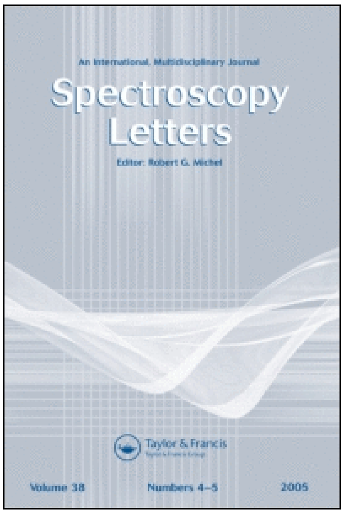

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Temperature Dependent Raman Scattering Study on Linbo$_3$:Zn Crystals

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TEMPERATURE DEPENDENT RAMAN SCATTERING STUDY ON $LiNbO_3$:Zn CRYSTALS

Key words: Raman scattering, $LiNbO_3$:Zn, Doping effect.

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ABSTRACT

In this paper the results of a Raman study on $LiNbO_3$:Zn crystals are presented. It is found that the symmetry , distribution and relative intensities of the vibrational modes show few changes , as compared to the results of pure $LiNbO_3$ crystals. Some vibrational modes are coupled to each other by doping ZnO into $LiNbO_3$ crystals, and the coupling effects disappear gradually with the decrease of temperature. It is suggested that $LiNbO_3$:Zn is substitute solution and the doped Zn ions substitute for the Nb_{Li} first and then the Li ions. The observed vibrational modes in $LiNbO_3$ crystals are mainly determined by the oxygen octahedra.

INTRODUCTION

$LiNbO_3$ is now widely used as a functional material in optoelectric region for its superior electronic and nonlinear properties. However, its utility in some applications is somewhat limited by photorefractive effects. $LiNbO_3$ doped with Mg higher than the concentration threshold(4.6mol.% in the melt) was found to show a substantial reduction in photorefractive damage[1,2]. Recently, $LiNbO_3$: Zn(>6.2mol.% in the melt) has also been found to be able to withstand much higher laser intensity than pure $LiNbO_3$[3,4] . It is found that the damage resistance is due to an essential increase in the photoconductivity σ_p[5] . In $LiNbO_3$ the increase in the σ_p is most pronounced at concentrations exceeding certain threshold (6mol.% ZnO in the congruent melt). The increase in σ_p is directly related to the reduction of the intrinsic defects Nb_{Li} because of their substitution by damage-resistant-impurities. It is known that the structure of $LiNbO_3$ is related to that of the ABO_3 perovskites[6]. The structure is different, however, essentially because Li^+ and Nb^{5+} have nearly identical ionic radii, unlike the perovskite A and B ions. In ferroelectric $LiNbO_3$ the environments of Li^+ and Nb^{5+} are similar (Fig.1); both ions are surrounded by distorted octahedra of six O^{2-} ions. Because of this similarity and since the Nb^{5+}-O^{2-} bond is stronger than the Li^+-O^{2-} one, $LiNbO_3$ has a tendency to non-stoichiometry with [Li]/[Nb]<1. Such crystals therefore have a very high concentration of intrinsic defects. This flexibility of the structure can also explain why $LiNbO_3$ can

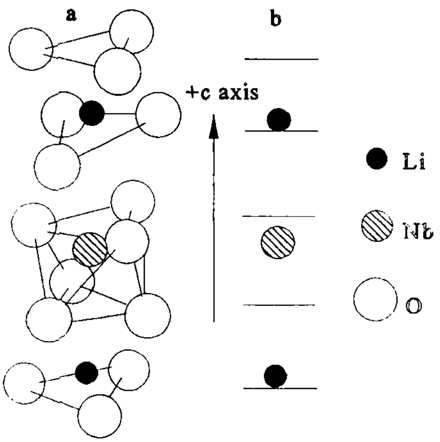

Fig. 1 Model of LiNbO$_3$ structure in the ferroelectric phase.

