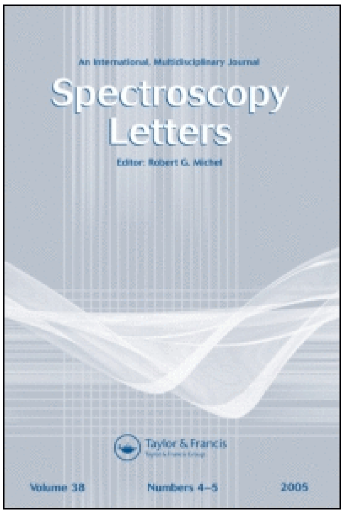

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POLARIZED RAMAN STUDY ON $LiNbO_3$

Key Words: polarized Raman spectrum, $LiNbO_3$, correlation analysis, internal vibration, external vibration

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Abstract

Polarized Raman was used to study the lattice vibrations in $LiNbO_3$ single crystals which temperature range from 291K to 11K. The 13 vibrational modes expected from group-theoretical analysis were obtained. The nine internal modes and four external modes of NbO_6 octahedra have been assigned for the first time.

Introduction

Lithium niobate is one of the most interesting materials for optics owing to its electro-optical and nonlinear optical properties[1,2]. The present study was made to assign the vibrational modes and to discover experimentally the Raman phonons in $LiNbO_3$.

The structure of $LiNbO_3$ is well established[3]. Below ferroelectric Curie point, the crystal has the $R3C(C_{3v}^6)$ space-symmetry, and primitive cell contains two formula units which allow 27 degrees of freedom to be assigned to optical-phonon modes. Fig.1 shows the structure of $LiNbO_3$ with nearly regular NbO_6 octahedra. After the pioneering work of Last[4], a lot of works have been poured onto the ABO_3 perovskite type ionic crystals, such as $LiNbO_3$, $NaNbO_3$, $KNbO_3$ and $BaTiO_3$, etc.[5-8]. In Raman spectra of these crystals, they found the similarity of the A_1(TO) modes. It is pointed that the structures of these compounds are similar, i.e. they all have BO_6 octahedra along c-axis. To a first-order approximation, the lattice interactions can be separate into internal vibrations of the octahedron and the external vibrations in which an octahedron vibrates as a unit.

A group-theoretical analysis of the $LiNbO_3$ structure below ferroelectric Curie point yields 18 lattice modes, of which 13 are Raman active: $4A_2 + 9E$. For the NbO_6 octahedra, table1 shows the correlation diagram between the O_h symmetry of an isolated regular octahedra, the ion-site symmetry and the C_{3v}^6 space group symmetry. In fact, the octahedron that has the symmetry of the point group O_h has six species of normal vibrations, i.e. A_{1g}, E_g, F_{1u}, F_{1u}, F_{2u}, F_{2g}. The requirement that atoms in equivalent positions in neighbouring cells must perform the same vibrational motion reduced this set of normal vibrations to two

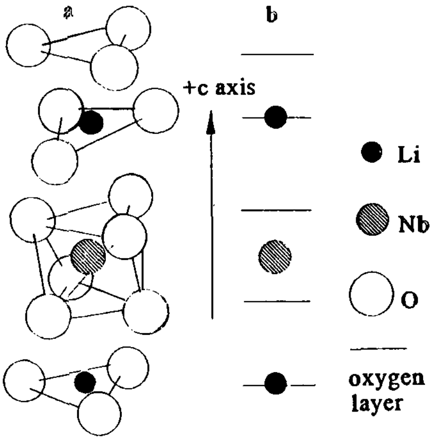


Fig.1 Structure model of $LiNbO_3$.

infrared-active vibrations of the species F_{1u} and one inactive vibration of the species F_{2u}, as pointed out by Last[9].

