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Review

Recent progress in research of optoelectronic materials

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광전자용 재료 연구의 최근현황

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Abstract It is well known that crystal growth is an essential area of research for optoelectronic materials. In the present paper the growth techniques and the advanced progress in development of crystal materials important for optoelectronic applications are described. New growth techniques, developed in the authors' laboratory, enabling the introduction of expanded applications of new materials are presented. After a review of recent developments of new techniques for optoelectronic materials, own experimental studies will be discussed.

요 약 결정성장은 광전자용 재료의 연구개발에 있어서 필수분야이다. 본 논문에서는 광전자 응용분야에서 중요한 결정재료의 성장기술과 개발 현황에 대해서 보고하였다. 특히 광전자용 재료의 최근 현황을 재검토, 새로운 재료개발의 확장영역을 소개하기 위해 저자들의 연구실에서 개발된 새로운 결정성장 기술의 실험적 연구를 검토하였다.

1. Introduction

It is well known that the development of oxide optoelectronic materials started at the moment the $LiNbO_3$ single crystal growth was achieved by Ballman [1] at the Bell Laboratories in 1965 using the Czochralski (CZ) method. Subsequently, many investigations on the crystal structure and ferroelectrical properties of optoelectronic materials have been carried out by numerous research groups [2-4]. New complex crystals such as $Ba_2NaNb_5O_{15}$ (BNN) with the tungsten bronze structure, for example, were developed to overcome some apparent shortcomings such as optical damage of the laser.

However, these crystals were not used as widely as expected because of the scaling back of research in the optical industry. Only a few crystals such as Y_3AlO_{12} (YAG), $LiTaO_3$ and

$LiNbO_3$ have been successfully used in industrial applications even though they show advantageous characteristics, because high-quality crystals have not yet been produced by the existing crystal growth techniques and due to the inherent problems of the materials themselves (composition inhomogeneity, for example).

Recently the growth of crystals from the melt has again become a focus of considerable interest due to the development of the optical industry including the industrialization of semiconductor lasers, emitting diodes and optical fibers. It appears that optoelectronic crystals are quite necessary for optical devices and systems. Optoelectronic crystals of new materials such as $KTiOPO_4$ (KTP), LiB_3O_5 and β-BaB_2O_4 (BBO) have been intensively developed in China and organic crystals with large nonlinear optical coefficients have been actively investigated.

In the authors' laboratory the development of optoelectronic and photonic materials has been carried out for several years by systematic investigations of the crystal growth process from the melt for numerous materials [5-8]. In this paper, the research and progress in development of optoelectronic materials (except semiconductors) are reviewed to promote a better understanding of the fundamentals of melt growth and new growth technologies.

2. Fundamental investigations on crystal growth

If oxide single crystals are grown by the CZ method, the heat transfer caused by radiation, conduction and convection is an important factor determining the growth behavior and quality of grown crystals. Therefore, it is necessary to understand and control the heat transfer process in the melt, crystal and growth furnace for obtaining high-quality bulk single crystals during the growth process. In the case of growth of transparent or semitransparent crystals with high melting temperature, the radiative heat transfer through the crystal is also of considerable importance.

In the case of crystal growth of $LiTaO_3$ by the CZ method the study aimed at gaining an understanding of the heat transfer by the internal radiation through transparent and semitransparent crystals of different colors and grown in N_2 and N_2+O_2 atmospheres [9]. Fig. 1 shows a good-quality $LiTaO_3$ crystal grown under N_2+O_2 atmosphere. It was found that crystal growth in N_2 atmosphere is unstable in comparison with that in N_2+O_2 atmosphere. Fig. 2 represents the emitted spectra from crystals grown in N_2 and N_2+O_2 atmospheres. It can be seen that both environments provide different growth conditions. As mentioned above, the unstable growth taking place in N_2 atmosphere is caused by the suppression of heat transfer through the crystal due to the decrease

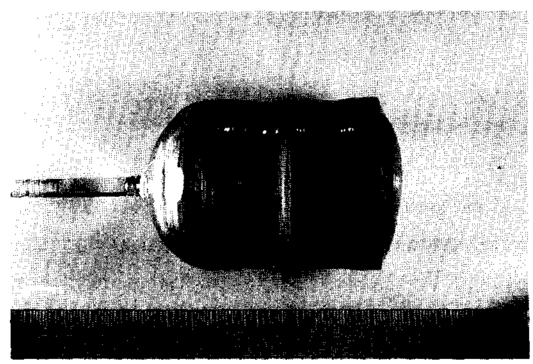

Fig. 1. $LiTaO_3$ single crystal grown along the <001> axis in N_2+O_2 atmosphere.

