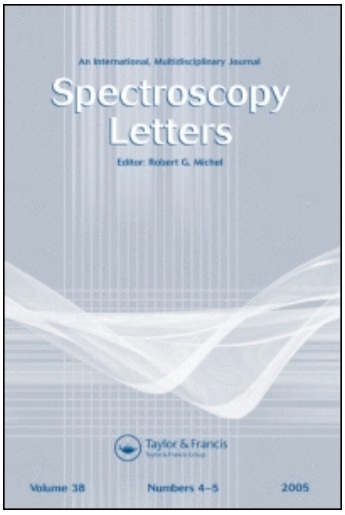

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RAMAN AND INFRARED TRANSMITTANCE SPECTRA OF DOPED KLN CRYSTAL

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RAMAN AND INFRARED TRANSMITTANCE SPECTRA OF DOPED KLN CRYSTAL

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ABSTRACT

Raman and Infrared Transmittance Spectra of KLN and Doped KLN Crystal have been carried out. The Raman spectra of KLN and doped KLN crystal were basically alike, which justified the fact that the ions of impurities entered the lattice by replacement of original ions of KLN crystal. The result of Infrared Transmittance Spectra showed that, compared with the KLN crystal, the number and site of absorption peaks of OH^{-1} vibration in doped KLN changed, only one peak existed in Fe:KLN and Cu:KLN, which located at higher wave numbers $3520\,cm^{-1}$ and lower wave numbers $3488\,cm^{-1}$ respectively, while, there existed two peaks in KLN at $3519\,cm^{-1}$ and $3504\,cm^{-1}$ respectively. It suggested that Fe cation replaced Nb cation, and Cu cation replaced K cation when they entered the lattice of crystal.

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Key Words: Doped KLN crystal; Raman spectra; Infrared transmittance spectra

INTRODUCTION

During recent years, many related studies[1–4] have suggested that the tetragonal tungsten bronze type potassium lithium niobate(KLN) single crystal is a potentially useful material for nonlinear optical applications because it is remarkably stable to intense laser radiation and has excellent second harmonic generation(SHG) and secondary electro-optic effects. Specifically it is expected to be a useful material for the blue laser radiation by SHG in a wavelength range from 790 to 920 nm, which takes place at room temperature and enables noncritical phase matching[5]. Also, it has found applications in the surface acoustic wave and piezoelectric devices. However, some of its undesirable properties have limited its practical applications. A big problem is that the KLN crystal is easy to crack when cooling through the paraelectric-ferroelectic phase transition. The useful bulk of centimeter dimensions was not obtained due to cracks induced by the change of composition and structural characteristics. Also, the change of composition in KLN crystal affects the electro-optical and nonlinear optical effects because the considerable change of the birefringence with variation of lithium content[6]. Recently, the very thin acicular KLN crystal grown via the micro-pulling-down method[4,7] can provide some practical applications. In this paper, we have grown the KLN, Fe:KLN and Cu:KLN crystals and studied their spectral properties. To our knowledge, it's the first time the spectral properties of the Cu:KLN crystal have been reported in detail.

EXPERIMENTAL

The crystals were grown via the Czochraski method. The starting composition was fixed by the mixture of K_2CO_3:Li_2CO_3: Nb_2O_5 = 33:23:24 mol%[8] in order to grow KLN crystal near the stochiometric composition($K_3Li_2Nb_5O_{15}$). The amount Fe_2O_3 and CuO was 0.05 mol% respectively, which was small, so the composition of K, Li and Nb was selected in the doped KLN as those in KLN crystals.