tolerate high concentrations of extrinsic defect ions. Possible charge misfits can easily be compensated by suitable intrinsic defects. The structure of LiNbO$_3$ in its ferroelectric, R3c, phase is shown in Fig. 1(a). A more abstract version is given in Fig. 1(b), indicating the existence of planes containing triangles of O^{2-} ions, being part of a hexagonal close-packed structure. The cations sit between these planes, Nb near the center of an octahedron, Li more off center. Then there is a problem that when the Zn ions are doped into the crystal, where do they occupy. In this paper, LiNbO$_3$:Zn crystals with various Zn concentration were studied by Raman scattering. It is found that the number of A$_1$(TO) modes and E(TO) modes, as well as their frequency shifts and relative intensities, show few changes. This implies that the symmetries of the crystals do not change largely, when the crystals are doped with Zn ions. However, with the increase of doped concentration of Zn ions, we observed that the two low-frequency A_1(TO) modes coupled to each other, and form a single peak when the doping concentration of Zn ions to 6 mol.%. For two low-frequency E(TO) modes the same phenomenon occurred. It is likely that the Zn ions substitute for the Nb ions at the Li ions sites(Nb_{Li}) dominantly below 6 mol.% Zn ions concentration, and the substitution of Li by Zn begins to occur when the Zn concentration is above 6 mol.%. To study the mode coupling effects, we measured the Raman spectra of $LiNbO_3$:Zn crystals from room temperature to the temperature as low as 10K. We found that the mode coupling phenomena disappeared gradually at low temperature, and the peak became narrower. Comparing with the results of pure $LiNbO_3$ crystals, apparently the coupling effect results from the doping of Zn^{++} ions, that make the band width increase as well.

EXPERIMENTAL

$LiNbO_3$:Zn crystals were grown from the melt using Czochralski technique. At a high concentration of the impurities, it is important to eliminate the defects in the growth process. The technique parameters were chosen as follows: temperature gradient 30-40°C/cm, growth speed 1-2mm/h. rotation speed 20-30rpm. The crystals of good optical quality were cut and polished into rectangular blocks of 10 x 10 x 4 mm^3 with edges within about 1 of the crystallographic axes, as determined by X-ray diffraction. The Raman spectra were measured in a JOBIN YVON HRD1 double grating spectrometer. The scattered light was recorded by an intensified diode-array detector connected with an OMA system. The detector was cooled to -20°C in order to decrease the noise signal. A Coherent Innova 70 Ar ion laser was used as the excitation source, the wavelength of excitation line is 514.5nm. The laser power was typically 200mW on the samples. A Ne lamp was used to calibrate the wavelength. For low temperature experiments an LTS-21 Cryogenic system was used. The temperature was controlled between 300K to 10K , the errors maintained within 0.1K.

RESULTS AND DISCUSSION

At room temperature (300K), $LiNbO_3$ crystallizes in the ferroelectric phase with C_{3v}^{6} space symmetry and has two formula units per unit cell. The expected distribution of the optical modes of lattice vibration is well known as follows[7]:

$$4A_1 + 9E + 5A_2$$

where A_1 and E are both Raman and infrared active modes, while A_2 are neither infrared nor Raman active modes. In our experiment all the Raman active modes were observed and their frequency shifts are in consistent with those reported in other work.

The Raman spectra of A_1(TO) and E(TO) modes for the $LiNbO_3$:Zn(6.0mol.%) crystals were observed, the A_1(TO) and E(TO) modes are shown in Fig.3(a) and Fig.4(a), respectively. Comparing with the results for pure $LiNbO_3$, it is found that the number of A_1(TO) modes and E(TO) modes are essentially unchanged, also the frequency-shifts and relative intensities of them are almost the same as the case in pure $LiNbO_3$. However, there are some differences between them, as we can see from Fig.3(a) and Fig.4(a). First, the two low-frequency A_1(TO) modes are coupled, so it is difficult to separate them. Similar phenomena occured in the E(TO) modes, the 236cm^{-1} mode and the 263cm^{-1} mode coupled to each other. Finally, the 614cm^{-1} mode could not be observed in Fig.4(a). It is clear that these phenomena result from the doping of Zn ions into the $LiNbO_3$ crystal. To clarify the doping effects, we measured Raman spectra of $LiNbO_3$:Zn crystals with various Zn ion concentrations: a)0%, b)1.0%, c)2.2%, d)4.0%, e)6.0%.The results are shown as Fig.2. Note two low-frequency A_1(TO) modes in Fig.2, the outline of them changes unclearly with the increase of doping concentration, the 276cm^{-1} -peak is difficult to observe as the concentration of Zn ions increases to 6 mol.%, The same phenomenon occured for two E(TO) modes at 236cm^{-1} and 263cm^{-1}. In order to study this phenomenon in detail, Raman spectra of the doped sample(with 6mol.% Zn ions) were measured at low temperature(300K to 10K), at temperature intervals of 10K. In Fig.3 and Fig.4, some representative spectra for A_1(TO) and E(TO) modes are shown. It is found in Fig.3, that the degree of superposition for the scattering peaks of the two low-frequency A_1(TO) modes reduce with decreased temperature. The 276cm^{-1}-mode appeared sharply at 140K, as shown in Fig.3(d). Further decreasing the temperature of sample makes the two