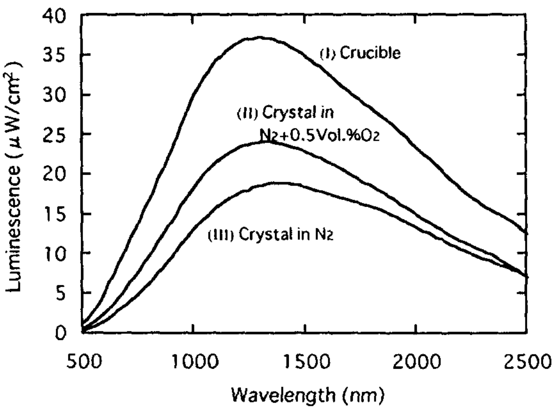

Fig. 2. Emitted spectra from the crucible wall (I), and crystal surface in N_2+O_2 atmosphere (II) and N_2 atmosphere (III).

of internal radiation. Furthermore, rutile (TiO_2) crystals affected the internal radiation and a spiral growth has appeared using the CZ method [10].

A numerical study was performed to understand the influence of the forced convection by crystal rotation as well as that of the thermal convection on the morphology of the melt/crystal interface and crystal radius during CZ growth of oxide single crystals. It was found that the order of magnitude analysis is useful for predicting the critical rotation rate during CZ growth of oxide single crystals [11].

3. New materials

In 1984 a national project in England on the $LiNbO_3$ crystal technology for the OEIC (opto-electronic integrated circuit) was launched by Grant et al. [12]. They reported the first successful evaluation of fundamental characteristics and industrialization of a high-quality waveguide technique for $LiNbO_3$ crystals.

In the United States a workshop on nonlinear materials was held in 1986. Many researchers discussed applications of this crystal material and the assessment was reported by Auston et al. [13]. From this discussion it can be concluded that crystal growth and crystal characterization of nonlinear optical materials such as BBO, KTP, $KNbO_3$, L-arginine phosphate, calcopylite and Tl_3AsSe_3, and photorefractive materials such as $KNbO_3$, $Bi_{12}TiO_{20}$, $KTa_xNb_{1-x}O_3$ (KTN), $Sr_{1-x}Ba_xNb_2O_6$ (SBN), $BaTiO_{20}$ and $Ba_{1-x}Sr_xTiO_3$ have been focused on and developed.

In Japan $LiNbO_3$ became of interest after the influence of research in England and the $LiNbO_3$ Crystal Committee was founded in 1988. A worldwide effort on characterization and device manufacture of $LiNbO_3$ was begun. The standardization of optical crystal was reported in 1992 [14]. Subsequently, the $LiNbO_3$ Crystal Committee became the Optical Crystal Committee charged to encompass the entire field of optical crystals.

As the source material of laser diode (LD) pumped lasers, Nd: Y_3AlO_{12} (Nd: YAG) with a wavelength of 1.06 μm and Tm: YAG with a wavelength of 2 μm have been used. These materials are required to control the temperature of the LD with electric Peltier coolers for obtaining highly efficient oscillation having a defined pump wavelength because of their narrow absorption spectra. Therefore, new excellent crystals with broad absorption spectra and high thermal conductivities are necessary for LD-pumped solid-state lasers. One such material is $Ca_3(NbGa)_{2-x}Ga_3O_{12}$ (CNGG) grown by the CZ method. It was revealed that the laser oscillation properties of CNGG are similar to those of Nd: YAG. However, its absorption spectrum was broader which renders it very attractive for a LD-pumped solid state laser [15]. Fig. 3 shows an example of an as-grown CNGG crystal pulled in the <111> direction. Crack-free CNGG crystals were grown without afterheater. It is expected that CNGG is a very promising crystal material for a new LD-pumped solid-state laser host.

