$ and -0.3 (see in Fig. 3) show a noncritical phase matching wavelength of about 820 and 790 nm. We think that the change of the SHG characteristic is caused by the displacement of Nb atoms, which will be described in future, due to different redistribution phenomena on an atomic scale.

Using the equipment presented in Fig. 4, we measured the SHG intensity dependent on temperature between 25℃ and 40℃ in the practical analysis of temperature allowance for SHG using a Nd : YAG pump laser (1064 nm). A sample with 2 mm long

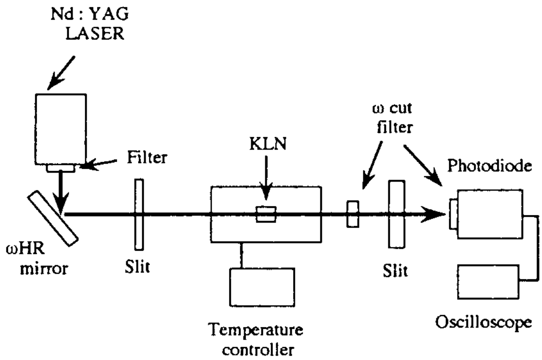

Fig. 4. Experimental arrangement for measurement of temperature allowance of SHG.

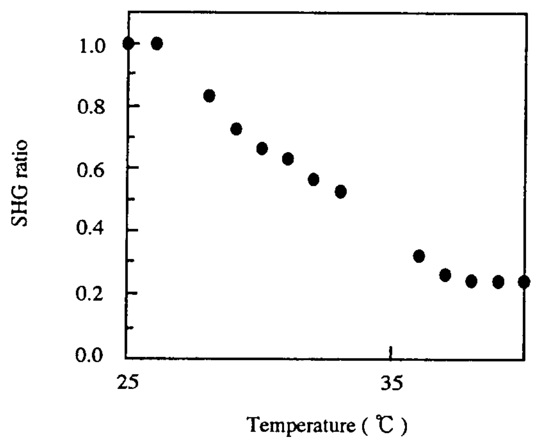

Fig. 5. Temperature allowance of SHG using a Nd : YAG pump laser.

segment cut from a-oriented KLN crystal was used. Figure 5 shows the result of the SHG intensity ratio dependent on temperature. The full width at half maximum is about 10.5℃, yielding an allowance of temperature of 2.1℃・cm. This indicates that KLN is competitive and superior to $KNbO_3$ and $LiNbO_3$ by factors of 7 and 3, respectively, as shown in Table 2.

Also, phase-matched frequency doubling

Table 2
Temperature allowance of SHG materials

Material	Temperature allowance (℃・cm)
KLN	2.1
$KNbO_3$	0.3
$LiNbO_3$	0.7

of (Ga, Al) As laser diodes at room temperature was achieved with pump power of 100 mW at 808 and 870 nm, respectively. We have applied 10 mm long a-oriented KLN crystal segments grown from melt compositions of $x = -0.3$ and $x = 0$. It has been found that the crystals favor phase matched frequency doubling at wavelengths of 808 nm and 870 nm, in depending upon the melt compositions of $x = -0.3$ and $x = 0$, respectively. The SHG wavelength increases on increasing the Nb content of the melt. However, no correlation between laser efficiency and crystal habit has been found. This is understandable because at the present state the dimensions of the cross sections still exceed the diameter of the exciting laser mode (≈ 100 μm for the (Ga, Al) As laser diode).

In summary, the μ-PD KLN crystals showed an excellent and a homogeneous SHG properties which is converted to blue laser light with half wavelength by the red irradiation of a Ti doped sapphire laser and/or semiconductor laser diode. Also, phase matched frequency doubling of the laser from 780 nm to 900 nm for blue SHG at room temperature has been obtained by the crystals dependence of the crystal compositions.

Acknowledgements

The authors wish to thank Dr. T. Taniuchi of Tohoku University (IMR) and Professor T. Sasaki of Osaka University for the SHG measurements.

References

[1] R.R. Neurgaonkar, W.K. Cory and J. Oliver, Ferroelectronics 51 (1983) 4.
[2] R.R. Neurgaonkar, J. Oliver and L.E. Cross, Ferroelectrics 51 (1984) 31.
[3] J.K. Yamamoto, S.A. Markgraf and A. S. Bhalla, J. Crystal Growth 123 (1992) 423.
[4] L.G. Van Uitert, S. Singh, H.J. Levinstein, J.E. Geusic and W.A. Bonner, Appl. Phys. Lett. 11 (1967) 161.
[5] L.G. Van Uitert, H.J. Levinstein, J.J. Rubin, C.D. Capio, E.F. Dearborn and W.A. Bonner, Mat. Res. Bull. 3 (1968) 47.
[6] J.J.E. Reid, Appl. Phys. Lett. 62 (1993) 19.
[7] W.A. Bonner, W.H. Grodkiewicz and L.G. Van Uitert, J. Crystal Growth 1 (1967) 318.
[8] T. Fukuda, Jpn. J. Appl. Phys. 8 (1969) 122.
[9] B.A. Scott, E.A. Giess, B.L. Olson, G. Burns, A.W. Smith and D.F. O'Kane, Mat. Res. Bull. 5 (1970) 47.
[10] D.H. Yoon, P. Rudolph and T. Fukuda, J. Crystal Growth 144 (1994) 207.
[11] D.H. Yoon, M. Hashimoto and T. Fukuda, Jpn. J. Appl. Phys. 33 (1994) 3510.
[12] D.H. Yoon, N. Shimo, M. Hashimoto, Y. Okano, T. Sasaki and T. Fukuda, The 37th Discussion Meeting of Synthetic Crystal (1992) A02.