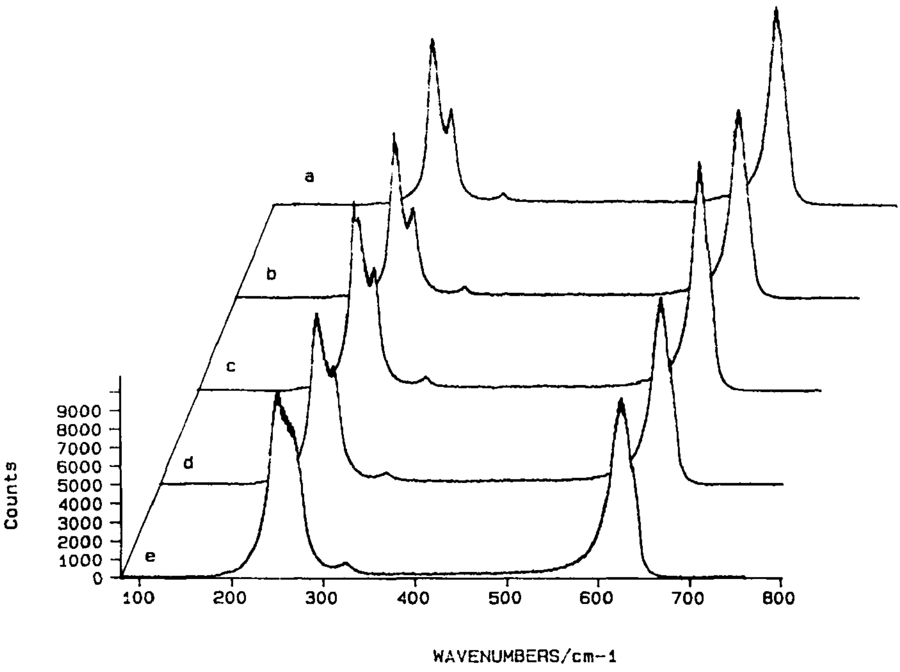

Fig.2 Raman spectra of $LiNbO_3$:ZnO with various Zn ion concentrations. a)0%; b)1.0%; c)2.2%; d)4.0%; e)6.0%.

peaks far apart from each other, implying that the coupling between the two modes is weakened. Similarly, in Fig.4 the two E(TO) modes(which located at 236cm^{-1} and 263cm^{-1}) separate as the temperature decreases, at 40K the 263cm^{-1}-mode can be resolved clearly.

From the results given above, it can be concluded that the $LiNbO_3$:Zn is substitution solid solution, so its symmetry properties are little