In the case of borates with the structure of natural huntite ($CaMg_3(CO_3)_4$) there are three different cation positions. The Ca^{2+} ion occupies the centers of the oxygen trigonal prism and can be completely substituted by cations of rare earth elements such as Bi^{3+}. The ions of Yb^{3+}, Mg^{2+} occupy the centers of oxygen octahedra and can be completely substituted by Al^{3+}, Ga^{3+}, etc. C^{4+} occupies oxygen triangles and can be substituted by B^{3+}. For investigation of crystal-chemical possibilities of this structure and each sublattice with different substitutional cations, single crystals of huntite borates $LnAl_3(BO_3)_4$ have been grown by the flux growth technique. This material shows the advantage of a congruent melting point [16]. Recently, the huntite borates have received considerable attention as promising materials for lasers and nonlinear optics.

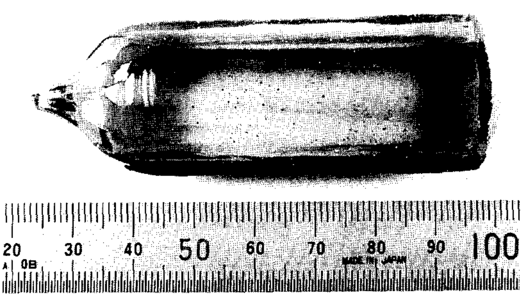

Fig. 3. CNGG single crystal grown along the <111> axis by the CZ method.

4. New growth techniques

The improvement of quality and demand for new crystals with multi-functions for devices and systems are, generally, requirements for industrialization. It is important not only to investigate new materials but also to improve the crystal growth techniques. Most crystals of optoelectronic materials including semiconductors, oxides and fluorides are grown by the conventional CZ method. However, the CZ method is not suitable for growth of high-quality single crystals from incongruent melts. A successful alternative is the top seeded solution growth (TSSG) method. Other methods, for example the floating zone (FZ) method as well as the hydrothermal method are applicable for high-temperature compound materials.

The crystal growth techniques were developed rapidly due to their practical applications. Surface acoustic wave (SAW) devices made from $LiNbO_3$ and $LiTaO_3$ present some problems for optical uses, i.e., optical strain and inhomogeneous dopant distributions within the crystals. Therefore, it is necessary to develop growth techniques for stoichiometric materials free of optical strain and optical damage having a homogeneous MgO doping distribution. It was not possible to obtain homogeneous compositions from the top to the bottom of crystals grown from incongruent melts by the conventional CZ method. In order to solve this problem a modified CZ method with the continuous charging (CC-CZ) method was developed for the silicon growth [17]. This method was also recently successfully employed for oxide single crystals [18-20]. Fig. 4 shows the schematic diagram of the modified method which guarantees a uniform composition distribution by continuous addition of raw materials to the melt. In Fig. 5 the axial distributions of Li_2O contents analyzed from refractive index (n_e) in $LiNbO_3$ crystal in comparison with conventional CZ grown samples are given. It can be seen that in CC-CZ crystals, the composition is always stoichiometric along the solidified fraction (g) and the homogeneity of MgO content [21] varies only by ±0.01 mol% Li and ± 0.01 mol% MgO.

$LiNbO_3$ crystals with stoichiometric composition and doped by 1% MgO show good resistance to optical damage and optical strain

