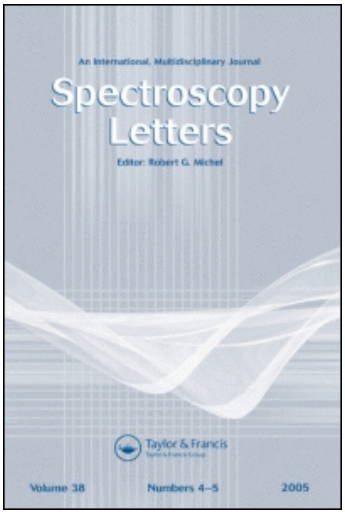

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Raman Spectrum Study on the Doping Effect in $LiNbO_3$: MgO Crystals

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ABSTRACT

Raman spectra of $LiNbO_3$:MgO crystals have been obtained and compared with Raman spectra of pure $LiNbO_3$ crystals. For both of the two kinds of Raman active modes ($4A_1 + 9E$), no changes of the numbers, frequency-shifts, and relative intensities of the Raman

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spectral lines are found. However, it is observed that some modes coupled to each other at room temperature. The observed modes coupling phenomena , disappeared at low temperature. It is shown from these results that the Raman spectral lines of A_1 (TO) and E (TO) vibrational modes are mainly determined by the (NbO_6) oxygen octahedra characteristic groups of $LiNbO_3$ crystals.

INTRODUCTION

$LiNbO_3$ crystal is now widely used in laser techniques for its superior electronic and nonlinear properties. However, its applications are somewhat limited due to its poor ability to resist the damage of laser. Recently, some researchers attempted to increase such ability for $LiNbO_3$ crystals, through doping Mg^{++} ions into $LiNbO_3$ crystals. Zhong Giguo et al. found[1] that the optical damage (alias: the photorefractive effect) is strongly reduced in samples grown from the congruent melt containing 4.6 mol% MgO as compared with those with a lower Mg concentrations. High Mg doping can thus lead to optical devices in which the light wavefronts are not distorted. This is a great achievement in the study of $LiNbO_3$ applications. Bryan et al.[2] confirmed the results

of Zhong et al.[1] and showed that the effect is due to a greatly increased photoconductivity short-circuiting the light induced space charges causing the photorefractive effect. This was also demonstrated by Arizmendi and Powell[3]. The structure of $LiNbO_3$ is related to that of the ABO_3 perovskites[4]. The structure are 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 strong 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 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 triangulars 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. In

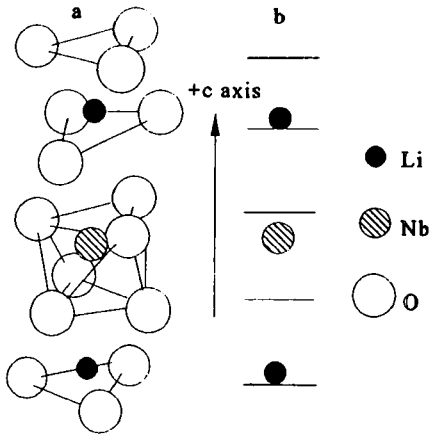

Fig.1 Models of $LiNbO_3$ structure in the ferroelectric R3c phase.

this paper, $LiNbO_3$ crystals with various Mg^{++} concentrations were studied by Raman scattering spectrum. It is found that the number of $A_1(TO)$ modes and E(TO) modes, as well as their frequency shifts and relative intensities are essiencially unchanged. Implying that the symmetry of the crystals do not changed when the Li^+ ions were substituted by the Mg^{++} ions and the Raman active modes (A_1 modes and E modes) are determined mainly by the characteristic vibrations of the oxygen octahedra(NbO_6). The doping effects were also observed that the two low-frequency $A_1(TO)$ modes coupled to the

outline of one peak. For the two low-frequency E(TO) modes the same phenomenon occurred. To clarify the mechanism of the modes coupling effects, we measured the Raman spectra of $LiNbO_3$:MgO (Mg^{++}:6.7mol%) crystals from room temperature to temperature as low as 10K. We found that the modes coupling phenomena disappeared gradually in low temperature, and meanwhile, the peak became narrower. Comparing with the results of pure $LiNbO_3$ crystals, apparently the coupling effect results from the doping of Mg^{++} ions, that make the band width increasing as well.