The crystals were grown under optimal technology conditions: temperature gradient of 28–32°C/cm, rotating rate of 10 rpm and pulling rate of 0.8 mm/h. The crystals as-grown along the [1 0 0] orientation were cubes about $7 \times 8 \times 30$ mm, but those grown along the [0 0 1] orientation were cylindrical, with a diameter of about 6 mm and a height of 20 mm. The color

of KLN, Fe:KLN and Cu:KLN crystals was pale-yellow, pale-brown and pale-green respectively. They were annealed at 800°C for 24 h to reduce residual stress formed during growth. The crystal structure was measured by a D/Max-rB x-ray powder diffractometer at room temperature. The result indicated that doped KLN crystals maintained the same structural characteristics as the pure KLN crystal, exhibiting tetragonal structure, but the lattice constants became a little smaller.

As mentioned above, the growth of crack-free KLN crystals of considerable size with required compositions is difficult. However, in our experiments, we found the growth of doped KLN crystals was easier than that of pure KLN.

The crystals were cut carefully, along a, b and c axes into samples with the size of about $1 \times 4 \times 4$ mm, then were optically polished. Room-temperature Raman spectra were measured on a Renishaw MKI 2000 Raman spectrometer with a incident slit width of 100 μm, using a 100-mw argon ion laser at 632.8 nm. Infrared transmittance spectra were obtained using an FT-IR spectrophotometer.

RESULTS AND DISCUSSION

Raman Spectra

The KLN single crystal has a completely filled TB type structure with the filling formula $(A_1)_2(A_2)_4(C)_4(B_1)_2(B_2)_8(C)_{30}$, the space group p4bm and point group 4 mm at room temperature.

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 representations of the lattice vibration of the KLN crystal are the following:[9]

$$21A_1 + 16A_2 + 15B_1 + 20B_2 + 39E$$

where A_1+E constitutes level modes, the pure vibration modes are:

$$20A_1(R, IR) + 15B_1(R) + 20B_2(R) + 38E(R, IR)$$

where R and IR represents Raman and Infrared active modes, respectively. It's clear that the theoretically observable Raman peaks are not more than 93 in number. In a primitive cell of the KLN crystal, there are ten $[NbO_6]^{7-}$ octahedral ions. Their vibration frequencies were not obviously different each other although $[NbO_6]^{7-}$ octahedral ions were distorted in different degree, resulting in the intensive overlap of peaks and forming muti-peaks envelop with irregular shape. Hence, in the experiments, the observable Raman peaks are much fewer in number than those calculated by the group theory.

Figures 1 and 2 show a typical Raman spectrum of the crystal with the $[NbO_6]^{7-}$ octahedral ions, recorded in the pure and doped KLN crystals at room temperature in a frequency range from 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 cm^{-1} to 400 cm^{-1}, the other from 400 cm^{-1} to 900 cm^{-1}, which was similar to some crystals with the octahedral ions, such as $LiNbO_3$, $LiTaO_3$, etc. But the vibration modes were too intensive from 50 cm^{-1} 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 resulted from the internal vibration of octahedral ions distorted. Compared with those in Raman for the symmetry species A, the values of peaks in Raman for the symmetry species E increased strongly, in contrast, the values of peaks with higher frequencies decreased.

On the other hand, the Raman spectra of doped KLN were similar to that of KLN crystal. There was no new scattering peaks, indicating that dopants have entered the lattice of crystal by replacing other cations, other than entered the space of lattice. However, compared with KLN crystal, the intensity of peaks of doped crystals changed.

Infrared Transmittance Spectra

Figure 3 shows the Infrared transmittance spectra of KLN and doped KLN crystals. In KLN crystal, there existed a peak at 3515 cm^{-1} and 3456 cm^{-1} respectively, which actually spilt into two peaks. This identified that hydrogen existed in KLN crystal, which was similar to that in $LiNbO_3$ crystal. OH^{-1} would exist in the KLN crystal grown via the Czochraski method in air and compensated the deviation of electric charge. In these two peaks, one peak at 3456 cm^{-1} resulted from the vibration of H_2O molecule was not considered, the other at 3515 cm^{-1} was resulted from the stretch vibration of OH^{-1} ions in crystal. As mentioned above, it split into two peaks, one at 3519 cm^{-1}, the other at 3504 cm^{-1}. The splitting of absorption peak might be due to the different circumstance around OH^{-1}. The electronic cloud of OH^{-1} around Nb^{5+} strongly tended to Nb^{5+} because the capability of Nb^{5+} attracting electron was stronger. The O-H bond was weakened, and the energy of its stretch vibration became lower. Thus, the absorption peak of OH^{-1} ion around Nb^{5+} located at the lower wave numbers. In contrast, the function between K^+, Li^+ and OH^{-1} ions around them was weaker because the capability of K^+ and Li^+ attracting electron was weaker, and the O-H bond was strengthen. Thus, the peak of OH^{-1}