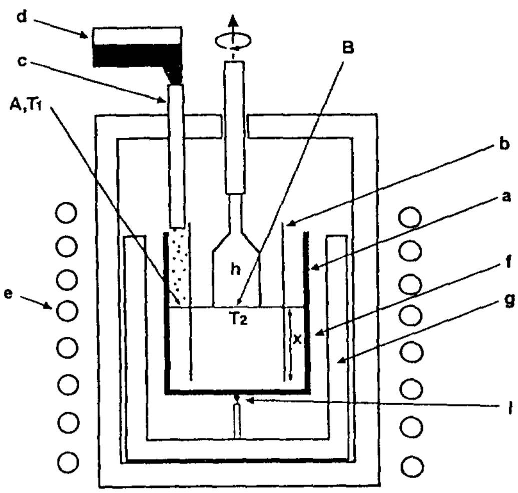

Fig. 4. Schematic diagram of CC-CZ apparatus. (a) Pt crucible, (b) Pt partition cylinder, (c) charging pipe, (d) feeder, (e) RF coil, (f) ZrO_2 bubble, (g) Al_2O_3 insulator, (h) $LiNbO_3$ crystal and (i) thermocouple; (A) material charging area and (B) crystal growth area.

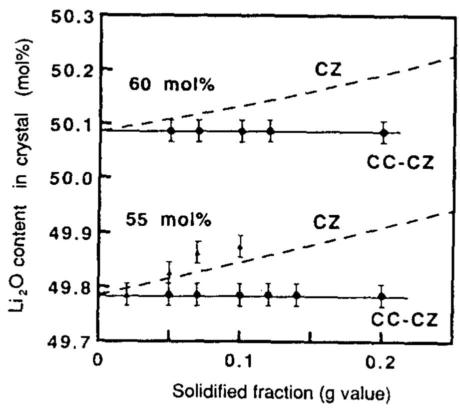

Fig. 5. The variation of crystal composition versus solidified fraction (g) for $LiNbO_3$ crystals grown from 55 and 60 mol% Li_2O melts.

[22]. Therefore, high-quality $LiNbO_3$ crystals are easily grown by the CC-CZ method. Moreover, this method is able to produce long crystals without extraordinary phenomena such as crystal twist.

The continuous charge method for prevention of composition variations is not only effective for the CZ method but also for the TSSG method. The TSSG method combined with continuous charging of raw material is of considerable interest for potassium lithium niobate (KLN) growth. KLN is the most competitive material among the blue SHG crystals due to its high figure of merits. It was grown recently and successfully developed for devices of good quality [23]. In the authors' laboratory KLN single crystals 5-10mm square were produced by the TSSG method [24]. It was demonstrated that the blue SHG of these crystals generated by a semiconductor laser diode is more stable than that of $KNbO_3$ which was investigated previously. However, a large change of composition is inevitable with the use of the conventional method. Therefore, the CC-TSSG method has been applied to guarantee composition control. The growth conditions of $(Nd_{1-x}Y_x)Al_3(BO_3)_4$ (NYAB) for self-frequency-doubling were studied carefully by the CC-TSSG method.

TiO_2 single crystals are of greatest interest for use as polarizers of optical isolators. Usually, the growth methods are either the FZ method or Verneuil method. However, the maximum diameter of the crystals obtained by the FZ method does not exceed 1 inch. Beyond that diameter the crystal growth is difficult to control along orientations other than the c-axis because of the dependence of thermal conductivity on the growth orientation. Large TiO_2 single crystals were examined under various growth conditions using the CZ method but the control of shape was very difficult [10]. Therefore, a modified edge-defined film-fed growth (EFG) method has been used to optimize the growth conditions. Ribbon-shaped single crystals were pulled with the control of interface temperature [25]. Special rod-shaped crystals with a diameter of 12 mm were also grown using a modified die, as shown in Fig. 6 [26].

The modified EFG method was also adopted for the growth of core-doped crystals [27]. A double-structured crucible was composed of inside and outside crucibles consisting Nd-doped and non-doped melts, respectively. A double-tube die was applied. Crystals doped with Nd only in the core have been grown. These crystals are suitable for generation of the single-mode laser. A high-power laser which is also of high efficiency can be obtained due to the high concentration of dopant in the center. Generally, the EFG method decreases the costs

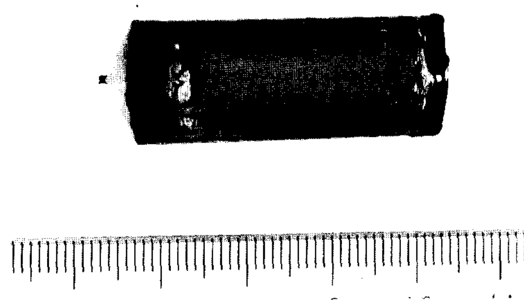

Fig. 6. TiO_2 single crystal of rod shape grown by the EFG method.

and enables control of the crystal shape. It is expected that this method is very suitable for growth of high-quality and highly functional materials.