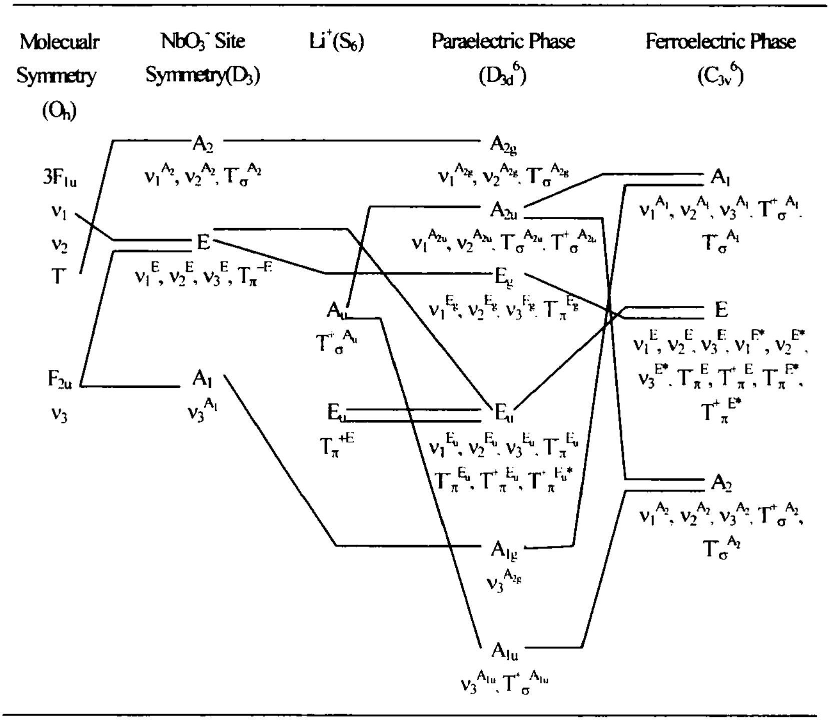
Degeneracies of the F_{1u}(three fold)and F_{2u}(three folds) are partially removed in the crystal, so five Raman-active modes are expected in paraelectric phase, A_{1g} + $4E_g$ and thirteen Raman-active modes in ferroelectric phase, $4A_2$ + 9E. The correlation diagrams of all the vibrational modes are shown in table1, it is similar to the case in $LiTaO_3$ which studied in our previous work[10].

Experiment

Single $LiNbO_3$ crystals were grown by Czochralski technique. The sample used in this work was optically transparent and colour free. It

TABLE1

Correlation Diagrams of Vibrational Modes in $LiNbO_3$



was cut and polished into a rectangular block 9x6x3mm^3 with edges within about 1° of the crystallographic axes, as determined by x-ray diffraction. The Raman spectra were obtained with the 514.5nm line of an Innova 70 argon-ion laser used as excitation source, the scattered light was analysed by an HRD1 double-grating monochromator and OMAIII photon-counting system. The spectra were recorded in the region 30~900cm^{-1} with a laser beam power of 100mW. The resolution of such a system is controlled to 1cm^{-1}.

Results and Discussions

In right angular scattering geometry, spectra were obtained between 11K and 291K in two different orientations which correspond to A_1(TO) and E(TO) modes, respectively. Figure 2 and figure 3 show the superposition of spectra for A_1(TO) and E(TO) modes at various temperature between 11K and 291K. The Raman frequency obtained at 291K are listed in table2, with their modes symmetry

In general, the internal vibrations of a tightly bound group of atoms have higher frequencies than the vibrations in which the more loosely bound groups vibrate against each other. So we can assign the internal modes and external modes on the basis of the Raman frequencies and correlation diagram of table1.

The modes assigned to internal vibrations of the NbO_6 octahedra are again listed in table3 and correlated to the vibrations of the isolated regular octahedra. Typical frequencies of NbO_6 octahedron and frequencies observed in the present study are also listed. The torsional vibration F_{2u} is infrared inactive in cubic symmetry, so one cannot observe it in $SrTiO_3$ and $BaTiO_3$(cubic phase), but it would be active when symmetry in lower symmetry, it appears in the infrared spectra of $BaTiO_3$(non-cubic phase), $KNbO_3$, $NaNbO_3$, etc[4]. So we can conclude that the "550cm^{-1} shoulder" in the infrared spectra of ref.4 which is

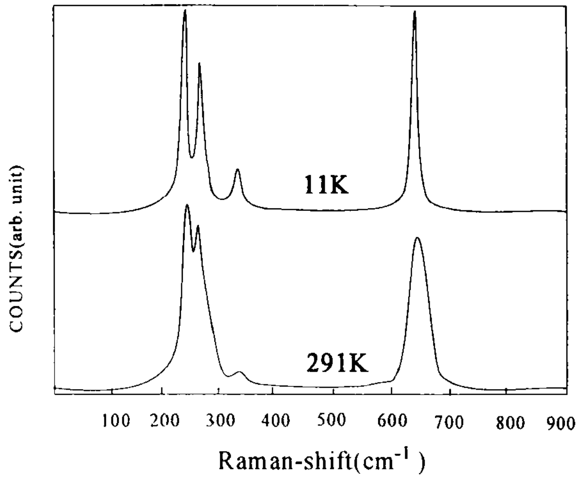


Fig.2 Raman spectra of A_1(TO) modes in $LiNbO_3$ measured at 11K and 291K with X(ZZ)Y configuration.