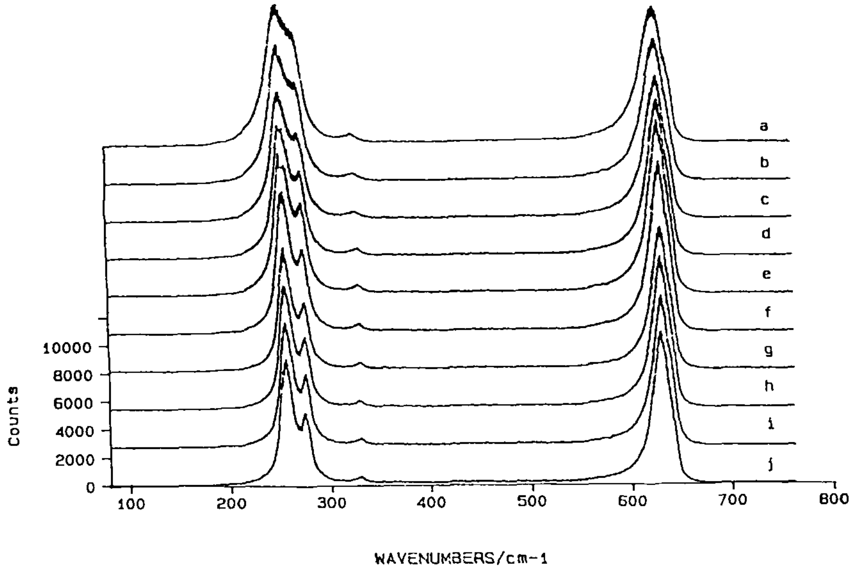

Fig.3 Raman spectra of A_1 modes in $LiNbO_3$:ZnO(6.0%) measured between 300K to 10K. a)300K; b)260K; c)200K; d)180K; e)140K; f)120K; g)80K; h)40K; i)20K; j)10K.

affected by Zn doping. No remarkable changes appear in the Raman specrtra of $LiNbO_3$:Zn cyrstals compared to pure $LiNbO_3$. It is likely that the Zn ions substitute for the Nb_{Li} ions first, i.e. the intrinsic impurities are substituted by the extrinsic impurities. As the doped concentration of Zn ions increases up to 6 mol.%, the Zn ions begin to substitute for the Li ions on normal lattice sites, increasing the concentration of impurities in the doped crystal. The lattice vibrational

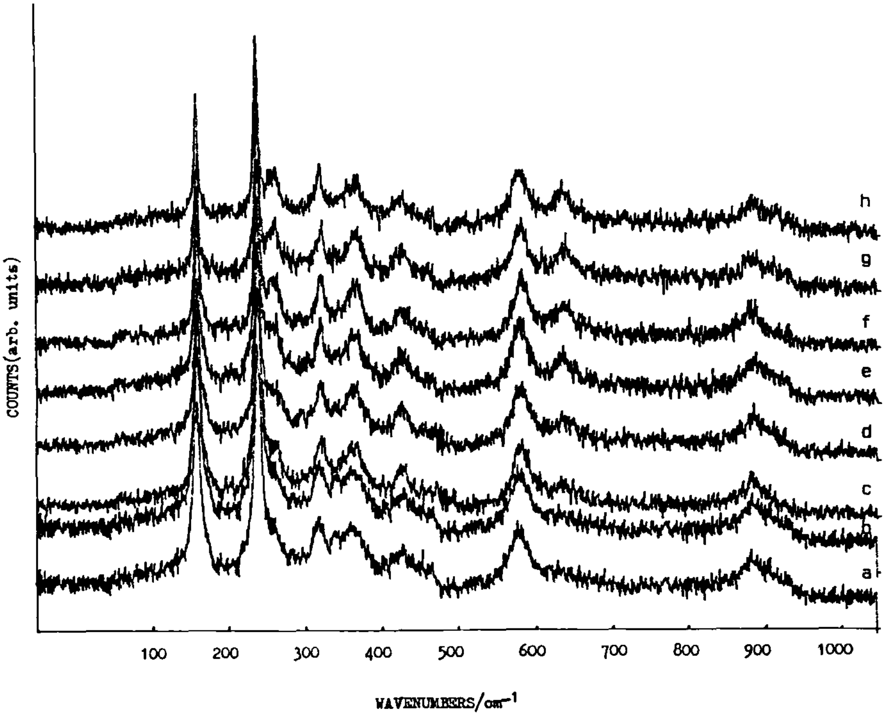

Fig.4 Raman spectra of E modes in LiNbO$_3$:ZnO(6.0%) measured between 300K to 10K. a)300K; b)200K; c)180K; d)140K; e)100K; f)60K; g)40K; h)10K.

modes associated with Li ions show some changes as compared to the pure LiNbO$_3$, such as the two low-frequency A$_1$ modes and two E modes coupled to each other. Also our results show that the A$_1$ modes and E modes in LiNbO$_3$ cyrstals are mainly determined by the oxygen octahedra(NbO_6), and the interaction between the cations and the oxygen octahedra is weak.

The increase in σ_p may relate to the reduction of the intrinsic defects Nb_{Li} for their substitution by damage-resistant-impurities Zn.

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