Usually, single crystals used in electronics and optoelectronics are grown to large sizes because of the cost of material. However, in large crystals it is easy to generate dislocations and subgrain boundaries because of the deformation of the thermal field. In contrast, in micro single crystals with diameters below 1 mm a low defect density can be expected if it is possible to develop a new low-cost growth process. There are several methods for the growth of micro single crystals in "fiber" form as shown in Fig. 7. The laser-heated pedestal (LHPG) method [28], the micro-CZ (μ-CZ) method [29] and the drawing down method [30] have been attempted. Fig. 8 represents the micro pulling down (μ-PD) method developed by the authors [31] by modification of the μ-CZ method. In this method the raw materials are melted within a crucible with a micro-nozzle at the bottom. Subsequently, the molten material is passed through the micro-nozzle to form a micro single crystal (rod shape) with a cross section not more than 1 mm in diameter. A typical sample of a KLN crystal grown by the μ-PD method is shown in Fig. 9. The crystal is colorless and free of cracks. This method shows several advantages: Firstly, crystals of very small sizes without degradation in quality or cracks can be grown; in comparison to the conventional growth method KLN crystals can be grown easily at a much faster rate and without cracks for blue SHG

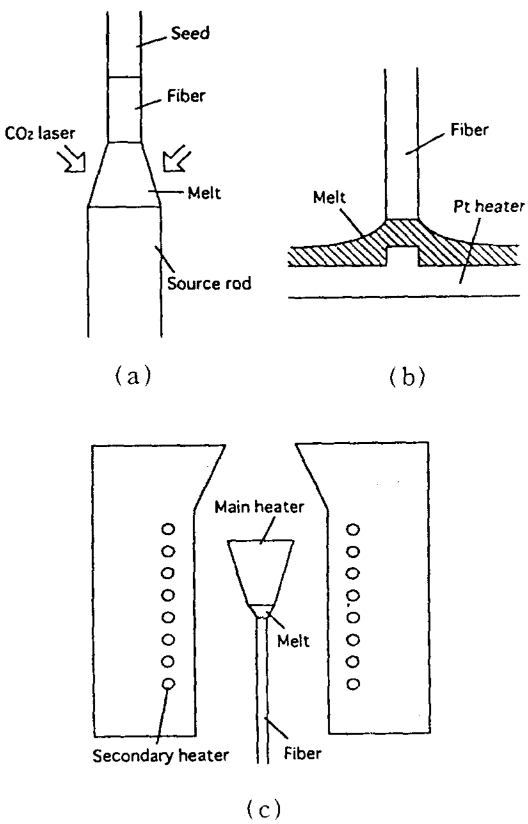

Fig. 7. Schematic diagram of fiber growth methods: (a) LHPG method, (b) μ-CZ method and (c) drawing down method.

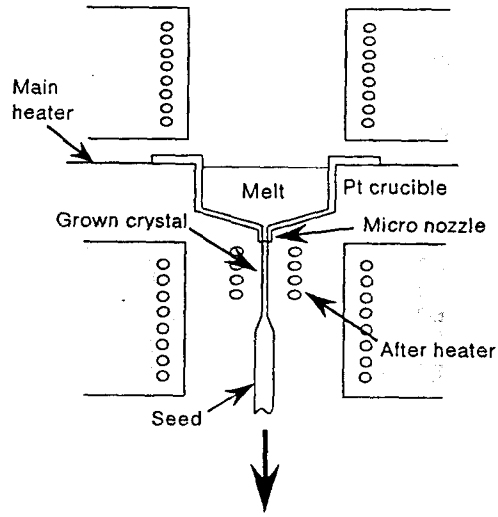

Fig. 8. Schematic diagram of μ-PD growth apparatus.

applications [32]. The dislocation density is nearly zero. Secondly, melt convection is suppressed by the use of a narrow-distance nozzle by the capillary effect; this allows the growth from incongruent KLN melts and Li-rich $LiNbO_3$ melts because of the effective segregation coefficient near unit. Thirdly, it is easy to control the crystal shape and composition. Finally, mass production at low cost is possible by the μ-PD method, reducing the preparation expenses considerably.

