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Journal of Crystal Growth 257 (2003) 161–164

JOURNAL OF CRYSTAL GROWTH

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Growth and optical properties of Zn:KLN single crystal

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Received 11 May 2003; accepted 1 June 2003
Communicated by M. Schieber

Abstract

KLN and Zn:KLN crystal were grown by the Czochralski method along the [1 0 0] orientation. All crystals were transparent from 380 to 760 nm by the ultraviolet-visible transmittance spectra of KLN and Zn:KLN crystals. Compared with KLN crystals, the transmittance of Zn:KLN increased and its absorption edge shifted to the ultraviolet band. The infrared transmittance spectra of KLN and Zn:KLN crystals were measured. The replacement of Zn^{2+} in the KLN crystals was analyzed. Laser lights of 420 and 405 nm were obtained through noncritical phase-matching second harmonic generation for KLN and Zn:KLN crystal, respectively. A shorter wavelength output was obtained for Zn:KLN crystal. The frequency efficiency for all crystals reached 6–7%.

PACS: 78.20−e

Keywords: A1. Infrared transmittance spectra; A1. Second harmonic generation; A1. Ultraviolet-visible transmittance spectra; B1. Zn:KLN crystal

1. Introduction

Potassium lithium niobate single crystal ($K_3Li_{2-x}Nb_{5+x}O_{15+x}$, KLN) is a promising material for second harmonic generation (SHG) blue lasers since it has a large nonlinearity, high damage threshold, low optical loss and wide noncritical phase-matching properties at room temperature [1–4]. It has been reported that a phase-matching wavelength can be adjustable at room temperature in the range of 790–920 nm by varying the lithium/niobate ratio of the starting melt [5]. In addition, it has applications in the surface acoustic wave and piezoelectric devices [6]. However, some of its undesirable properties have limited its practical applications, for example, KLN crystal cracks easily and the lithium content in the as-grown crystal deviates from stoichiometry [7]. KLN crystal is a transparent oxide with a tetragonal tungsten bronze structure, space group p4bm and point group 4 mm. It can be grown by many methods, such as Kyropoulos, Czochralski, top seeded solution growth, micro-pulling-down and laser heated pedestal growth.

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doi:10.1016/S0022-0248(03)01420-9

However, high-quality KLN crystal with centimeter dimensions and good properties is very difficult to obtain due to its incongruent melt. In our previous studies, it was shown that crystal growth is easier by doping [8]. In order to obtain a KLN crack free crystal with high quality and a shorter wavelength, Zn:KLN was successfully grown by the Czochralski method in an air atmosphere in our laboratory.

2. Experimental procedure

KLN and Zn:KLN crystal were grown by the Czochraski method along the [1 0 0] orientation. The raw materials were K_2CO_3, Li_2CO_3, Nb_2O_5 and ZnO with a purity of 99.99%. The melt compositions of K_2CO_3, $LiCO_3$, Nb_2O_5 were 35, 22 and 43 mol% for both pure and doped KLN crystal according to the Li_2O–K_2O–Nb_2O_5 phase diagram studied by Scott et al. [9], respectively. The doping level of Zn for Zn:KLN crystal was 0.1 wt%.

The raw materials were placed in a platinum crucible with the diameter of 70 mm and height of 30 mm. They were heated to 800°C and soaked for 2 h to remove CO_2, and then soaked for 12 h at 1100°C. The seed orientation was [1 0 0]. The growth rate was 0.8–1 mm/h, with a temperature gradient of 30°C/cm and a rotation rate of 15 rpm. The crystal was cut into samples with dimensions of $3 \times 8 \times 6\,\mathrm{mm}^3$ ($a \times b \times c$). The crystal was poled into a single ferroelectric domain along the c-axis. The polarization current was $1\,\mathrm{mA/cm}^2$. The polarization temperature for KLN and Zn:KLN crystal were 435°C and 425°C, which was slightly higher than the Curie temperatures. The Curie temperatures of KLN and Zn:KLN crystal were 420°C and 410°C according to differential thermal analysis, respectively.

The crystal structure was measured by a D/Max-rB X-ray powder diffractometer at room temperature. The crystal ultraviolet-visible and infrared transmittance spectra were measured by a CARY 2390 ultraviolet-visible spectrophotometer and an infrared spectrophotometer. SHG properties were studied at room temperature using a (Al, As) Ga laser diode.

3. Results

Fig. 1 shows the photographs of as-grown crystals.

The X-ray diffraction patterns of KLN and Zn:KLN crystals showed that all crystals exhibited the tetragonal bronze structure. Compared with pure KLN, there was no new peak for Zn doped KLN. This showed that the Zn dopant entered the crystal lattice. However, the size of the Zn^{2+} ion was different from that of K^+, Li^+ and Nb^{5+}, which resulted in a change of the lattice size. So the location and relative intensity of peaks of Zn:KLN were changed.

Fig. 2 showed the ultraviolet-visible transmittance spectra of KLN and Zn:KLN crystals. All crystals were transparent from 380 to 760 nm. Compared with KLN crystals, the transmittance of Zn:KLN increased and its absorption edge shifted to the ultraviolet band. The absorption of KLN crystals was determined by the minimum energy of valence electrons of O^{2-} transiting from

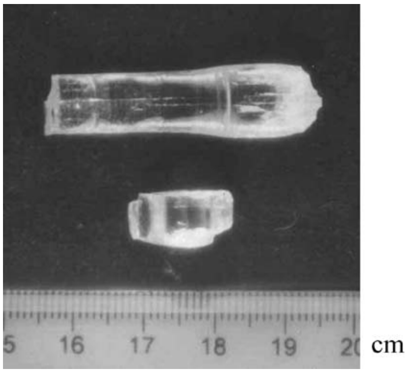

Fig. 1. Photograph of (a) Zn:KLN and (b) KLN crystal.

