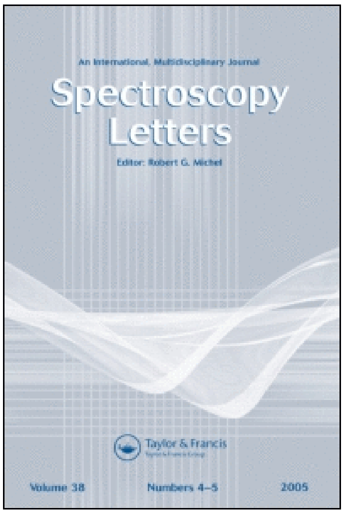

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Raman Spectra Study on $LiTa_{0.9}Nb_{0.1}O_3$ Single Crystal

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RAMAN SPECTRA STUDY ON $LiTa_{0.9}Nb_{0.1}O_3$ SINGLE CRYSTAL

Key Words: $LiTa_{0.9}Nb_{0.1}O_3$ crystal, Vibrational modes, Raman spectra, Doping effects

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ABSTRACT

In this letter, Raman spectra of $LiTa_{0.9}Nb_{0.1}O_3$ single crystal in both of its ferroelectric phase and paraelectric phase are presented for the first time. Comparing with $LiTaO_3$ crystal, we find that the distribution and Raman shifts of normal vibrational mades are similar, but the line-shape and relative intensities of these modes have changed.

INTRODUCTION

$LiTa_{0.9}Nb_{0.1}O_3$ crystal is a new type of doped ferroelectric material(1)(2), it has similar properties and structure as $LiTaO_3$ crystal. Below ferroelectric Curie point(900K), it is in ferroelectric phase with the C_{3v} point symmetry, and it will transform to paraelectric phase with the D_{3d} point symmetry when the temperature is above the Curie point. There are two formula units in the primitive cell of both of its two phases, so there are 27 degrees of freedom to be assigned to optical-phonon modes(3). Group theoretical analysis of the $LiTa_{0.9}Nb_{0.1}O_3$ structure yields 18 lattice modes in both of the ferroelectric phase and the paraelectric phase, of which 13 are Raman active in the ferroelectric phase and 5 are Raman active in the paraelectric phase, as shown below in TABLE 1.

In this paper, the doped effects on the lattice **vibration** of $LiTa_{0.9}Nb_{0.1}O_3$ single crystal are studied by Raman scattering spectra with right angle scattering geometry and forward geometry. All Raman active modes are observed in both of its two phases ,

TABLE 1

Normal Vibration Modes in Both Phases of $LiTa_{0.9}Nb_{0.1}O_3$ Crystal

Paraelectric Phase	$A_{1g}(R)+3A_{2g}+4E_g(R)+2A_{1u}+3A_{2u}+5E_u$
Ferroelectric Phase	$4A_1(R)+5A_2+9E(R)$

"(R)"Indicates that the mode just before it is Raman active mode.

the informations about doping effects are also given by comparing with the results of $LiTaO_3$ crystal.

EXPERIMENT

Good optical quality $LiTa_{0.9}Nb_{0.1}O_3$ crystal was grown by czochralski technique. The sample was cut and polished into rectangular block of 10*6*6 mm^3 with edges within about 1° of the crystallographic axes, as determined by X-ray diffraction. The Raman spectra were recorded digitally using a SPEX 1403 double gratings monochromator spectrometer. Radiation of 514.5 nm from an argon ion laser(Innova 70), adjusted to 100mW was used for excitation and detection was made using a thermoelectrically cooled photomultiplier(Hamamatsu RCA C 31014). The spectrometer was totally controlled by a DM1B microcomputer. The spectra slits were 50μm-100μm-50μm. Under these conditions, the estimated frequency error was less than 1 cm^{-1}. For high temperature experiment, the sample was located in an electrically heated oven which controlled by a DWT 702 type temperature controlling apparatus produced in China and the temperature error was within 1 K.