Nonlinear optical properties of organic materials have received much attention due to their large second-order nonlinearities and potential applications to the OEIC. 4'-nitrobenzylidene-3-ethylcarbonylamino-4-methoxy aniline (MNBA-Et) is a potential non-linear material for heteroepitaxy in combination with 4'-nitrobenzylidene-3-acetamino-4-methoxy aniline (MNBA) which is promising for the fabrication of waveguides [33]. Generally,

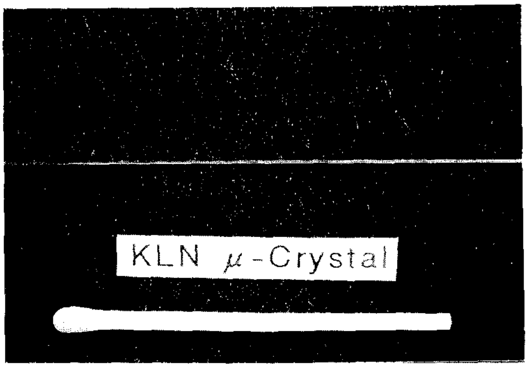

Fig. 9. KLN micro single crystal grown by the μ-PD method.

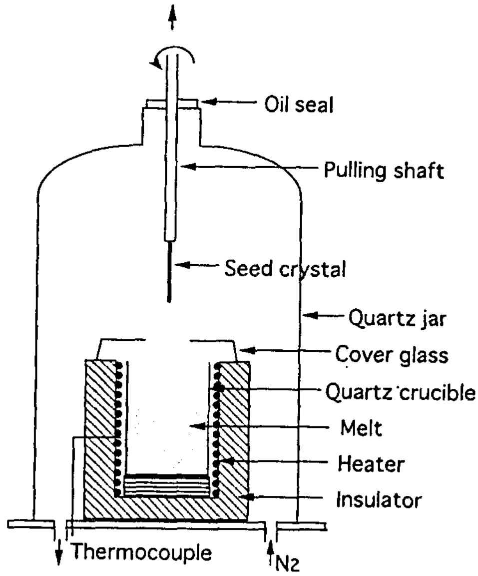

Fig. 10. Schematic diagram of mini-CZ apparatus for organic growth.

organic crystals have been grown from aqueous solution. However, major obstacles in the successful development of organic nonlinear materials include the considerable difficulties in the growth of large crystals and directional growth of crystals. In order to overcome these problems MNBA-Et single crystals have been grown by the mini-CZ method shown in Fig. 10. MNBA-Et single crystals were grown with diameters between 3-15 mm and length of 15 mm [34]. This method is probably suitable for the growth of some organic and low-melting point materials.

5. Conclusions

The progress in growth of optoelectronic crystals based on experimental observations of the fundamental characteristics, new materials and new techniques was reported. The development of optoelectronic crystals is important for optical devices and systems. However, even at present the quality of most crystals is too low and the cost is too high for widespread use in industry. A breakthrough in crystal growth techniques is necessary for future optoelectronic applications. Therefore, new materials and new modified growth techniques important for optoelectronic applications have been developed. For further optimization, research on the melt properties, melt flow and specific growth phenomena is of considerable importance.

References

[1] A.A. Ballman, J. Am. Ceram. Soc. 48 (1965) 12.
[2] J.A. Giodmaine, Physics Today (1969) 39.
[3] S.C Abrahams, J.M Reddy and J.L.

Bernstein, J. Phys. Chem. Solids 27 (1966) 997.

[4] N. Niizeki, T. Yamada and H. Toyada, Jpn. J. Appl. Phys. 6 (1967) 318.

[5] K. Kawasaki, Y. Okano, S. Kan, M. Sakamoto, K. Hoshikawa and T. Fukuda, J. Crystal Growth 119 (1992) 317.

