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Optical properties of potassium lithium niobate single crystal grown by TSSG method

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TSSG법에 의해 육성한 KLN단결정의 광학적 성질

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Abstract Large size potassium lithium niobate (KLN) crystals with dimensions of 8 × 6 × 2 mm^3 were grown by the top-seeded solution growth (TSSG) method. The extraordinary refractive index n_e at the second harmonic frequency for KLN crystal depends on the composition and decreases in this crystal due to the large Li content. KLN crystal was characterized by observation in UV-VIS spectrometry. It is transparent from the ultraviolet to infrared spectral regions that the transmission limit and cut-off wavelength are about 350 and 380 nm.

요 약 대형 단결정 육성을 위해 TSSG법에 의해 결정성장을 시도, 8 × 6 × 2 mm^3 크기의 KLN 결정을 육성하였다. 육성된 결정으로부터 제2고주파 발생영역에서의 이상광 굴절률 n_e는 조성에 따라 변화하며, 조성중의 Li량이 많을수록 감소함을 알았다. 또한 광투과 특성평가에 의해 자외영역으로부터 적외영역에 걸쳐 광이 투과함을 관측하였으며, 자외영역에서의 투과 한도는 350 nm, cut-off 파장은 380 nm임이 확인되었다..

1. Introduction

Potassium lithium niobate (KLN) exhibits large longitudinal pyroelectric and piezoelectric effects very useful for SAW and photorefractive applications [1]. Further, the electro-optical coefficients of KLN are significantly larger than those of $LiNbO_3$ [2]. It can be seen that it is difficult to grow good quality crystals from incongruent compositions because of compositional changes up to 63 mol% [3] and ths generation of other phase (KNb_3O_8) near 64 mol% [4].

KLN with tetragonal bronze structure (point group 4 mm) is optically negative, and has type I phase matching [5]. Thus, the effective nonlinear optical coefficient for type I phase matching is given by $d_{eff} = d_{31} \sin(\theta)$, where the angle θ is that between the crystal c-axis and the propagation vector of the fundamental pump laser radiation. Very successful second harmonic generation (SHG) of blue light has been obtained in KLN crystals [6] grown by the micro pulling down (μ-PD) method. The compositional range of the tetragonal phase has been emphasized [7]. However, few papers are discussed optical properties such as refractive index and absorption coefficient relevant to SHG characteristics.

In this paper the theory and measurement of optical properties are described. Also, we discuss efforts to grow high quality and large size KLN crystals using the top-seeded solution growth (TSSG) method.

2. Experimental

A TSSG equipment, which is composed by

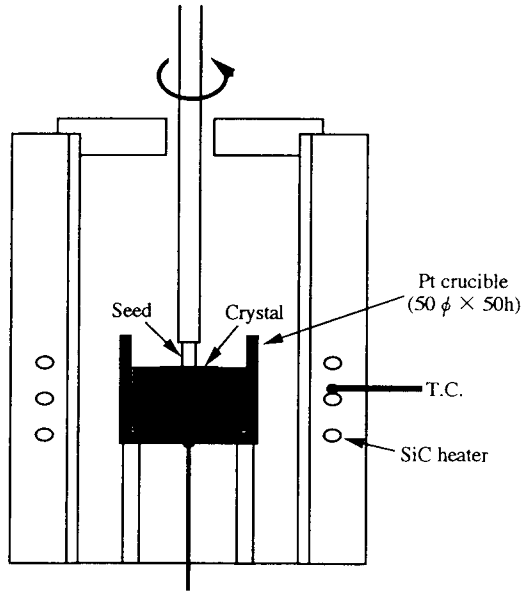

Fig. 1. Schematic diagram of the TSSG apparatus.

a resistance furnace of SiC heater with a temperature gradient of 5℃/cm, and a Pt crucible (50 mmϕ × 50 mmH) and driving system as shown in Fig. 1, was used for growth process. The raw materials are prepared by mixing and sintering (920℃, 5 h). The composition was fixed by a mixture of 33 mol% K_2O, 23 mol% Li_2O and 44 mol% Nb_2O_5 because of a decrease in K_2O content during grwoth [4]. A seed was cut from an as-grown Czochralski (CZ) KLN crystal [8].

During the growth process, the preheated seed was lowered into a melt at a temperature 20℃ above the melting point, and rotated at a rate of 30 rpm. Then the temperature was lowered step by step to the melting point. This process was employed for 1 ~ 2 days. After that, the temperature was lowered less than 0.5℃/day during the crystallization stage. After the crystal growth the crystal was pulled out from the flux. The temperature was lowered at rates of 4.8℃/h between 600℃ and 400℃ and 18℃/h in other ranges. Special attention was necessary when the crystal was cooling near the phase transition temperature.

