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# Preparation and defect structure analysis of near-stoichiometric lithium tantalate wafers

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A vapour transfer equilibrium (VTE) method has been used to prepare near-stoichiometric lithium tantalate (NSLT) crystals with different Li contents. The NSLT crystals were tested and analyzed by differential thermal analysis (DTA) and X-ray photoelectron spectroscopy (XPS) to investigate the effect of Li content on the Curie temperature and internal defects of NSLT crystals. This study found that when the Li content increased in the NSLT wafer, the binding energy corresponding to the peak of the Ta<sub>4f</sub> electron layer in the XPS spectrum first decreased and then increased, indicating that the proportion of Ta valence states was different in wafers with different Li contents. From XPS energy spectrum analysis, it can be seen that the lithium tantalate crystal contains Ta<sup>5+</sup>, Ta<sup>4+</sup>, Ta<sup>3+</sup> and lower-valence Ta. As the Li content increases in the NSLT wafer, Ta<sup>4+</sup> disappears and the proportion of Ta<sup>5+</sup> decreases initially, follows by a later increase and then subsequent further decrease. However, the change in proportion of Ta<sup>3+</sup> and lower-price Ta is completely opposite to that of Ta<sup>5+</sup>, showing a trend of first rising, then falling and then finally rising again. Moreover, when the Li content is 49.751% in the NSLT wafer, the proportion of Ta<sup>5+</sup> reaches a maximum, showing that at this Li concentration the NSLT crystal has a more perfect lattice structure. In this study, we propose a mixed defect model in which polarons coexist with Li vacancies and Ta inversion, explaining the change in Ta valence state in lithium tantalate crystals. This model is more in line with the observed results in this work. The new hybrid defect model and the variation law of Ta valence state with Li concentration proposed in this paper provide a new direction and experimental proof for the defect study of NSLT crystals, and also provide a theoretical basis to explore the Li content at the best physical properties of NSLT crystals.

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## 1 Introduction

Lithium tantalate (LiTaO<sub>3</sub>, LT) crystal is an excellent piezoelectric, ferroelectric and optical crystal with good piezoelectric, pyroelectric and electro-optical properties.<sup>1,2</sup> It can be used to make filters, lasers, oscillators and other devices, and is known as the “universal crystal”. LT crystals are also known as the most important basic material for wireless communication because of their unique advantages in making SAW filters.<sup>3</sup> In addition, LT crystals have important applications not only in acoustics but also in optics, especially in lidar, air pollution detection and medical examination. At present, there are many studies on the optical application of NSLT crystals, including the application of NSLT crystals in lasers when doped with other ions.<sup>4–8</sup>

The crystals are divided into congruent lithium tantalate (CLT) and near-stoichiometric lithium tantalate (NSLT) crystals,

according to the Li-to-Ta ratio in LT crystals. Among these, the ratio of Li and Ta in CLT crystals is approximately 48.5 : 51.5, while the ratio of Li and Ta in NSLT crystals is close to 1 : 1. Due to the reduced Li content in CLT, a large number of defects appear in the crystal,<sup>9</sup> including Li vacancies (V<sub>Li</sub>)<sup>10</sup> and Ta inversion defects (Ta in Li position, Ta<sub>Li</sub>).<sup>11</sup> Li vacancy defects will increase the coercivity field inside the crystal<sup>12</sup> and Ta<sub>Li</sub> defects cause optical damage.<sup>13</sup> Therefore, Li content has a great influence on the internal defect structure and crystal properties of LT, as the internal defects of LT crystals affect the crystal lattice and conductive carriers.<sup>14,15</sup> Therefore, the Li concentration in LT crystals has an impact on the thermal conductivity and conductivity of the crystal and, thus, on the performance of the device.

The crystal structures of LT and lithium niobate (LN) crystals are similar, so the defect structure of LN crystals is investigated in this paper. Initially, Lerner *et al.* proposed the most widely-used defect model, the Nb anti-occupancy defect model.<sup>16</sup> Later, Kim *et al.* perfected the model, proposing that the anti-occupied Nb is surrounded by three Li vacancies and one Li vacancy along the *c*-axis.<sup>17</sup> More recently, Chen *et al.* used density functional theory, X-ray diffraction (XRD) and high-

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temperature Raman spectroscopy to study the defects of LN and near-stoichiometric lithium niobate (NSLN) crystals.<sup>18</sup> It was found that Nb in Li positions ( $\text{Nb}_{\text{Li}}$ ) and  $\text{V}_{\text{Li}}$  defects are the most stable defects in LN crystals, further proving the applicability of  $\text{Nb}_{\text{Li}}$  and  $\text{V}_{\text{Li}}$  defects.

