Journal of Korean Association of Crystal Growth
Vol. 4, No. 4 (1994) 405-410

Compositional homogeneity of potassium lithium niobate crystals grown by micro pulling down method

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

μ-PD법에 의해 육성한 KLN 단결정의 조성적 균일성

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

Abstract KLN crystals were grown with various melt compositions by μ-PD method. The composition of KLN crystals was determined by DTA and X-ray diffraction measurements. It can be obtained that KLN micro crystals have a nearly homogeneous composition along the growth axis because of the absence of convection in melt growth interface.

요 약 μ-PD법에 의해 융액 조성을 변화시키면서 KLN결정을 육성하였다. 육성된 결정은 DTA 측정 및 X-선 회절법에 의해 조성을 변화를 측정하였다. 이 결과로부터 μ-PD KLN 단결정은 육성축 방향에 따라 균일한 조성을 갖음을 알 수 있었으며, 이는 고액계면에서의 대류제어 효과에 기인된다고 사료된다.

1. Introduction

Potassium lithium niobate, $K_3Li_{2-x}Nb_{5+x}O_{15+2x}$ (KLN), crystals with $0.1 \leqq x \leqq 0.5$ crystallizes in the tetragonal tungsten bronze structure with unit cell dimensions of $c \approx 4.04$ Å and $a_1 = a_2 \approx 12.56$ Å [1]. Large electro-optic and nonlinear coefficients combined with remarkable stability under intense laser radiation has been described by Reid [2] for this composition range. He has shown that KLN is a very suitable material

for frequency doubling of a (Ga, Al)As diode laser at 300 K. Usually, KLN single crystals are grown by conventional methods, e.g. the Czochralski (CZ) [3] and top-seeded solution growth (TSSG) methods [4]. However, useful bulk of centimeter dimensions have not been obtained due to cracks resulting from composition changes and due to structural characteristics of the material. A change of composition in KLN crystals affects electro-optical and nonlinear optical properties [5].

We investigated growth of crack-free KLN micro single crystals from incongruent compositions by the μ-PD method [6, 7]. We also obtained very successful second harmonic generation (SHG) of blue light using Ti sapphire laser [6]. Micro single crystals exhibiting nonlinear optical behavior are of increasing interest because of their improved laser processing efficiency and phase matching behavior [8-10].

There is a close relation bewteen the properties and the composition of KLN crystals. Also, the homogeneity of crystal composition has a direct influence on the optical quality. However, up to now the homogeneity of crystals grown from various melt compositions has not been reported. In this paper we report the compositional homogeneity of μ-PD KLN single crystals associated dependence on melt compositions.

2. Experimental

We have used starting compositions between $-0.6 \leqq x \leqq 0.5$ (in $K_3Li_{2-x}Nb_{5+x}O_{15+2x}$), scaled before sintering. Using the μ-PD method described in ref. 6 and 7, the sintered raw material was loaded and melted in a Pt crucible with a micro nozzle at the bottom. A seed crystal with a-axis orientation