The optical transmission of KLN has been measured by a UV-VIS spectrophotometer between 200 and 1100 nm. The sample used was cut parallel to the (110) face and polished mechanically at both faces to a thickness of 1 mm. The refractive indices were obtained by the prism method [9]. Measurements were made with both a tungsten lamp (375 ~ 700 nm) and a semiconductor laser (> 700 nm) source.

3. Results and discussion

When a KLN solid solution crystal is grown by the temperature lowering method, its composition along the growth axis will change from the top to the bottom. Therefore, we tried to use a large crucible and a large amount of starting material relative to the crystal size to obtain relatively homogeneous samples.

Figure 2 shows an as-grown KLN crystal along the [110] orientation. Crack-free and transparent crystals were obtained with dimensions of 8 × 6 × 2 mm^3. A distinct facet plane was obtained, having a rectangular shape elongated along the c-axis. We think that the stability of the temperature gradient (5℃/cm) and low solidification fraction ($g < 0.01$) were responsible for the prevention of cracks. Growth of [001] oriented crystals were also attempted, but crack-free samples were not obtained. All crystals showed fractures normal to the c-axis comparison with the result of CZ growth [10].

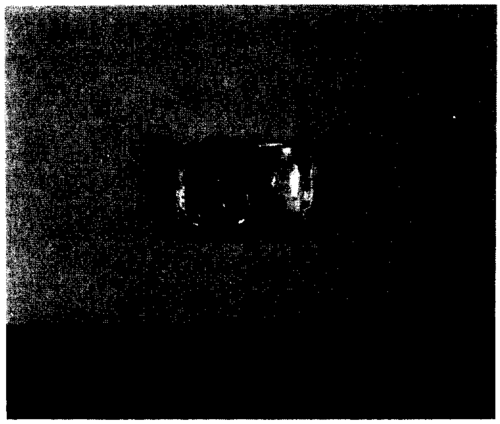

Fig. 2. As-grown KLN crystal with [110] orientation, along the growth axis.

For light polarized perpendicular to the optic axis, the material appears isotropic and the index of refraction is independent of the direction of propagation. This angularly independent index is the ordinary index of refraction (n_0). If light is not polarized perpendicular to the optic axis, the index of refraction varies as a function of the direction of propagation. The angularly sensitive index is the extraordinary index of refraction (n_e).

The refractive indices were obtained by the prism method using the TSSG crystal $K_3Li_{2-x}Nb_{5+x}O_{15+2x}$ with $x = -0.27$ ($Li = 2.27$) (determined by chemical analysis [11]), as shown in Table 1. Nonlinear optical properties are closely tied to the refractive index. KLN is a negative uniaxial crystal, and the phase matching condition is $n_o(\omega) = n_e(2\omega)$. A propagation direction might be found in which the ordinary index at the fundamental frequency $n_o(\omega)$ is equal to the extraordinary index at the second harmonic frequency $n_e(2\omega)$.

In Fig. 3 the wavelength dependence of the refractive indices of a KLN crystal is compared to Philips data for KLN (Li = 1.97) [2]. The wavelength dependence of the refractive index was determined by a fit to the Sellmeier equation [12] written by,

$$n = \{A + B/(\lambda^2 - C) - D \times \lambda^2\}^{1/2} \qquad (1)$$

where n is refractive index, λ is wavelength, and A, B, C, and D are constants,

Table 1
Refractive index of KLN

λ (nm)	n_o	n_e
1337	2.192	2.092
700	2.262	2.133
600	2.263	2.135
575	2.271	2.142
550	2.276	2.145
525	2.288	2.153
500	2.300	2.158
475	2.309	2.166
450	2.325	2.175
425	2.341	2.187
400	2.361	2.201
375	2.387	2.215

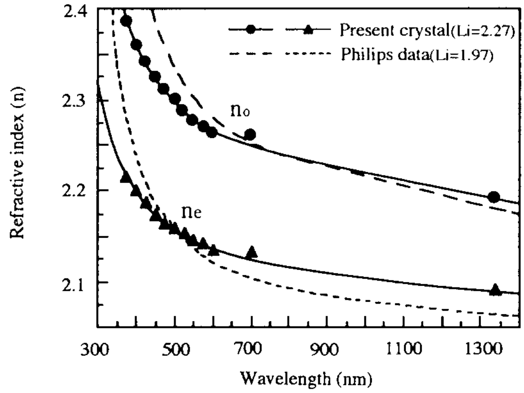

Fig. 3. The wavelength dependence of the refractive index of a KLN crystal.

represented in Table 2 for the TSSG crystal (Li = 2.27). In comparing refractive indices for a KLN crystal with those for another composition, it is important to consider that the ordinary refractive index n_o is almost independent on the composition, whereas the extraordinary refractive index n_e strongly depends on composition and decreases due to the large Li content for the phase matching condition.

