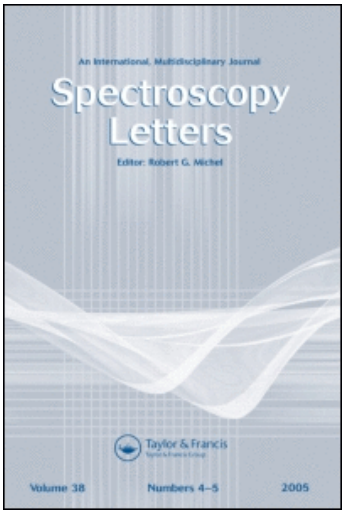

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CORRELATION ANALYSIS AND RAMAN STUDY ON THE LATTICE VIBRATION IN BOTH PHASES OF LITHIUM TANTALATE

Key Words: Group theory, Correlational Analysis, Raman scattering, Lithium tantalate.

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INTRODUCTION

Lithium tantalate ($LiTaO_3$) and the isomorphic lithium niobate ($LiNbO_3$) are uniaxial ferroelectric with a single phase transition of second order. Their dynamics properties have been the subject of considerable interest over the last two decades.

The structure of lithium tantalate ($LiTaO_3$) is well established[1]. Below Curie point(900K), the crystals are in the ferroelectric phase and have the space symmetry C_{3v}^6. When the temperature is higher than the Curie point (900K), they transform to the paraelectric phase and have the space symmetry D_{3d}^6. The lattice vibrations and the phase transition of $LiTaO_3$ crystals have been studied for thirty years[2-7,9]. The observations of lattice vibrations are mainly on the ferroelectric phase, and seldom works related to the vibrations of paraelectric phase, as well as the correlationships between the normal vibrational modes in the paraelectric phase and that of ferroelectric phase. In this paper the

correlation of modes in both of the ferroelectric phase and that of paraelectric phase are presented, and the correlationship between the modes in the two phase are discussed in detail. Using Raman scattering, the Raman active modes in the two phases are observed and analysed.

EXPERIMENT

The poled single crystal of $LiTaO_3$ was obtained from the Institute of Crystal Materials of Shandong University. Optically good quality samples were cut and polished into rectangular blocks of 10x10x4 mm^3 with edges within about 1^0 of the crystallographic axes, as determined by x-ray diffraction. The Raman scattering spectra were recorded digitally using a Spex1403 double-grating monochromator. Radiation at 514.5 nm from an argon ion laser (Innova70) adjusted to 100mW was used for excitation, and detection was effected using a thermoelectrically cooled photomultiplier(Hamamatsu RCA C31034). The spectrometer was totally controlled by a IBM-microcomputer. For high-temperature experiments, the sample was located in an electrically heated oven which was controlled by a DWT702-type temperature controlling apparatus which was produced in China. The temperature was maintained within 1K. Rectangular scattering configuration was adopted in all the measurements.

GROUP-THEORETICAL ANALYSIS

The $LiTaO_3$ crystal has two formula units (10 ions) per primitive unit cell. Figure 1(a) shows the unit -cell structure of $LiTaO_3$ crystal. The positions of Ta and Li ions in $LiTaO_3$ crystal in the ferroelectric phase are shown in Figure 1(b). Figures 1(c)and 1(d) show the two types of the models for the positions of Li and Ta ions in the paraelectric phase.[2,3] It can be seen from Fig.1(a) that the TaO_6 octahedra repeated periodically along the z-axis of the crystal, and this is a predominant feature of the $LiTaO_3$ crystals. Some other crystals also have similar oxygen octahedron structure, such as $LiNbO_3$, $NaNbO_3$ and $BaTiO_3$ etc.[4-7]

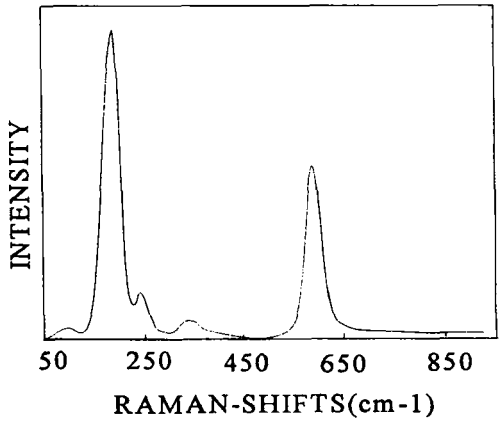

Fig.1 Raman spectra of A_1 modes in $LiTaO_3$ crystal measured with X(ZZ)Y geometry at room temperature(300K).