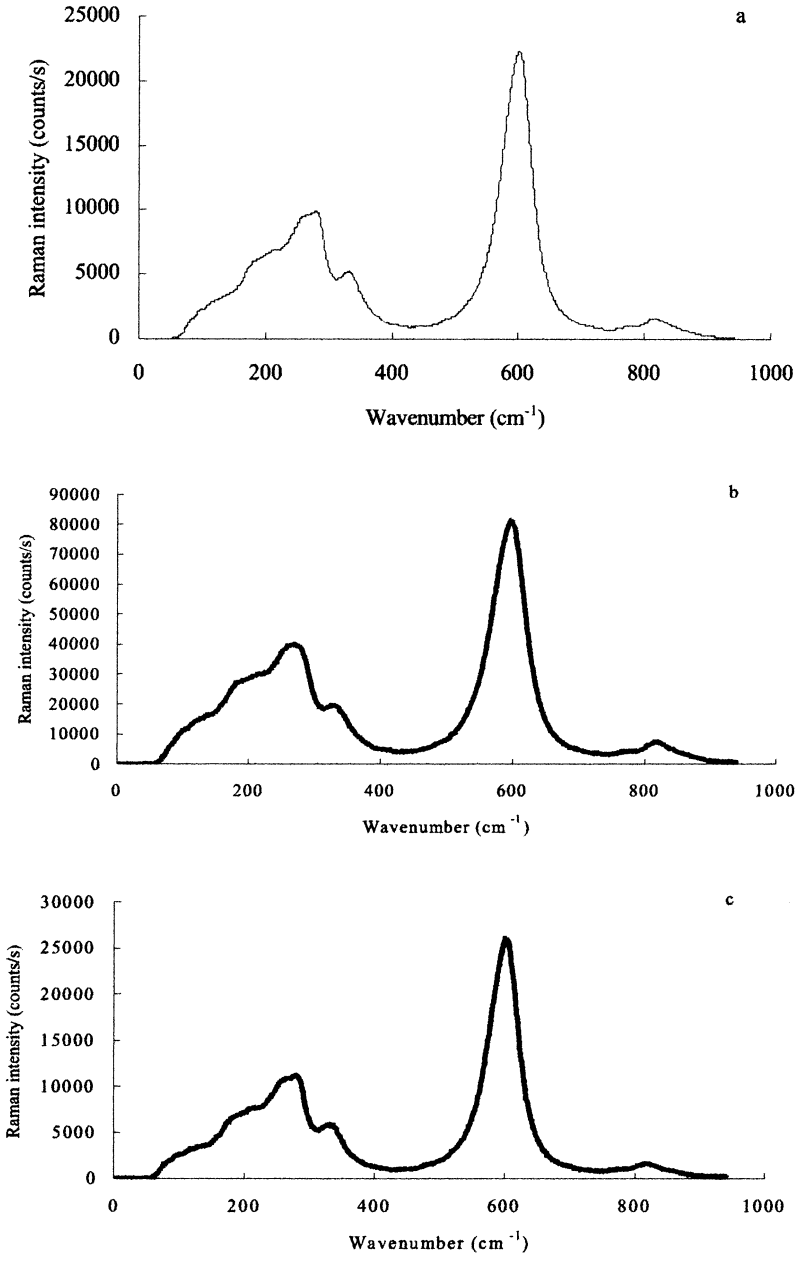

Figure 1. Raman spectra recorded in (a) KLN, (b) Fe:KLN, and (c) Cu:KLN crystals for the symmetry species A_1 with the scattering geometry X(ZZ)Y.