EXPERIMENTAL

$LiNbO_3$ crystals were grown using Czochralski technique. Samples 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 gratings spectrometer, the scattering light was recorded by an intensified diode-array detector connected with an OMA system. The detector was cooled to the temperature of -20 degrees centigrade, in order to decrease the noise signal. A Coherent Innova 70 Ar 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 experiment 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 have two formula units per unit cell. The expected distribution of the optical modes of lattice vibration are well known as follows:

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

where A_1 and E are both Raman and infrared active modes, while A_2 are neither infrared nor Raman active modes. Different scattering geometries were used to observe A_1 and E modes, i.e. X(ZZ)Y geometry for the A_1 modes and X(ZX)Y geometry for the E modes. The results are presented in Fig.2 and Fig.3, respectively. In Fig.2 there are four A_1 modes appeared in the Raman spectrum with X(ZZ)Y configuration, and nine E modes were observed in the

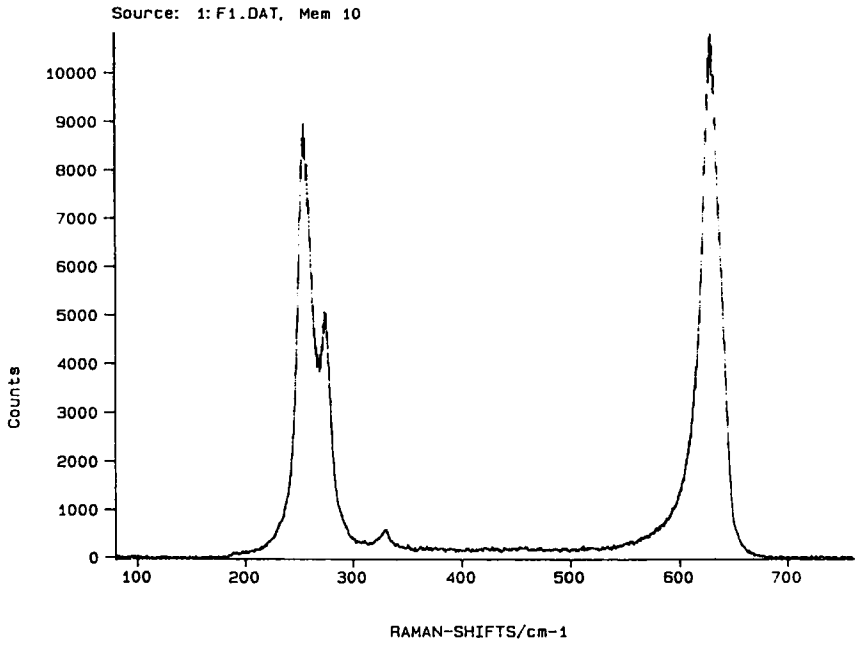

Fig.2 Raman spectrum of the A1 modes in $LiNbO_3$ crystal, measured with X(ZZ)Y geometry at room temperature.

Raman spectrum with X(ZX)Y geometry as shown in Fig.3, their frequency shifts are all listed in Table 1.

To study the doping effects of MgO, the samples doped with MgO were measured. The Mg^{++} concentrations are 3mol%, 5mol% and 6.7mol%, respectively. Using rectangular scattering configuration, the Raman spectra of A_1(TO) and E(TO) modes for all the three