Although the structure of octahedra is tight, they will still be distorted under the inteaction with their neighbour ions in the crystals. So the symmetry of them will be affected by the symmetry of the crystals. In free state the oxygen octahedron has the cubic O_h symmetry. It can be obtained from group-theoretical analysis that the isolated regular oxygen octahedron has the six species of normal vibrations:

$$A_{1g} + E_g + F_{1u} + F_{1u} + F_{2u} + F_{2g}$$

The requirement that atoms in equivalent positions in neighbouring unit cells must perform the same vibrational motion reduces this set of normal vibrations to the two infrared-active vibrations of the species F_{1u} and one inactive vibration of the species F_{2u}, as pointed out by Last.[8]

The degeneracies of the F_{1u} (three fold) and F_{2u} (three fold) are partially removed in the paraelectric $LiTaO_3$ crystals which have the point symmetry of D_{3d}. In this case the site symmetry of oxygen octahedron (TaO_6) is D_3. The three fold degeneracy normal vibrations are splited into A_1, A_2 and E modes, the correlations between them are shown as Tab.1.

TABLE 1

Correlations of the Normal Vibrations Between TaO_6 in Free, TaO_6 in D_3 Site and TaO_6 in the Unit Cell of Paraelectric Phase $LiTaO_3$

TaO_6 in free O_h	TaO_6 in D_3 site D_3	$LiTaO_3$ unit cell D_{3d}	Li^+ in S_6 site S_6
		$3A_{2g}$	
	$3A_2$		
		$4A_{2u}$	
$3F_{1u}$			A_u
		$4E_g$	
	$4E$		
		$6E_u$	E_u
F_{2u}		A_{1g}	
	A_1		
		$2A_{1u}$	

As pointed above, the normal vibrations of the TaO_6 octahedron are reduced to

$$3F_{1u} + F_{2u}$$

And one of the three F_{1u} modes is translation vector T. These modes will split into other low symmetry modes when the symmetry of the octahedron is lowered, as shown in Tab.1. In D_3 site these three fold degeneracy modes splited into:

$$3A_2 + 4E + A_1$$

And the translation vector is

$$E + A_2.$$

The A_2 mode is the motion of the octahedron along z-axis, and the E mode is the motion in the xy-plane.

In the crystal lattice of paraelectric phase, the Li ions have the sites of S_6 symmetry, their translational vectors split into

$$A_u + E_u.$$

A_u: motion of ion along z-axis; E_u: motion of ion in the xy-plane

The paraelectric primitive unit cells formed by the oxygen octahadra and Li ions have the point symmetry of D_{3d}. The normal vibrational modes of the crystals in paraelectric phase are correlated with that of the two components, as given in Tab.1.

In paraelectric phase the optical vibrational modes are distributed among irreducible representations as follows:

$$A_{1g} + 3A_{2g} + 4E_g + 2A_{1u} + 3A_{2u} + 5E_u$$

where the A_{1g} and E_g modes are Raman active, the A_{2u} and E_u modes are infrared active, and the A_{1u} modes are silent for both of Raman and infrared.

As to the ferroelectric phase with the symmetry of C_{3v} point group, there are eighteen vibrational modes.

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

of which the four A_1 modes and nine E modes are Raman active modes, and the five A_2 modes are silent modes, i.e. nonactive for both of Raman and infrared. The correlation between the modes of ferroelectric phase and that of paraelectric phase are presented as below(Tab.2).

