The composition dependence and new assignment of the Raman spectrum in lithium tantalate

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Abstract

The Raman scattering spectra of lithium tantalate crystals with different compositions were investigated. The comparison of the Raman data obtained for the congruent and the near-stoichiometric crystals reveals some differences in the shape and the number of Raman peaks, which lead to a new assignment of the long-wavelength optical phonons. And quantitative relationships between the linewidth of Raman peaks (142 cm^{-1} for E-phonon and 861 cm^{-1} for A_1-phonon) and the crystal composition were firstly presented. Two local Raman lines, 278 and 750 cm^{-1}, were found for the congruent crystals and attributed to the intrinsic defects, Li vacancy and anti-site Ta ion, respectively.
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1. Introduction

Lithium tantalate ($LiTaO_3$, LT) is one of the most excellent and useful materials for piezoelectric, electro-optic, and nonlinear optical applications [1,2]. The lattice dynamics of $LiTaO_3$ has been the object of numerous investigations using the Raman spectroscopy [3–6]. But some disagreements have been reported between various authors and the assignment of the long-wavelength optical phonons was not clearly established. Since all these investigations were carried out on congruent lithium tantalate (CLT), which is grown from the congruent melt of Li/Ta=48.74/51.26. However, many experiments have

prove that the near-stoichiometric lithium tantalate (SLT) with the Li/Ta ratio of nearly one has better performance in the optical applications [7,8]. In order to find out the origin of performance improvement, SLT crystal was investigated by many methods, in which Raman scattering spectrum has been proved to be a powerful tool. Especially, the Raman scattering technique could be used to determine the composition from the measurement of the width of some particular lines [9]. However the possible variation of Raman lines (shape and positions) with the composition or the Li/Ta concentration ratio has been investigated rarely.

The goal of this paper is to give a complete and clear assignment of the long-wavelength optical phonons. A quantitative relationship between Raman linewidth and compositions of the $LiTaO_3$ samples was presented. And two new local Raman lines related to intrinsic defects were also introduced.

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2. Experiments

LiTaO$_3$ crystals with various compositions were investigated in this paper. The starting crystals were grown from a congruent melting composition by the Czochralski method. Then, these as-grown crystals were cut into y- and z-cut plates of 1.2 mm thickness. In order to obtain nearly stoichiometric LiTaO$_3$ crystals, the vapor transport equilibration (VTE) technique was employed [10]. The congruent plates were wrapped with Pt wire to avoid contact with the mixing LiTaO$_3$ powder. The reaction crucible containing the crystal and the powder, was positioned within the hot zone of a platinum wound resistance furnace, heated (10 °C/min) to the desired reaction temperature (1200 °C), and maintained at this temperature for a given time (140 h). At last, these plates were removed from the furnace and cooled down to room temperature. Each sample was then polished to optical grade.

Raman scattering experiments were carried out in a Renishaw Ramanscope 2000 spectrometer using the 632.8 nm exciting line of a He–Ne laser with 30 mW output power in backward scattering geometry and a SPEX-1403 monochromator in right angle scattering geometry. And the transmission spectrum of LiTaO$_3$ crystal in the ultraviolet and visible wavelength regions was measured using a UV-365 spectrometer at room temperature in wavelength of 240–380 nm.

3. Results and discussion

LiTaO$_3$ samples were obtained using the VTE method, and the compositions of these samples were determined by the ultraviolet absorption edge [11]. The absorption edge wavelengths was defined as the wavelength where the absorption coefficient is $\alpha = 20$ cm^{-1}. The compositions of these samples vary from 48.74 to 49.8 mol% Li$_2$O. The relationship between the compositions of these samples and Raman linewidth was presented. One SLT sample (composition 49.8 mol%) and one CLT sample (composition 48.74 mol%) were selected for the assignment of the Raman modes.

3.1. The assignment of Raman modes

Transverse E(TO) modes can be detected in the $y(zx)y$ configuration in backward scattering geometry whereas E(LO) and A$_1$(TO) phonons are simultaneously detected in $y(xx)y$ configuration. Figs. 1 and 2 exhibit the Raman spectra in these two configurations for both SLT and CLT samples, respectively. It is easily seen that the peaks for SLT sample are thinner, better resolved and more intense compared with CLT sample. So, it is advantaged to attribute peaks in the spectrum for SLT to first-order phonons unambiguously.

According to the group theory, 9 and 13 Raman peaks are respectively expected in the $y(zx)y$ and $y(xx)y$
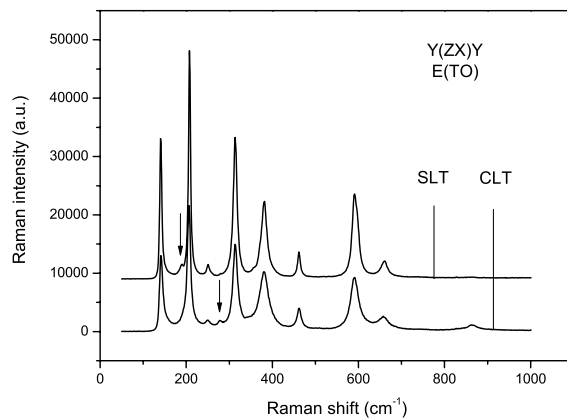

Fig. 1. The Raman spectra in the $y(zx)y$ configuration for CLT and SLT (the arrows point the frequency where new peaks clearly appear for SLT sample and the peak which related to Li vacancy (V$_{Li}^-$) for CLT sample).

configurations. The $y(zx)y$ spectrum for SLT sample (Fig. 1) exhibits nine well resolved peaks which correspond to all E(TO) phonons. In our experiment, we can't find the band around 90 cm^{-1} in Raman spectrum for both SLT and CLT crystals (Fig. 1), which is the main disagreement in the literature. This experimental evidence is consistent with the observation of Ridah et al. [12], who showed that this band was absent in the near-stoichiometric lithium niobate (SLN) samples. The well resolved peak (around 190 cm^{-1}) is observed for SLT sample, which is hidden in the strong peak at 208 cm^{-1} for CLT crystal. The appearance of this peak should thank to the high stoichiometry of crystal. We assign this peak to the first-order E(TO) phonons, which is reasonable because one corresponding phonon of SLN also occurs in the range from 150 to 200 cm^{-1} [12].

However, the total number of Raman-active modes does not accord with the group theory in Fig. 2, which may be due to the localization of the assignment used. Instead of 9
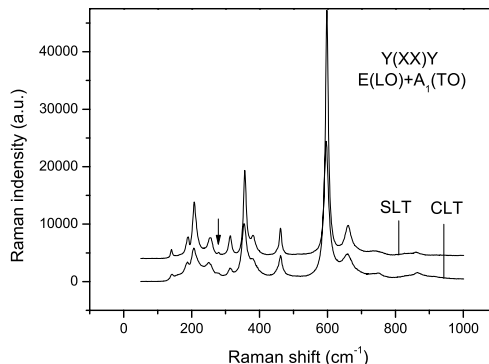

Fig. 2. Raman spectra of E(LO)+A$_1$(TO) modes for both SLT and CLT samples in the backward scattering configurations (the arrows point the frequency where new peaks clearly appear for SLT sample).