Leroux *et al.* used high-resolution electron microscopy to study the defects of LN crystals and found many 1 nm defects.<sup>19</sup> Based on this phenomenon, a  $\text{Nb}_2\text{O}_5$  cluster defect model was proposed. Among these clusters, the cation arrangement along the c-axis changes from normal  $\text{-LiNb-}\square\text{-LiNb-}\square\text{-}$  to ilmenite stacking  $\text{-LiNb-}\square\text{-NbLi-}\square\text{-}$ . Maaider K *et al.* found a characteristic peak of  $738\text{ cm}^{-1}$  in the Raman spectrum of LN, which is characteristic of titanite.<sup>20</sup> Therefore, it was concluded that the defect structure of LN crystal is suitable for modelling using the  $\text{Nb}_2\text{O}_5$  cluster defect model.

Although VNb (Nb vacancies) cannot exist from the energy point of view, Abdi *et al.* verified the possibility of coexistence of  $\text{V}_{\text{Li}}$  with  $\text{V}_{\text{Nb}}$  using Raman spectroscopy, with  $\text{V}_{\text{Li}}$  dominating.<sup>21</sup> Meanwhile, the study of LN crystal spectra revealed the presence of polaritons in LN crystals.<sup>22</sup> Shi *et al.* studied the defect structure of LN using high-temperature optical reduction spectroscopy, and concluded that LN crystal contains not only free polarons (quasiparticles composed of trapped electrons and local distortion), but also bound polarons and bipolarons.<sup>23</sup> Diffraction density tests also support the existence of polarons, and  $\text{Nb}_{\text{Li}}$  absorbs electrons more easily than  $\text{Nb}_{\text{Nb}}$ .<sup>24</sup> Schmidt *et al.* calculated various defect models of near-stoichiometric lithium niobate crystals using density functional theory (DFT), and found that the  $\text{Nb}_{\text{Li}}^{4+}$  defect is equivalent to an  $\text{Nb}_{\text{V}} + \text{V}_{\text{Li}}$  defect.<sup>25</sup> Moreover, O and Nb in LN crystals can capture excess electrons to form polarons.

At present, there are three defect models of LN. The most applicable and accepted models are the  $\text{V}_{\text{Li}} + \text{Nb}_{\text{Li}}$  defect model, the  $\text{Nb}_2\text{O}_5$  cluster defect model, and the model based on the  $\text{Nb}_{\text{Li}} + \text{V}_{\text{Li}}$  defect model with the addition of polaritons.<sup>16–25</sup> Since the structure of LT crystals is similar to that of LN crystals, the defect model of LT crystals is considered to be the same as that of LN crystals, which also conforms to the above three defect models.

In this work, NSLT wafers with different Li concentrations were prepared using a VTE method. The effects of Curie temperature and internal Li content on the atomic valence of NSLT crystals were studied. The binding energies and valence change law of Ta and O were studied by XPS. The change law of internal defects in NSLT crystals with changing Li concentration was obtained, and the defect model was verified experimentally as being in line with the change law of NSLT defects.

## 2 Experiment

### 2.1 Preparation of NSLT wafer

Lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) and tantalum oxide ( $\text{Ta}_2\text{O}_5$ ) were fully mixed with a roller ball mill in a fixed molar ratio, and the LT polycrystalline material was made by holding at  $1300\text{ }^\circ\text{C}$  for 6 h in a high-temperature furnace. The polycrystalline material was placed in a ceramic crucible and grown by a pulling