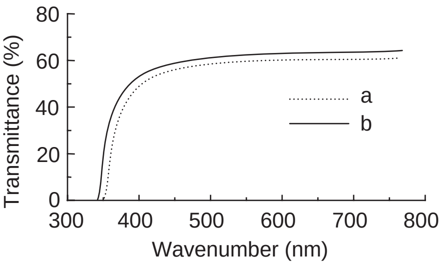

Fig. 2. Ultraviolet-visible transmittance of (a) KLN and (b) Zn:KLN crystal.

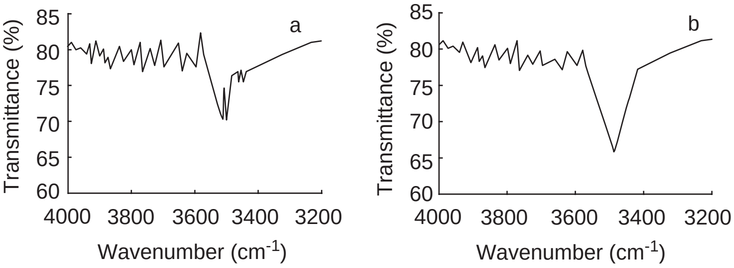

Fig. 3. Infrared transmittance of (a) KLN and (b) Zn:KLN crystal.

the valence band to the conduction band, which was composed of the valence electron orbit of K^+ and Li^+, and the 5p and 5s orbits of Nb^{5+} [10]. So the valence electronic state of O^{2-} directly affected the location of the absorption edge. There are different numbers of O^{2-} around K^+, Li^+ and Nb^{5+} in KLN crystals. The energy required by electron transition would increase if the capability of the dopant to attract the electron were stronger than that of the replaced ions. Thus, the absorption edge shifted to ultraviolet band. Otherwise, the absorption edge shifted to infrared band if the capability of the dopant to attract the electron were weaker than that of the replaced ions. The capability of the Zn ion to attract electrons was stronger than that of Li^+ and K^+, but weaker than that of Nb^{5+}. The absorption edge of Zn:KLN shifted to ultraviolet band, and the Zn ion substituted on the sites of K^+ or Li^+.

Fig. 3 showed the infrared transmittance spectra of KLN and Zn:KLN crystals. There were peaks at around 3515 and 3456 cm^{-1} in the KLN crystal. This identified the presence of hydrogen in the KLN crystal, which was similar to that in the $LiNbO_3$ crystal. OH^- would exist in the KLN crystal grown by the Czochraski method in air and would compensate the deviation of electrical charges. The two at around 3456 cm^{-1} peaks of these peaks resulted from the vibration of the H_2O molecule, which was not considered. The other two peaks (one at 3519 cm^{-1}, the other at 3504 cm^{-1}) at 3515 cm^{-1} were split by the same peak, which resulted from the stretch vibration of OH^- ions in the crystal. The splitting of absorption peak might be due to the different ions around OH^-. The electronic cloud of OH^- around Nb^{5+} strongly was close to Nb^{5+} because the capability of Nb^{5+} to attract electrons was stronger. The O–H bond was weakened, and the energy of its stretch vibration became lower. Thus, the absorption peak of the OH^- ion around Nb^{5+} was located at lower wave numbers. In contrast, the interaction between K^+, Li^+ and OH^- ions around them was weaker because the capability of K^+ and Li^+ to attract electrons was weaker, and the O–H bond was strengthened. Thus, the peak of OH^- around K^+ and Li^+ ions was located at the higher wave numbers. Therefore, we could analyze the replacement of Zn^{2+} in the KLN crystals according to the change of their infrared transmittance spectra.

Compared with KLN crystal, only one peak existed at 3486 cm^{-1} in Zn:KLN (the absorption peak of H_2O molecule is at 3454 cm^{-1}). It was suggested that the Zn ions replaced K^+ or Li^+ when they entered the lattice of the crystal. The capability of Zn ions to attract electrons was stronger than that of K^+ or Li^+, so that the O–H bond was weakened when Zn ions replaced K^+ and Li^+ ions, and the OH^- energy of vibration decreases. Thus, the absorption peak of this kind of OH^- shifted to the infrared band, covering the absorption peak of OH^- around Nb^{5+}. The analysis results for Zn replacement site by infrared transmittance spectra were well identified with that by ultraviolet-visible spectra.

Laser lights of 420 and 405 nm were obtained through noncritical phase-matching SHG of a (Al, As)Ga laser diode at a wavelengths of 840 nm and 810 nm for KLN and Zn:KLN crystal, respectively, and for Zn:KLN crystal, a shorter wavelength output was obtained. The frequency efficiency for all crystals reached 6–7%.

Acknowledgements

This paper was sponsored by the National Science Foundation (No.50202005) and National Research Fund for Fundamental Key Projects of China "the Fundamental Research of Super-high density, Super-high speed Optical Information Storage and Process (No.19990330) of China".

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