

Influence of Zn doping on the optical properties of KLN single crystal

Y. J. GUO

Department of Chemistry Engineering, Harbin Engineering University, Harbin 150001, People's Republic of China

Y. H. XU, C. H. YANG

Department of Applied Chemistry and Electro-Optics Research Center, Harbin Institute of Technology, Harbin 150001, People's Republic of China
E-mail: yangchh69@yahoo.com

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 [1–3]. 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 [4]. In addition, it has applications in the surface acoustic wave and piezoelectric devices [5]. 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 [6]. 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, micropulling-down and laser heated pedestal growth. 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 made easier by doping [7]. 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.

KLN and Zn:KLN crystals were grown by the Czochralski method along the [100] orientation. The raw materials were K_2CO_3 , $LiCO_3$, Nb_2O_5 , and ZnO with a purity of 99.99%. According to the Li_2O - K_2O - Nb_2O_5 phase diagram studied by Scott *et al.* [8], the melt compositions of K_2CO_3 , $LiCO_3$, Nb_2O_5 were 35, 22, and 43 mol% for both pure and doped KLN crystals, respectively. The doping level of Zn for Zn:KLN crystal was 0.1 wt%.

The raw material was placed in a platinum crucible of dimensions 70 mm diameter and 30 mm height and heated to 800 °C for 2 hr to remove CO_2 . Then it was soaked at 1100 °C for 12 hr. The growth rate was 0.8–1 mm/hr, with a temperature gradient of 30 °C/cm and a rotation rate of 15 rpm. The seed orientation was [100]. The crystal was cut into samples with dimensions of $3 \times 8 \times 6$ mm ($a \times b \times c$). The crystal was poled into a single ferroelectric domain along the c -axis, with a polarization current of 1 mA/cm². The polarization tem-

peratures for KLN and Zn:KLN crystals were 435 and 425 °C, respectively, slightly higher than the Curie temperatures. The Curie temperatures of KLN and Zn:KLN crystals were 420 and 410 °C, respectively, according to differential thermal analysis. Fig. 1 shows the photographs of as-grown crystals.

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. Second harmonic generation (SHG) properties were studied at room temperature using an (Al, As)Ga laser diode. Room-temperature Raman spectra were measured on a Renishaw MKI 2000 Raman spectrometer with an incident slit width of 100 μ m, using a 100-mw argon ion laser at 632.8 nm.

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 were no new peaks for Zn-doped KLN. This showed that the Zn dopant entered the crystal lattice. However, the location and relative intensity of the peaks of Zn:KLN were changed because 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.

Fig. 2 shows the ultraviolet–visible transmittance spectra of KLN and Zn:KLN crystals. All crystals were transparent from 380 to 760 nm. Compared with the 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 the valence electrons of O^{2-} transiting from the valence band to the conduction band, which is composed of the valence electron orbit of K^+ and Li^+ , and the 5p and 5s orbits of Nb^{5+} [9]. 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 the ultraviolet band. Otherwise, the absorption edge shifted to the infrared band if the capability of the dopant to attract the electron were weaker than that of the replaced ions. The capability of

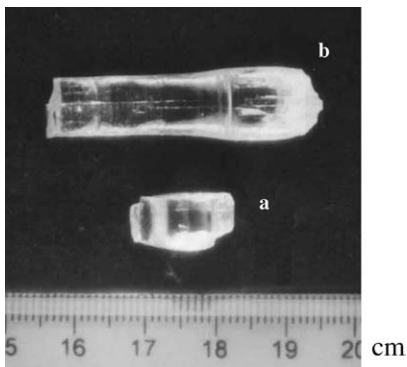


Figure 1 Photograph of (a) Zn:KLN and (b) KLN crystals.

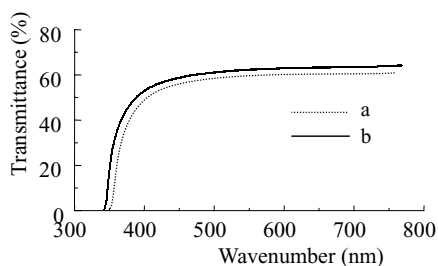


Figure 2 Ultraviolet–visible transmittance of (a) KLN and (b) Zn:KLN crystals.

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 the ultraviolet band, and the Zn ion substituted on the sites of K^+ or Li^+ .

Fig. 3 shows the infrared transmittance spectra of KLN and Zn:KLN crystals. In the KLN crystal, there were peaks at around 3515 and 3456 cm^{-1} . This identified the presence of hydrogen in the KLN crystal, which was similar to that in the LiNbO_3 crystal. OH^{-1} would exist in the KLN crystal grown by the Czochraski method in air and would compensate the deviation of electrical charges.

The two peaks at around 3456 cm^{-1} 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^{-1} ions in the crystal. The splitting of absorption peak might be due to the different ions around OH^{-1} . The electronic cloud of OH^{-1} around Nb^{5+} was strongly 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. So, the absorption peak of the OH^{-1} ion around Nb^{5+} was located at lower wavenumbers. In contrast, the interaction between K^+ , Li^+ , and OH^{-1} 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^{-1} around K^+ and Li^+ ions was located at the higher wavenumbers. Therefore, we could analyze the replacement of Zn^{2+} in the KLN crystals according to the change of their infrared transmittance spectra.

Compared with the KLN crystal, only one peak existed at 3486 cm^{-1} in Zn:KLN (the absorption peak of H_2O molecule was 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^{-1} energy of vibration decreased. The absorption peak of this kind of OH^{-1} shifted to the infrared band, covering the absorption peak of OH^{-1} around Nb^{5+} . The analysis results for Zn replacement site by infrared transmittance spectra were well identified with that by ultraviolet–visible spectra.