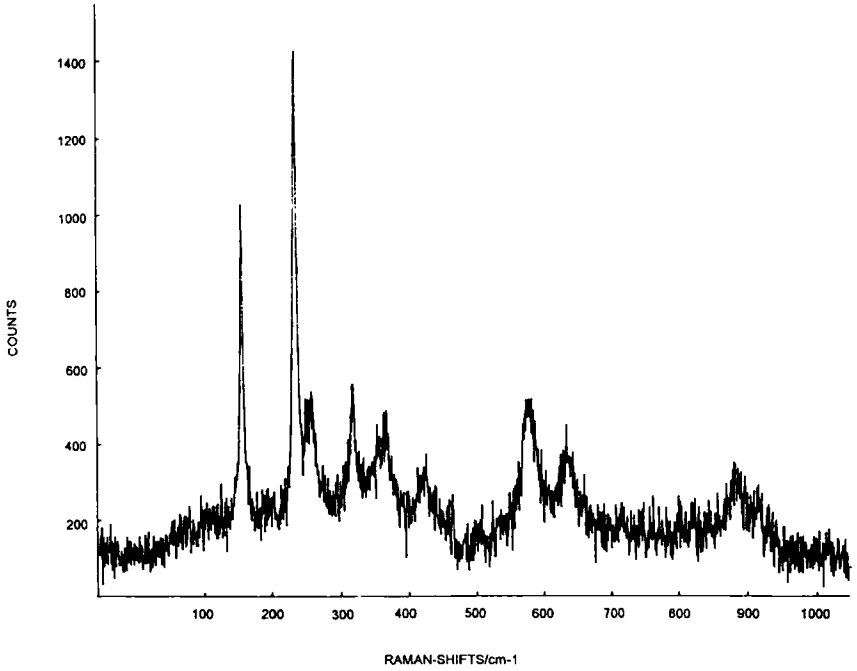

Fig.3 Raman spectrum of the E modes in $LiNbO_3$ crystal, measured with X(ZX)Y geometry at room temperature.

Table1 Frequency shifts(cm^{-1}) of A_1 modes and E modes in $LiNbO_3$ crystal at room temperature.

A_1	251		267		334		622		
E	155	236	263	325	371	431	582	665	886

samples were observed. Comparing with the results of 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 the same as the case in pure $LiNbO_3$. However, there are some difference between them, as shown in Fig.4 and Fig.5. First note the two low-frequency $A_1(TO)$ modes in Fig.4, the border of them changes unclearly with the Mg^{++} ions upto 6.7mol%, the $276cm^{-1}$ -peak is difficult to observe. Another point should be note is the same case for the two low-frequency E(TO) modes, appeared in Fig.5, it is difficult to resolve the $263cm^{-1}$-mode for the sample doped with 6.7mol% Mg^{++} ions. In order to clarify the mechanism of the phenomena above, Raman spectra of doped samples and pure $LiNbO_3$ crystal were studied at low temperature, during the range of 300K to 10K, the temperature interval was 10K. In Fig.6 and Fig.7, some representatives for the results of measured $A_1(TO)$ modes and E(TO) modes are shown. It is found in Fig.6, that the degree of superposition for the scattering peaks of the two low-frequency $A_1(TO)$ modes reduces with temperature decreasing. The $276cm^{-1}$-mode appeared sharply at 140K, as shown in Fig.6(e). Further decreasing the temperature of sample makes the two peaks

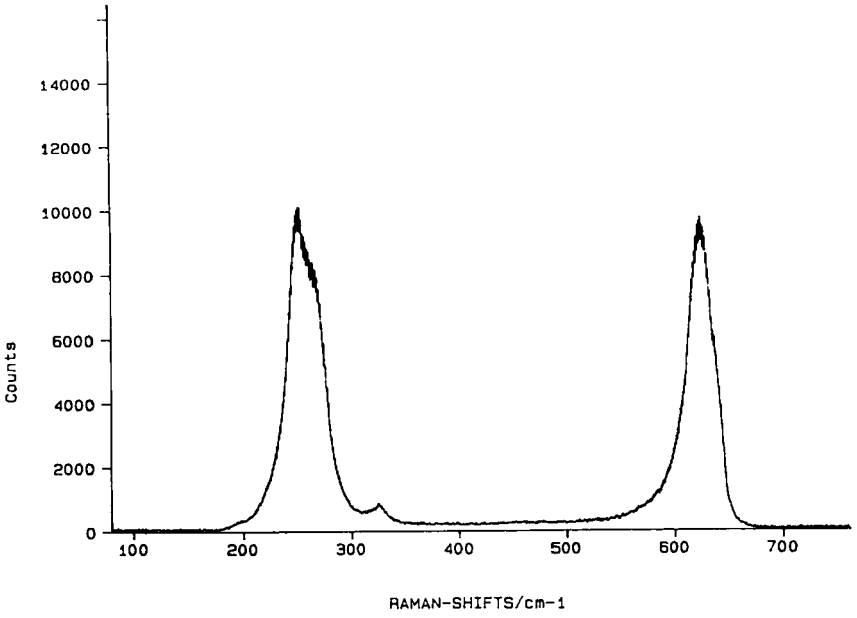

Fig.4 Raman spectrum of the A1 modes in $LiNbO_3$:MgO(6.7mol.%) crystal measured with X(ZZ)Y geometry at room temperature.