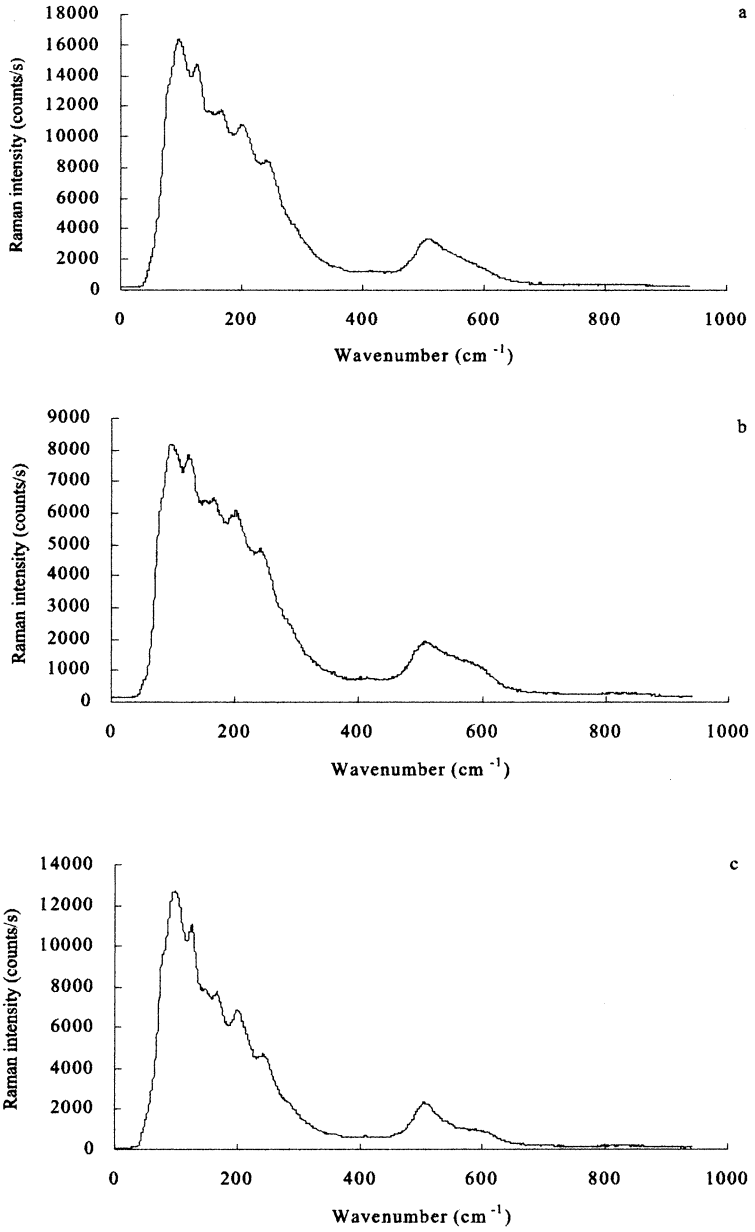

Figure 2. Raman spectra recorded in (a) KLN, (b) Fe:KLN, and (c) Cu:KLN crystals for the symmetry species E with the scattering geometry X(YZ)Y.