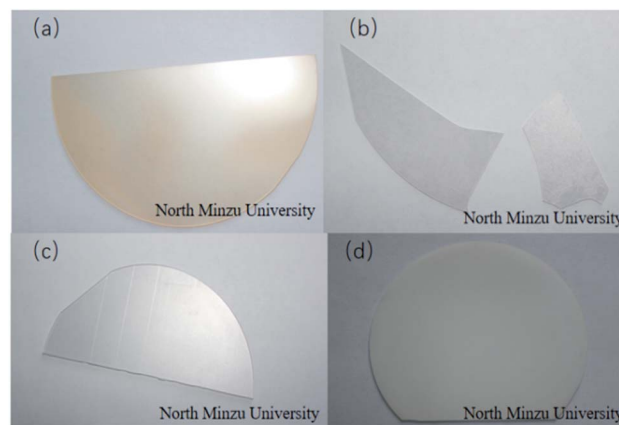


Fig. 1 LT wafers (a) #1 (b) #2 (c) #3 (d) #4.

method. The grown crystal was processed by grinding, slicing, grinding and polishing to make the LT wafer.

$\text{Li}_2\text{CO}_3$  (99.99%) and  $\text{Ta}_2\text{O}_5$  (99.99%) were mixed according to a certain molar ratio, and then mixed evenly and kept at a high temperature for a period of time as standby diffusion material. Then, the LT wafer and diffusion material were alternately placed into the ceramic crucible and heated in the high-temperature furnace to make the NSLT wafer. NSLT wafers processed by VTE were labelled as #1 and NSLT wafers processed by VTE were numbered as #2, #3 and #4. All chips were  $\text{Y36}^\circ$  LT chips. As shown in Fig. 1, #1 chips are light yellow, while #2, #3 and #4 chips are white. Wafer #1 was an untreated LT wafer, wafer #2 was insulated in the diffusion material at  $1300\text{ }^\circ\text{C}$  for 60 h, wafer #3 was insulated in the diffusion material at  $1250\text{ }^\circ\text{C}$  for 60 h, and #4 wafer was insulated in the diffusion material at  $1160\text{ }^\circ\text{C}$  for 60 h.

### 2.2 Differential thermal analysis (DTA) testing

Testing was performed using a Shimadzu DTG-60AH differential thermal analyser (DTA) with  $\text{N}_2$  as a pure protective gas. The heating rate was  $20\text{ }^\circ\text{C min}^{-1}$  from room temperature to  $800\text{ }^\circ\text{C}$ . The argon flow rate was  $50\text{ mL min}^{-1}$ . Samples #1, #2, #3 and #4 were all tested under the same conditions.

### 2.3 X-ray photoelectron spectroscopy (XPS) testing

The XPS spectra of all LT samples were measured using a ThermoFisher Scientific *k*-Alpha X-ray photoelectron spectrometer. Each test sample was etched twice. The XPS spectra of the sample surface, with etching depths of 40 and 80 nm were both tested. All samples were tested under the same conditions.

Table 1 Sample quality, Curie temperature and Li content of wafer

Sample number	#1	#2	#3	#4
Quality (mg)	16.57	26.59	31.54	31.90
Curie temperature ( $^\circ\text{C}$ )	604.06	648.60	677.23	691.01
Li content (%)	48.710	49.344	49.751	49.947