far apart from each other, implying that the nonharmonic interaction between the two modes are weakened. Similarly, in Fig.7 the two low-frequency E(TO) modes become apart during the temperature decreasing process, at 100K the 263cm^{-1}-mode can be resolved clearly. Additionally, the 665cm^{-1} mode(E mode) which cannot be observed in the Raman spectrum measured at room temperature,

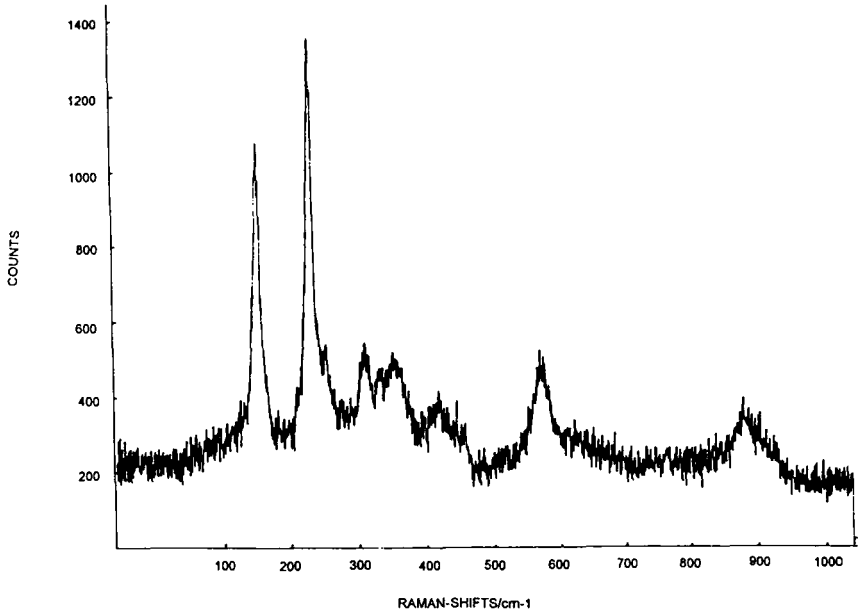

Fig.5 Raman spectrum of the E modes in $LiNbO_3$:MgO(6.7mol.%) crystal measured with X(ZX)Y geometry at room temperature.

appeared in the Raman spectrum obtained at 160K, and its intensity relative to the 582cm^{-1}-mode increases with temperature decreasing.

By measuring the concentrations of Li_2O, MgO and Nb_2O_5 in $LiNbO_3$:MgO crystals, it is determined that the doped Mg^{++} ions are substituted for the Li^+ ions, and $LiNbO_3$ is substitutional solid solution. For the doped crystals are substitution solid solutions, the symmetry

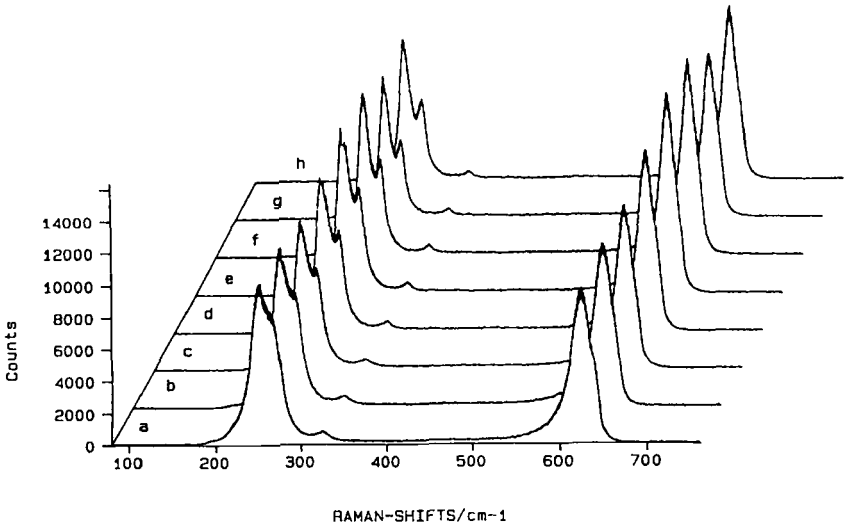

Fig.6 Raman spectra of the A1 modes in $LiNbO_3$:MgO(6.7mol.%) crystal measured between the temperature range from 300K to 10K: a) 300K, b) 260K, c) 200K, d) 180K, e) 140K, f)100K, g)60K, h)10K.