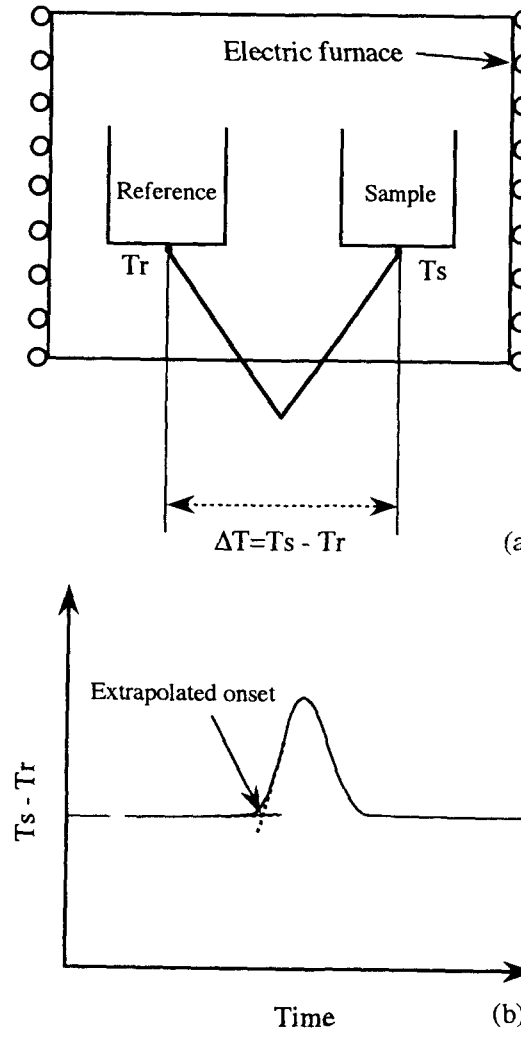

Fig. 1. Illustration of the DTA technique : (a) schematic diagram of the general type of DTA cell, (b) signal of $T_s - T_r$ by exothermic reaction.

was attached to the tip of the micro nozzle and after wetting of the melt pulled down, at a velocity of 6 mm/h. Diameter control of crystals has been achieved by using a narrow micro-nozzle and by maintaining a particular, steady after-heater temperature.

Composition and homogeneity of the grown crystals have been measured by differential temperature analysis (DTA) using a Rigaku High Temperature TG-DTA apparatus (TAS 100) and X-ray powder diffration method using a Philips PW 1700 (CuK_α, 45 kV, 35 mA). All measurements were done in an air atmosphere.

A schematic diagram of DTA measurement system is shown in Fig. 1. This is a technique by which one can compare sample temperature (T_S) to a reference temperature (T_r) to obtain a temperature difference as a sample is heated or cooled. A constant heating or cooling rate is normally programmed. For a measured temperature range, a reference material such as α-Al_2O_3 is usually chosen. Cylindrical platinum cups of 5 mm diameter, 2.5 mm height and 0.1 mm thickness were used as containers for the sample and the reference material. The temperature was analyzed by Pt-Pt/Rh 13 % thermocouples. The crystal samples were cut from a single crystal in dimensions of 5 $\times$ 0.5 $\times$ 0.4 mm^3 and subsequently enclosed in a thin platinum cup.

3. Results and discussion

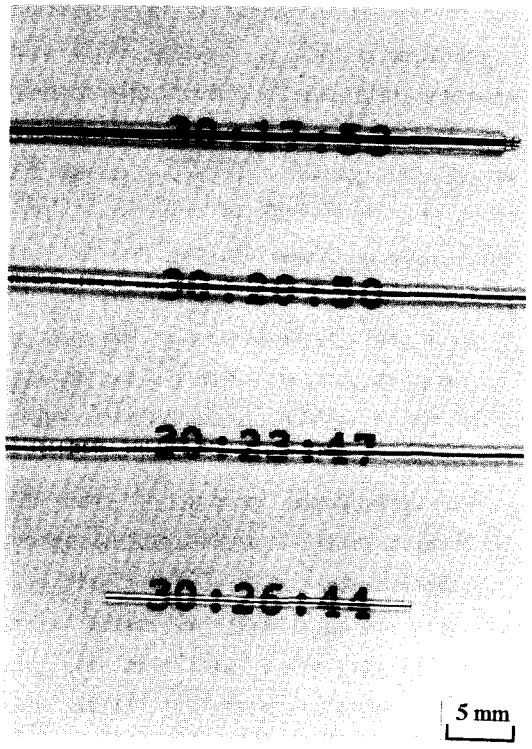

Fig. 2. Photograph of KLN micro single crystals grown along the a-axis with growth rate of 6 mm/hr and various melt compositions in K : Li : Nb ratio.