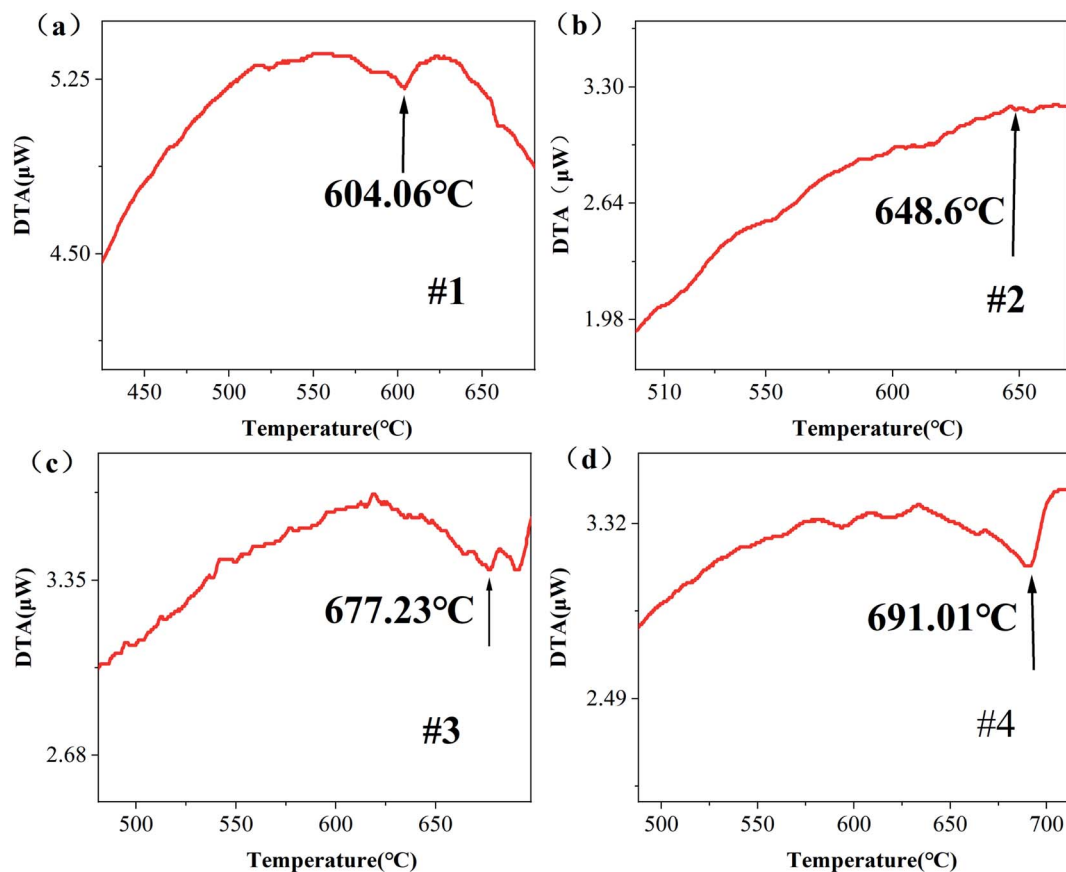


Fig. 2 DTA diagram of wafers (a) #1 (b) #2 (c) #3 (d) #4.

## 2.4 Raman spectrum testing

The Raman spectra of the LT and NSLT crystal samples were tested using an inViaTM laser confocal micro Raman spectrometer from Renishaw, UK. A 532 nm laser with an exposure time of 10 s was used and scanned in the range of 100–1000  $\text{cm}^{-1}$ . All samples were tested under the same conditions.

## 2.5 Raman imaging testing

An array of 4800 Raman spectra was sequentially acquired at 1  $\mu\text{m}$  step intervals in the selected 60  $\mu\text{m} \times 80 \mu\text{m}$  region for Raman imaging of the target peaks. The 4800 acquired Raman spectra were subjected to uniform cosmic ray removal and the imaging peaks were fitted using analytical software, and then microscopic Raman imaging was performed using the peak positions of the fitted spectral peaks. All samples were tested under the same conditions.

# 3 Results and discussion

## 3.1 Differential thermal analysis

After a series of processes of cleaning, drying and grinding, the NSLT wafers with different Li contents were made into powder samples for DTA. The sample mass is shown in Table 1. When the test sample changes phase, the LT powder goes through an endothermic process; that is, when the LT sample changes from

ferromagnetic to paramagnetic, there will be a step-wise shape first, and then a clear inflection point. At this time, the transformation of the LT sample from ferromagnetic to paramagnetic will first appear as a step, and then an obvious inflection point, which corresponds to the Curie temperature of the LT wafer.<sup>26</sup> It can be seen from Fig. 2 that the Curie temperatures of #1, #2, #3 and #4 samples are 604.06, 648.6, 677.23 and 691.01  $^{\circ}\text{C}$ , respectively. The LT wafers treated using the VTE method have higher Curie temperatures than the untreated LT wafer. The Curie temperature may reflect the lithium content inside the LT wafer. According to Yang *et al.*,<sup>27</sup> the formula relating Curie temperature and lithium content is as follows:

$$T_c = -2821.1 + 70.3143C_{\text{Li}} \quad (1)$$

$$C_{\text{Li}} = 40.121 + 1.422 \times 10^{-2} T_c \quad (2)$$

Table 2 O content of samples at different etching depths

O Atomic (%)	Sample number			
	#1	#2	#3	#4
Surface	57.11	50.81	50.06	49.57
Etching depth 40 nm	46.70	49.26	48.12	47.70
Etching depth 80 nm	47.29	44.21	46.19	46.75
Average	50.40	48.09	48.12	48.00