of the crystals does not change essentially by doping Mg^{++} into them. So there are no obvious changes in the Raman spectra of $LiNbO_3$:MgO crystals, in spite of the doping concentration attained as high as 6.7mol%. Meanwhile, our results support the conclusion that $LiNbO_3$:MgO crystals are substitution solid solutions. It should be noted that the doped Mg^{++} ions substitute for the equal amount of Li^{+}

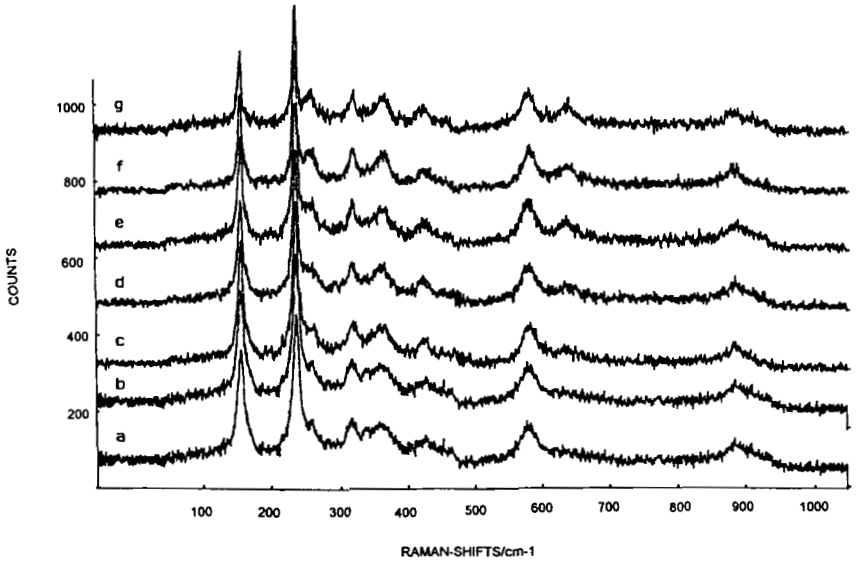

Fig.7 Raman spectra of the E modes in $LiNbO_3$:MgO(6.7mol.%) crystal measured between the temperature range from 300K to 10K: a) 300K, b) 200K, c) 180K, d) 140K, e)100K, f)60K, g)10K.

ions, which will make the constitution and properties of the cations changed largely, however, there are no obvious changes in their Raman spectra. Thus we can conclude that the A_1 modes and E modes are mainly determined by the oxygen octahedrons(NbO_6), meanwhile it also implying that the interaction between the cations

and the oxygen octahedra is weak. For the radii of Li^+ ions and Mg^{++} ions are the same—0.78 angstrom, the superposition of electron clouds and the interaction between ions are almost unchanged. But we should note that the electricity of Mg^{++} ions and the Li^+ ions are different, according to the theory of electroneutrality, as one Mg^{++} ion substituting for two Li^+ ions a lattice vacancy is formed. And the lattice constants will be changed. We conclude that such "disorder substitution" results in the scattering bands' broadening somewhat, explaining the unclear borders of the two low-frequency $A_1(TO)$ modes and two low-frequency E(TO) modes.

REFERENCES

1. Zhong Gi-guo, Jin Jian, Wu Zhong-Kang, 11th International Quantum Electronics Conference, P.631. IEEE Cat. No.80 CH 1561-0(1980).
2. Bryan D.A., Rice R.R., Gerson R., Tomaschke H,E., Sweeney K.L. and Hilliburton L.E., Opt. Engng vol.24, 143, (1985).
3. Arizmendi L. and Powell R.C., J. Appl. Phys. vol.61, 2128, (1987).

4. Megaw H. and Darlingrton C.N.W., Acta crystallogr. A31, 161 (1965).

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