RESULTS AND DISCUSSION

Ferroelectric Phase

The Raman shifts of four $A_1(TO)$ modes in $LiTaO_3$ are 203 cm^{-1}, 250cm^{-1}, 356 cm^{-1} and 598cm^{-1}, measured in our experiments.We defined them as $A_1(TO)_1$, $A_1(TO)_2$, $A_1(TO)_3$ and $A_1(TO)_4$, respectively as shown in Fig.1(a). For the E(TO) modes, similar defination are given: $E(TO)_1$-149cm^{-1}, $E(TO)_2$-211cm^{-1}, $E(TO)_3$-242cm^{-1}, $E(TO)_4$-314 cm^{-1}, $E(TO)_5$-377cm^{-1}, $E(TO)_6$-461cm^{-1}, $E(TO)_7$-593cm^{-1}, $E(TO)_8$- 656 cm^{-1}, $E(TO)_9$-746cm^{-1}, as denoted in Fig.3(a).

From Fig.1(b), we can see a broad peak at 209 cm^{-1}, it must be the result of overlapping between $A_1(TO)_1$ and $A_1(TO)_2$, for these two $A_1(TO)$ modes are close in frequencies, and it is easy for them to couple with each other when perturbation appearing as we found for the $A_1(TO)_1$ mode and the $A_1(TO)_2$ mode in ferroelectric phase transformation process in $LiTaO_3$ crystal(4). On the other hand, peaks broadening of the vibrational modes in doped matter should be considered when we discuss the overlapping phenomenon above, for it is shown in the scattering peaks of $A_1(TO)_3$ mode and $A_1(TO)_4$ mode, clearly. In order to clarify the machanism of the overlapping phenomenon, we measured the Raman spectra of the crystal with forward scattering geometry to move the $A_1(TO)_1$mode to lower frequency using dependence of frequency on wave vector of the polariton. The result is represented in Fig.2.

We find that the $A_1(TO)_2$ mode almost does not change while the $A_1(TO)_1$ mode moving to lower frequency range. So it is indicated that the overlapping phenomenon is essentialy the result of peaks' broadening under doping.

For the E(TO) modes, similar results were observed, i.e. the overlapping phenomenon appeared for the $E(TO)_2$ and $E(TO)_3$ modes while no frequency shifts' changes were found in the other

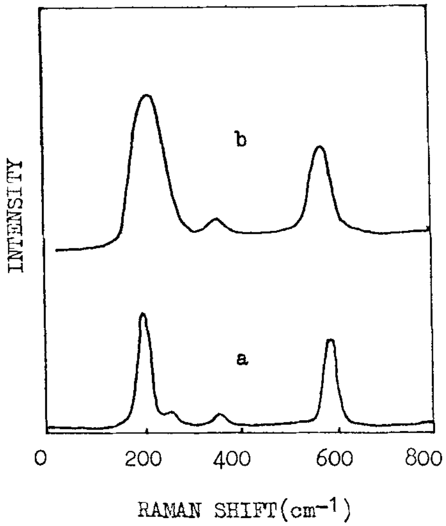

Fig. 1 Raman spectra of A_1(TO) modes in $LiTaO_3$ crystal(a) and $LiTa_{0.9}Nb_{0.1}O_3$ crystal at room temperature.

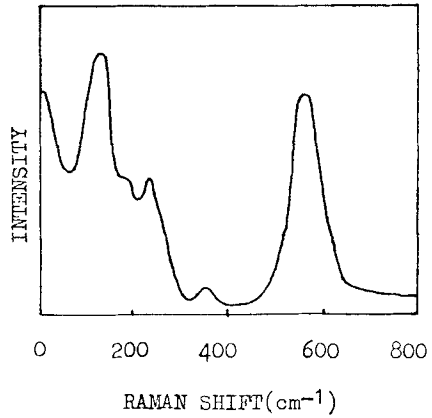

Fig. 2 Raman spectra of A_1 type polaritons in $LiTa_{0.9}Nb_{0.1}O_3$ crystal with forward scattering geometry.

modes. However, the relative intensities of the scattering peaks of these E(TO) modes changed. As shown in Fig.3.