Figure 4 presents the transmittance curve of this crystal. It can be seen that KLN is transparent from the ultraviolet to infrared region, with a transmissivity of about 70 %. The transmission limit and cut-off wavelength are about 350 and 380 nm, respectively. The transmission region constrains

Table 2
The constants of Sellmeier equation

	A	B	C	D
n_o	4.973	0.067	0.051	0.114
n_e	4.449	0.046	0.042	0.054

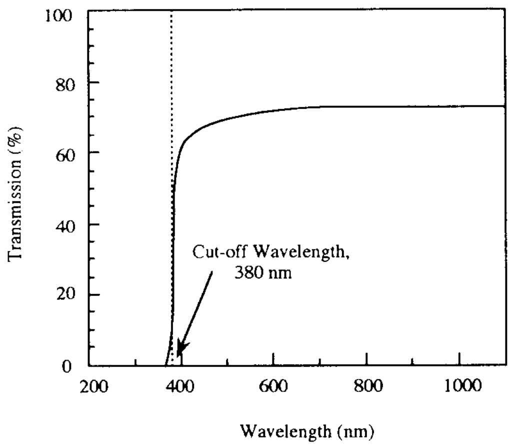

Fig. 4. Transmission curve of KLN grown by TSSG method.

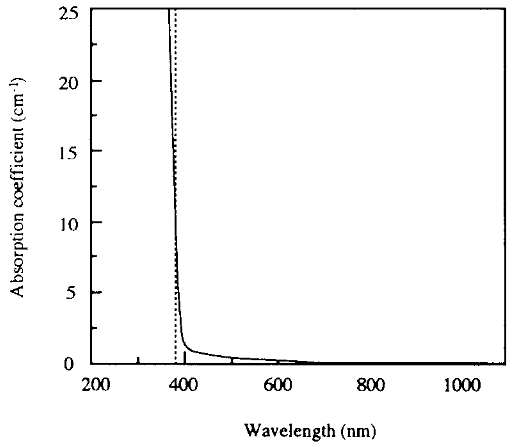

Fig. 5. Absorption coefficient of KLN grown by TSSG method.

the spectral range of SHG generation wavelengths. Therefore, it is expected that the phase matching is possible until the ultraviolet region (about 350 nm) in KLN.

The transmissivity is also dependent on the refractive index and the reflectivity. From the results of Fig. 4 and Table 1, we obtain the absorption coefficients because the optical behavior is determined by the refractive index n. The reflectivity (R) and the transmissivity (T) of a plate at normal incidence are given by Cardona [13],

$$R = (n-1)^2/(n+1)^2 \quad (2)$$

$$\begin{aligned} T &= (1-R)^2 e^{-\alpha d}/(1-R^2)\, e^{-2\alpha d} \\ &= (1-R)^2/(1-R^2) = (1-R)/(1+R), \\ &\quad \text{if } \alpha d \ll 1 \\ &= (1-R)^2 e^{-\alpha d}, \text{ if } \alpha d \gg 1 \end{aligned} \quad (3)$$

where n is the refractive index, α is the absorption coefficient and d is the sample thickness. The absorption coefficient α, as shown in Fig. 5, is obtained from equation 3,

$$\alpha = (-1/d) \ln \{T/(1-R)^2\} \quad (4)$$

The absorption coefficient is nearly zero until the wavelength of about 700 nm, and increases in the short wavelength region under the wavelength 700 nm. Absorption under the wavelength 700 nm is considered to cause the distribution of inhomogeneous refractive index and the exist of crystal color in a TSSG KLN crystal.

4. Summary

Using the TSSG method, crack-free KLN crystals with dimensions of $8 \times 6 \times 2$ mm^3 have been obtained. A distinct faceting plane with a rectangular shape elongated along the c-axis has been obtained. Refractive indices for KLN crystal can be considered that the ordinary refractive index n_o is almost independent on the composition, whereas the extraordinary refractive index n_e strongly depends on composition. KLN is transparent from the ultraviolet to infrared spectral regions. The transmission limit and cut-off wavelength are about 350 and 380 nm, respectively. Also, the absorption coefficient in the short wavelength region increases due to the inhomogeneous refractive index and the crystal color in a TSSG KLN crystal.

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