The grown KLN crystals with diameters of about 500 μm are free of cracks shown in Fig. 2. Good control of the crystal diameter is dependent of the melt compositions. In fact, very good control of the crystal diameter at melt compositions $x \geqq -0.3$ (at high Nb concentration, Nb $\geqq$ 47 mol% in K : Li : Nb ratio) has been demonstrated. However, at low Nb content ($x = -0.6$) the diameter drops drastically and changes uncontrollably. We can predict that the melt composition of KLN for μ-PD crystal growth influences the growth kinetics and the diameter

self-consistency.

For DTA, we measured the temperature at the starting point as used extrapolated onset [11] which it enables accurate detection of small signals by taking the difference between Ts and Tr (Fig. 1 (b)), where this signal can be amplified. However, if the reaction rates are too fast, the DTA measurement system is not able to monitor them because of its finite response time. On the other hand, if they are slow, the DTA system is able to discriminate between them clearly. The system was heated and cooled between room temperature and 1150℃, and held for 20 minutes after heating to attain a steady state. Then the temperature was increased to 1175℃ with a programmed heating rate. The selected heating and cooling rates were 20℃/min, 10℃/min, 5℃/min and 1℃/min, respectively.

Table 1 presents the measured solidifying point of the melt with $x = 0.5$, as a function of the cooling rate. It can be seen that it is difficult to obtain the melting point during the heating process for KLN because of the large subsolidus region of the melt from the phase diagram [1]. Thus far, cooling has been more useful for revealing incremental temperature differences due to chemical reactions. Table 2 presents DTA results measured for a cooling rate of 1℃/min, indicating the melting point of crystals grown from various compositions and also temperature differences along the growth axis at points 30 mm apart. The temperature differences are about 1 ~ 2℃, and a composition change is almost undetectable. This means that composition changes are reduced by the μ-PD method and, therefore, the crystals show a high degree of compositional homogeneity.

In the following we compare the analysis of chemical composition and lattice constant distribution. The lattice constants a and c, shown in Fig. 3, depend on the melt composition and change in $K_3Li_{2-x}Nb_{5+x}O_{15+2x}$ between $-0.6 \leqq x \leqq 0.3$ from 12.555 Å and 4.050 Å to 12.590 Å and 3.965 Å, respectively. Whereas in a-oriented crystals

Table 1
The solidifying point and the cooling rates (melt composition with 55 mol% Nb_2O_5)

Cooling rate	Solidifying point
20℃/min	1085℃
10℃/min	1088℃
5℃/min	1091℃
1℃/min	1097℃

Table 2
Solidifyng points of crystals grown from melts of various compositions, at two points along the growth axis (cooling rate of 1℃/min)

Melt composition (K_2O : Li_2O : Nb_2O_5)	Upper	Lower
30 : 17 : 53	1090℃	1091℃
30 : 20 : 50	1080℃	1079℃
30 : 22 : 48	1074℃	1072℃
30 : 23 : 47	1071℃	1072℃
30 : 26 : 44	1071℃	1073℃

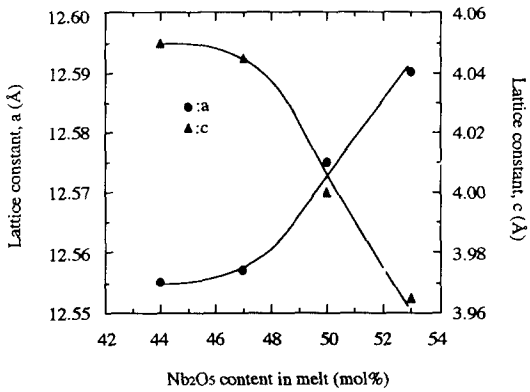

Fig. 3. Lattice constants a and c of grown crystals dependent on the melt compositions.