Paraelectric Phase

All the five Raman active modes were observed for $LiTaO_3$ and $LiTa_{0.9}Nb_{0.1}O_3$ crystals, as presented in Fig.4.

It is seen that the frequncy shifts of the Raman active modes in $LiTa_{0.9}Nb_{0.1}O_3$ crystal are almost the same as the case in $LiTaO_3$ crystal, but the scattering peaks are broadened and the differences in relative intensities are also observed. In order to distinguish the A_{1g} mode and the E_g modes of these two crystal in their paraelectric phase, polarised Raman spectra of them should be measured. For $LiTaO_3$ crystal, the results were presented in our previous work(5), i.e.the A_{1g} and E_g modes were observed in two different scattering geometry, respectively,i.e. A_{1g}mode in the X(ZZ)Y geometry and E_g modes in the X(ZY)Z geometry. However, in $LiTa_{0.9}Nb_{0.1}O_3$ crystal, all the five modes appeared in the X(ZZ)Y and X(ZY)Z geometries as nonpolarised Raman spectra. The A_{1g} and E_g modes in $LiTa_{0.9}Nb_{0.1}O_3$ crystal can not be distinguished in the polarised Raman spectra which geometry is defined under the axes of ferroelectric phase.

From the discussion above, it is shown that the behaviour of lattice vibrations of $LiTa_{0.9}Nb_{0.1}O_3$ crystal is similar to the $LiTaO_3$ crystal, i.e. the modes' distribution and the frequency shifts are similar. But the doping effects are also ob-

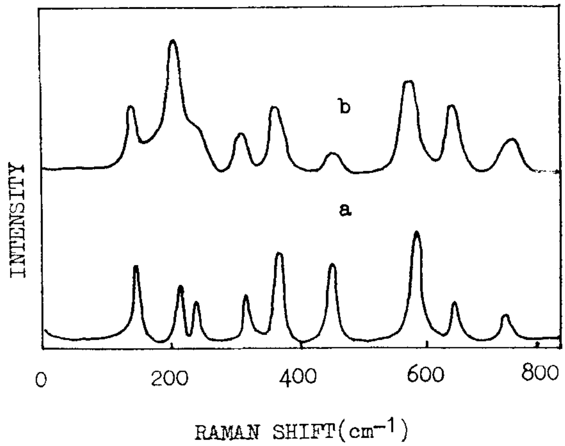

Fig. 3 Raman spectra of E(TO) modes in$LiTaO_3$ crystal(a) and $LiTa_{0.9}Nb_{0.1}O_3$ crystal(b) at room temperature.

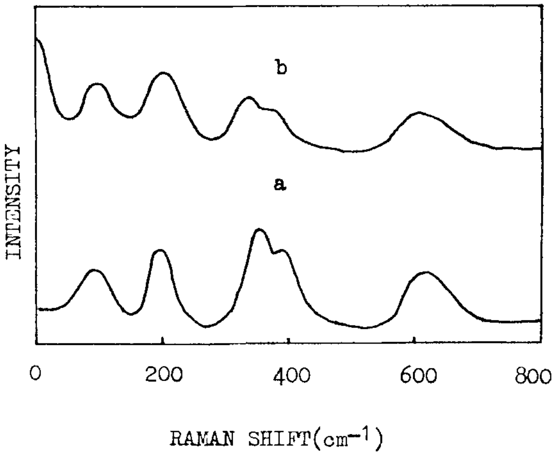

Fig. 4 Nonpolarised Raman spectra of $LiTaO_3$ crystal(a) and $LiTa_{0.9}Nb_{0.1}O_3$ crystal(b) at 1100K.

served, such as the broadening, coupling and relative intensity changing of scattering peaks, also the changes of the scattering geometry occured in the paraelectric phase.

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