MEASUREMENT RESULTS AND DISCUSSION

A. Ferroelectric Phase

In ferroelectric phase the A_1 (TO) modes can be observed with the X(ZZ)Y configuration, and the E(TO) modes can be observed in the X(ZX)Y geometry. Figures 1 and 2 show the two kinds of normal vibrational modes respectively. From Fig.1 we can see that all the four Raman active A_1 modes are shown. The frequency-shifts are $203cm^{-1}$, $252cm^{-1}$, $356cm^{-1}$, $598cm^{-1}$. which are in accordant with the previours work.[9] In Fig.2 the nine Raman acttive E modes are presented,

TABLE 2

Correlation Between the Normal Vibrational modes of Ferroelectric Phase and That of Paraelectric Phase in $LiTaO_3$ Crystals

Paraelectric Phase D_{3d}	Ferroelectric Phase C_{3V}
A_{2g}	
	A_2
A_{1u}	
A_{2u}	
	A_1
A_{1g}	
E_g	
	E
E_u	

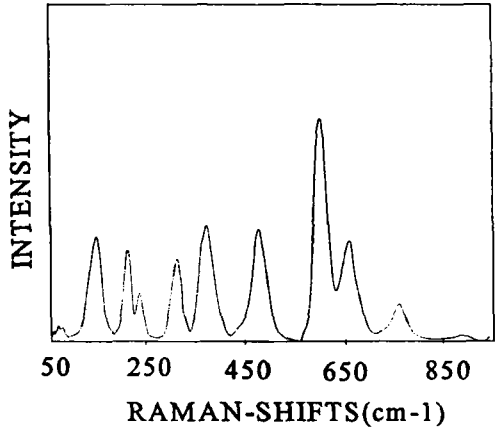

Fig.2 Raman spectra of E modes in $LiTaO_3$ crystal measured with X(ZX)Y geometry at room temperature(300K).

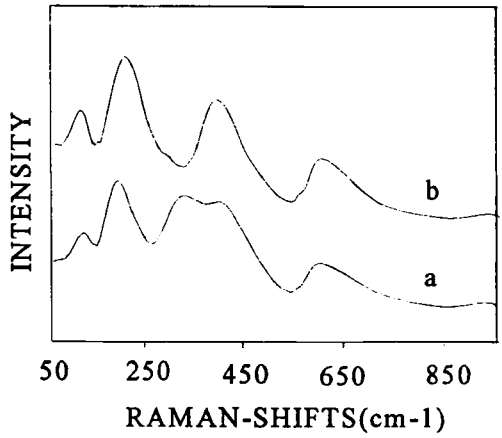

Fig.3 Raman spectra of A_1 and E modes of $LiTaO_3$ in paraelectric phase measured at 1000K.

their frequency-shifts are 149cm^{-1}, 211cm^{-1}, 242cm^{-1}, 314cm^{-1}, 377cm^{-1}, 461cm^{-1}, 593cm^{-1}, 656cm^{-1}, and 746cm^{-1} which are also similar to the results of ref.9.

B. Paraelectric Phase

As pointed above only the A_{1g} and E_g modes are Raman active in the paraelectric phase, nonpolarized measurement was performed. The measurements temperature was set at 1000K, the results are shown in Fig.3. From the changing process of the Raman spectra via the temperature of samples, it is shown that the A_{1g} mode in the paraelectric phase is correlated with one A_1 mode which located at ~350cm^{-1} in the ferroelectric phase. And the other three A_1 modes in the ferroelectric phase are correlated with the three A_{2u} modes in paraelectric phase which are non-Raman active, so cannot be observed in the Raman spectra. It should be note that the A_{1g} mode correlated with the 350cm^{-1}- A_1 mode does not show remarkable frequency changes during the phase transition. The other four scattering peaks in the Fig.3 are attributed to the four E_g modes. Their frequencies

do not shift much compare to the correlated E modes. From the results given above it can be concluded that the phase transition does not affect the lattice vibration largely, so that the vibration frequencies of the corresponding modes do not show much changes.

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