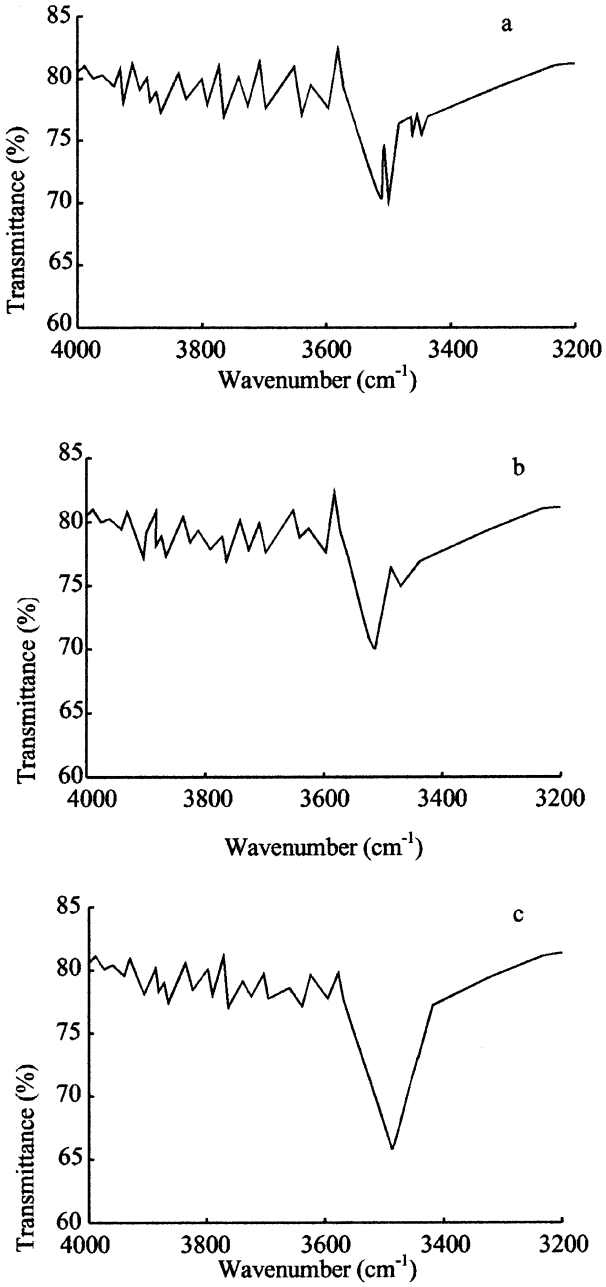

Figure 3. Infrared transmittance spectra of (a) KLN, (b) Fe:KLN, and (c) Cu:KLN crystals.

around them located at the higher wavenumbers. Therefore, we could analyze the replacement of dopants in the doped KLN crystals according to the change of their infrared transmittance spectra.

For example, compared with the KLN crystal, only a peak exited at 3520 cm^{-1} in Fe:KLN (the absorption peak of H_2O molecule at 3456 cm^{-1}). It suggested that Fe ions replaced Nb^{5+} when they entered the lattice of crystal. The capability of Fe ions attracting electrons was weaker than that of Nb^{5+}, so the O-H bond was strengthen when they replaced Nb^{5+} and the energy of OH^{-1} vibration became higher. Thus, the absorption peak of the kind of OH^{-1} shifted to ultraviolet band, covering the absorption peak of OH^{-1} around K^+ or Li^+. In Cu:KLN crystal, there only existed a absorption peak at 3488 cm^{-1}. Compared with the KLN, the site of peak shifted to infrared band. Accordingly, it suggested that Cu ions replaced K^+ or Li^+ because the capability of Cu ions was stronger than that of K^+ or Li^+ and weaker than that of Nb^{5+}. It covered the absorption peak of OH^{-1} around Nb^{5+}. Otherwise, according to x-ray powder diffraction analysis, we obtained data that the lattice constants of Cu:KLN were smaller than that of KLN. So Cu ion should replace the larger ion. There existed Cu^+ and Cu^{2+} in Cu:KLN due to Cu ionic variable valence (similarly, Fe^{2+} and Fe^{3+} existed in Fe:KLN). The radii of Cu^+/Cu^{2+} were 0.96/0.69 A, and that of K^+ and Li^+ were 1.33 A and 0.60 A respectively. Thus, Cu ion replaced K^+. The results of Infrared transmittance and Ultra-violet absorption spectra[10] were obtained.

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