The KLN single crystal has a completely filled TB-type structure with the filling formula $(\text{A}_1)_2(\text{A}_2)_4(\text{C})_4(\text{B}_1)_2(\text{B}_2)_8(\text{C})_{30}$. There are two chemical formulas of the KLN in a unit cell, a total of 50 atoms. Based on the factor group theory, the irreducible representation of the lattice vibration of the KLN crystal is as follows [10]:

$$21\text{A}_1 + 16\text{A}_2 + 15\text{B}_1 + 20\text{B}_2 + 39\text{E}$$

where $\text{A}_1 + \text{E}$ constituted translation modes. The pure vibration modes were

$$20\text{A}_1(\text{R, IR}) + 15\text{B}_1(\text{R}) + 20\text{B}_2(\text{R}) + 38\text{E}(\text{R, IR})$$

where R and IR represented Raman and infrared active, respectively. It was clear that the theoretically observable Raman peaks were not more than 93 in number. There were ten $[\text{NbO}_6]^{7-}$ octahedral ions in a primitive cell of the KLN crystal. Their vibration frequencies were not obviously different from each other although the $[\text{NbO}_6]^{7-}$ octahedral ions were distorted to a different degree, resulting in the intensive overlap of peaks

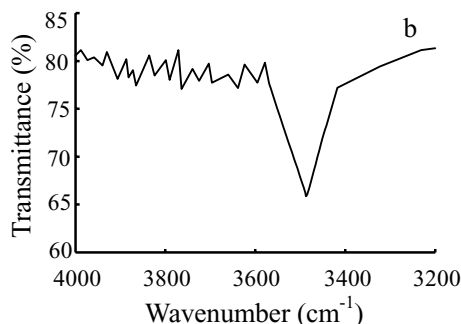
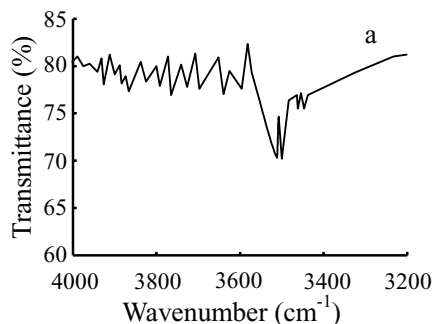


Figure 3 Infrared transmittance of (a) KLN and (b) Zn:KLN crystals.

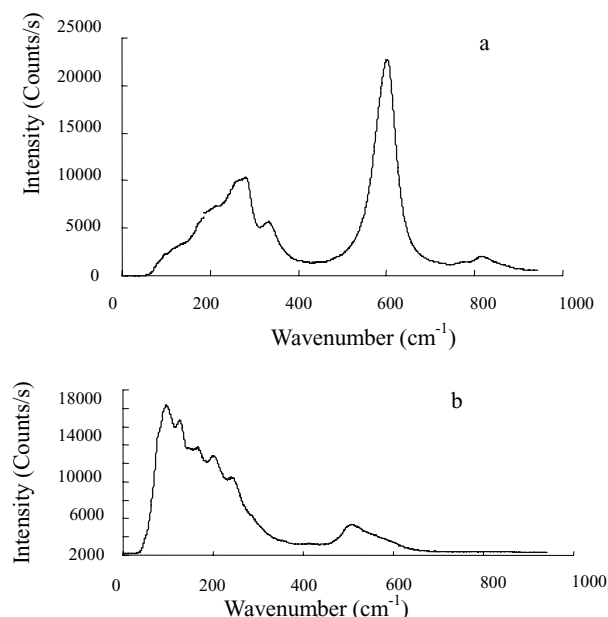


Figure 4 Raman spectra recorded for the symmetry species E with the scattering geometry: (a) X(ZZ)Y and (b) X(YZ)Y in KLN and Zn:KLN crystals.

and forming a multi-peak envelop with an irregular shape. The observable Raman peaks in the experiments were much fewer in number than those calculated by the group theory.

Fig. 4 shows a typical Raman spectrum of the crystal with the $[\text{NbO}_6]^{7-}$ octahedral ions, recorded in the pure and doped KLN crystals at room temperature in a frequency range of 50 to 1000 cm^{-1} , corresponding to the symmetry species A_1 with the scattering geometry X(ZZ)Y and the symmetry species E with the scattering geometry X(YZ)Y. It was found that the vibration modes could be divided into two groups, one was from 50 to 400 cm^{-1} , the other from 400 to 900 cm^{-1} , which is similar behavior to some crystals with octahedral ions, such as LiNbO_3 , LiTaO_3 , etc. But the vibration modes were too intensive from 50 to 900 cm^{-1} to identify. However, it was clear that the peaks with lower frequencies were resulted from the vibration of octahedral ions corresponding to metal cations, and the peaks with higher frequencies were resulted from the internal vibration of distorted octahedral ions. Compared with the Raman peaks with the scattering geometry X(YZ)Y, the intensities of Raman peaks at higher wavenumbers with the scattering geometry X(ZZ)Y increased strongly; in

contrast, the peaks' intensities at lower wavenumbers decreased.

On the other hand, the Raman spectra of Zn:KLN were similar to that of KLN crystal. There were no new scattering peaks, indicating that dopants have entered the lattice of the crystal, replacing other cations, rather than entering the space of lattice. However, compared with the KLN crystal, the intensity of the peaks of Zn:KLN crystals slightly decreased.

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

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