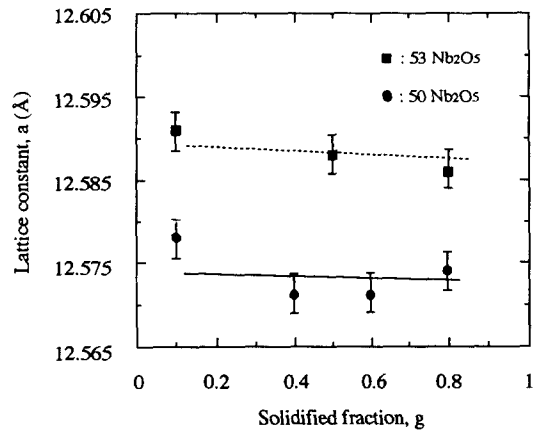

Fig. 4. The change of lattice constant along the solidified fraction grown from melts with 50 and 53 mol% Nb_2O_5.

with high Nb content ($x \geqq -0.3$) a sensitive change with composition was detected, at low Nb concentration ($x \leqq -0.3$) the lattice constant was markedly uniform and relatively independent of the variation of the composition of the melt. We explain this constancy of the lattice parameter by the segregation phenomena, comparison with the DTA measurement.

Fig. 4 presents the change of lattice constants, which are resulted in $a = 12.590 \pm 0.002$ Å and $a = 12.575 \pm 0.002$ Å along the solidified fraction g in a-oriented crystals, grown from melts with 50 and 53 mol% Nb_2O_5, respectively. A nearly homogeneous distribution has been observed independent on the melt compositions. By conventional growth techniques, it is problematic to obtain crack-free crystals from incongruent melts with 50 or 53 mol% Nb_2O_5 because of a considerable axial composition change by segregation. Theoretically the value of the lattice constant a decreases along the growth axis from 12.60 to 12.575 Å and from 12.60 to 12.565 Å, accompanying changes of the melt compositions from 53 and 50 mol% Nb_2O_5, respectively. We think the lattice constant decreases in conventional crystals due to the axial decreasing of the Nb content by segregation during the normal freezing process with complete convective mixing of the melt for techniques like CZ or TSSG. By contrast, the μ-PD method is characterized by an absence of convection in very small meniscus [7]. Additionally, the high pulling rate prevents an effective rediffusion of the rejected Li excess at the growth interface. Thus the effective distribution coefficient is unity. This results in a homogeneous chemical composition and crack-free growth.

4. Conclusion

Crack-free KLN micro single crystals

have been successfully grown by the μ-PD method. Good control of the micro crystal diameter has been observed for melt compositions $x \geqq -0.3$. A low cooling rate (1℃/min) using by the DTA analysis was most favorable for revealing small temperature difference due to chemical reactions. A nearly homogeneous composition has been observed, independent of melt composition. Crystals grown from melts with 50 and 53 mol% Nb_2O_5 are homogeneous along the solidified fraction g by measurement of the lattice constant. In contrast to the CZ and TSSG methods, the μ-PD method is characterized by an absence of convection in the very small meniscus and also by a high pulling rate.

References

[1] 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.

[2] J.J.E. Reid, Appl. Phys. Lett. 62 (1993) 19.

[3] W.A. Bonner, W.H. Grodkiewicz and L.G. Van Uitert, J. Crystal Growth 1 (1967) 318.

[4] T. Fukuda, J. Crystal Growth 6 (1970) 293.

[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] D.H. Yoon, M. Hashimoto and T. Fukuda, Jpn. J. Appl. Phys. 33 (1994) 3510.

[7] D.H. Yoon, P. Rudolph and T. Fukuda, J. Crystal Growth 144 (1994) 207.

[8] C.A. Burrus and J. Stone, J. Appl. Phys. 49 (1978) 3118.

[9] D.H. Jundt, M.M. Fejer and R.L. Byer, Appl. Phys. Lett. 55 (1989) 2170.

[10] S. Sudo, I. Yokohama, A. Cordova-Plaza, M.M. Fejer and R.L. Byer, Appl. Phys. Lett. 56 (1990) 1931.

[11] G. Lombardi, in For Better Thermal Analysis (International Confederation for Thermal Analysis, 1977).