[6] T. Suzuki, Y. Okano, K. Hoshikawa and T. Fukuda, J. Crystal Growth 128 (1993) 435.

[7] S. Pan, Y. Okano, S. Tsunekawa and T. Fukuda, J. Crystal Growth 129 (1993) 365.

[8] F. Matsumoto, Y. Okano, I. Yonenaga, K. Hoshikawa and T. Fukuda, J. Crystal Growth 132 (1993) 348.

[9] D.H. Yoon, Y. Okano, T. Tsuji and T. Fukuda, J. Crystal Growth (to be published) & J. Korean Crystal Growth (The Autumn Extended Abstracts), (1992) A04.

[10] H. Machida and T. Fukuda, J. Crystal Growth 112 (1991) 835.

[11] Y. Okano, T. Fukuda, A. Hirata, N. Takano, T. Tsukada, M. Hozawa and N. Imaishi, J. Crystal Growth 109 (1991) 94.

[12] M.F. Grant, A. Donaldson, D.R. Gibson and M. Wale, Opt. Eng. 27 (1988) 2.

[13] D.H. Auston et al., Appl. Optics 26 (1991) 211.

[14] Reports of LN Crystal Committee in Japanese Optical Industry, 1992.

[15] K. Shimamura, M. Timoshechkin, T. Sasaki, K. Hoshikawa and T. Fukuda, J. Crystal Growth 128 (1993) 1021.

[16] V.I. Chani, K. Shimamura, K. Inoue, T. Fukuda and K. Sugiyama, J. Crystal Growth 132 (1993) 173.

[17] W. Lin and D.W. Hill, in: Silicon Processing, ASTM STP 804 (1983) 24.

[18] S. Kan, M. Sakamoto, Y. Okano, K. Hoshikawa and T. Fukuda, J. Crystal Growth 119 (1992) 215.

[19] K. Kitamura, J.K. Yamamoto, N. Iyi, S. Kimura and T. Hayashi, J. Crystal Growth 116 (1992) 327.

[20] Y. Furukawa, M. Satoh and K. Kitamura, Jpn. J. Crystal Growth 18 (1991) 64.

[21] S. Kan, M. Sakamoto, Y. Okano, K. Hoshikawa and T. Fukuda, J. Crystal Growth 128 (1993) 915.

[22] S. Kan, M. Sakamoto, Y. Okano, K. Hoshikawa, T. Fukuda, O. Oguri and T. Sasaki, Jpn. Soc. Appl. Phys. & Rel. Soc. (The 39th Extended Abstracts), (1992) 241.

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

[24] M. Hashimoto, D.H. Yoon, T. Fukuda and T. Sasaki, Jpn. Soc. Appl. Phys. & Rel. Soc. (The 40th Extended Abstracts), (1993) 222.

[25] H. Machida, K. Hoshikawa and T. Fukuda, J. Crystal Growth 128 (1993) 829.

[26] H. Machida, K. Hoshikawa and T. Fukuda, Jpn. Soc. Appl. Phys. & Rel. Soc. (The 40th Extended Abstracts), (1993) 226.

[27] K. Shimamura, H. Kiyoku, N. Kodama and T. Fukuda, Jpn. J. Crystal Growth 20 (1993) 128.

[28] R.S. Feigelson, J. Crystal Growth 79 (1986) 669.

[29] N. Ohnishi and T. Yao, Jpn. J. Appl. Phys. 28 (1989) L278.

[30] H. Oguri, H. Yamamura and T. Orito, J. Crystal Growth 110 (1991) 669.

[31] D.H. Yoon, N. Ohnishi and T. Fukuda, J. Crystal Growth (to be published).
[32] D.H. Yoon, M. Hashimoto and T. Fukuda, Jpn. J. Appl. Phys. (to be published).
[33] T. Gotoh, S. Fukuda and T. Yamashiki, The Fifth Toyota Conference, Nonlinear Optical Materials (1991) 26.
[34] D.H. Yoon, M. Hashimoto and T. Fukuda, Jpn. J. Crystal Growth 20 (1993) 185.