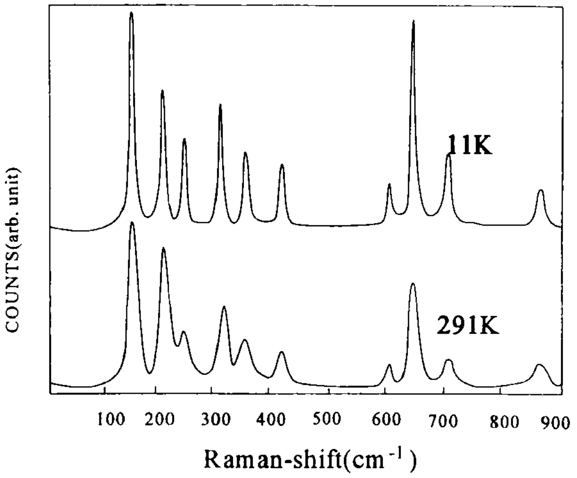


Fig.3 Raman spectra of E(TO) modes in $LiNbO_3$ measured at 11K and 291K with X(ZX)Y configuration.

TABLE2

Raman Active Bands Observed in $LiNbO_3$

	1	2	3	4	5	6	7	8	9	10	11	12	13
ν	713	665	630	614	428	365	334	314	274	263	251	236	155
type	E	E	A_1	E	E	E	A_1	E	A_1	E	A_1	E	E

TABLE3

Symmetry and Frequency of internal modes at room temperature

Symmetry	Internal modes(cm^{-1})	NbO_6(cm^{-1})	Symmetry
E	713		
E	665	$\rightarrow$675	ν_1 (F_{1u})
A_1	630		stretching
E	614		
E	428	$\rightarrow$510	ν_3(F_{2u})
A_1	334		torsion
E	365		
E	314	$\rightarrow$375	ν_2 (F_{1u})
A_1	274		bending

neglected by Last is the torsional vibration $n_3(F_{2u})$, the "660cm^{-1} peak" is the stretching vibration $n_1(F_{1u})$ and the "375cm^{-1} peak " is the bending vibration $\nu_2(F_{1u})$. The stretching vibration is expected to occur at frequencies higher than the bending vibration. The two $\nu_1(F_{1u})$ (stretching modes) of the two octahedra in a ferroelectric primitive cell split into A_1+A_2+2E of which A_2 is inactive mode and ν_1^{A1}~630cm^{-1}, ν_1^{E}~713cm^{-1}, ν_1^{E*}~665cm^{-1}. The two $\nu_2(F_{1u})$(bending modes) also split into A_1+A_2+2E, A_2 is inactive mode and ν_2^{A1}~274cm^{-1}, ν_2^{E}~365cm^{-1}, ν_2^{E*}~314cm^{-1}. The two torsional modes-$\nu_3(F_{2u})$ split into A_1+A_2+2E, A_2 is inactive mode, and ν_3^{A1}~334cm^{-1}, ν_2^{E}~614cm^{-1}, ν_2^{E*}~428cm^{-1}. The other A_1 mode(251cm^{-1}) is assigned to the vibration of NbO_6 group and Li ion along z axis, so that this mode may take part in the structure phase transition[11,12,13]. The other three E modes (155cm^{-1}, 236cm^{-1}, 263cm^{-1}) are assigned to the vibration of Li^+ ions, NbO_6 groups, and the vibration of Li^+ ions with NbO_6 groups, respectively, in accordance with table1. Note that one A_1 mode and one E mode should be assigned to unit cell motion modes.

Experimentally, we may also be able to assign the internal modes and external modes on the basis of the temperature dependence of the Raman frequencies. In fact, the modes indicated by asterisk in table2 have nearly the same frequencies at 11 and 291K, and are thus assigned to internal vibrations of the NbO_6 octahedra. Notice that there are $3A_1$ and 6E modes assigned to the internal vibrations, in agreement with the results analysed above. The frequencies of the remaining four modes decrease more rapid with temperature decreasing. Temperature-dependence details of these modes will be presented elsewhere later.

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