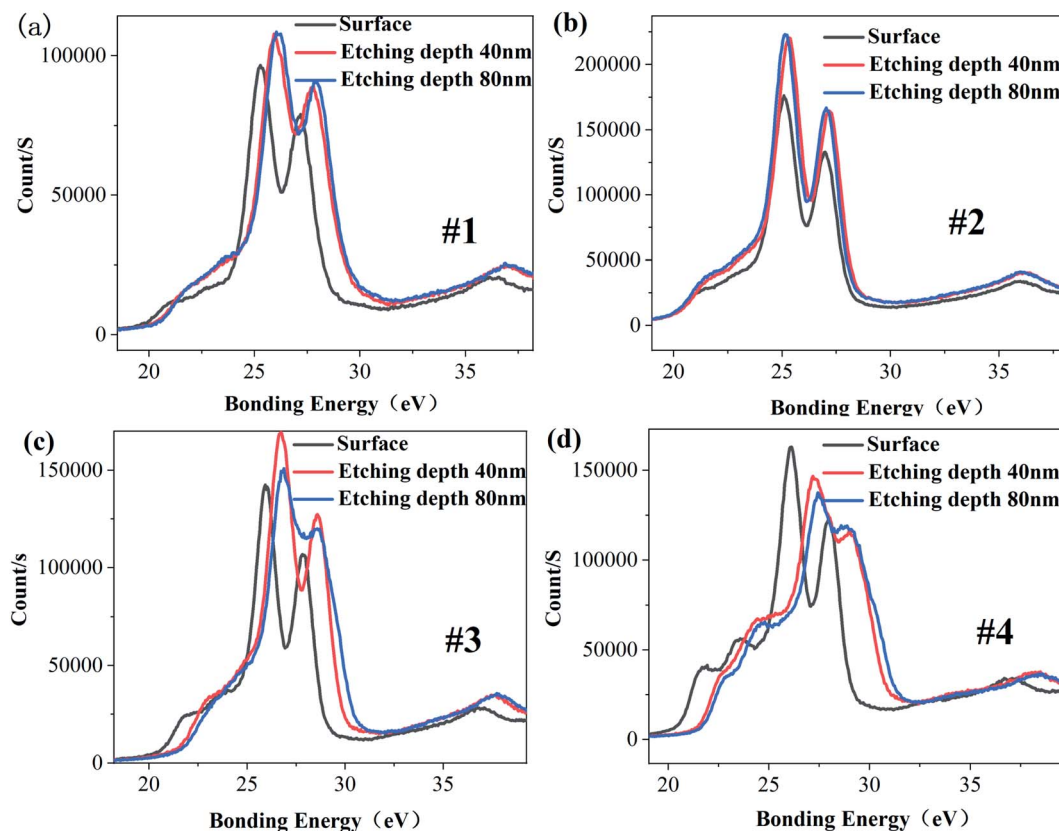


Fig. 3 XPS spectra of Ta4F electron layer on the surface and etching depth of 40 nm and 80 nm (a) #1 (b) #2 (c) #3 (d) #4.

According to the above formula, the Li concentration of samples #1–3 and #4 is 48.710%, 49.344%, 49.750% and 49.947%, respectively. From the calculated Li concentrations, it can be seen that chip #1 is the CLT chip, and the Li/Ta of sample #4 is the closest to 1 : 1.

### 3.2 X-ray photoelectron spectroscopy (XPS) analysis

It can be seen from Table 2 that the O content on the surface of samples #1–4 is 57.11%, 50.81%, 50.06% and 49.57%, respectively, showing that the O atomic content on the surface of crystals #2–4 crystals is less than that of #1. When the etching depth is 40 or 80 nm, samples #1–4 show little difference in O

Table 3 Binding energy corresponding to each peak of Ta4F electron layer

Etching depth (nm)	0	40	80
#1 peak binding energy (eV)	25.28	27.18	25.93
#2 peak binding energy (eV)	25.08	26.98	25.33
#3 peak binding energy (eV)	25.93	27.83	26.73
#4 peak binding energy (eV)	26.08	27.98	27.18

atomic content. Therefore, the use of the VTE method causes the surface of the wafer to lose a small amount of O atoms at high temperatures. However, this will not have a great impact

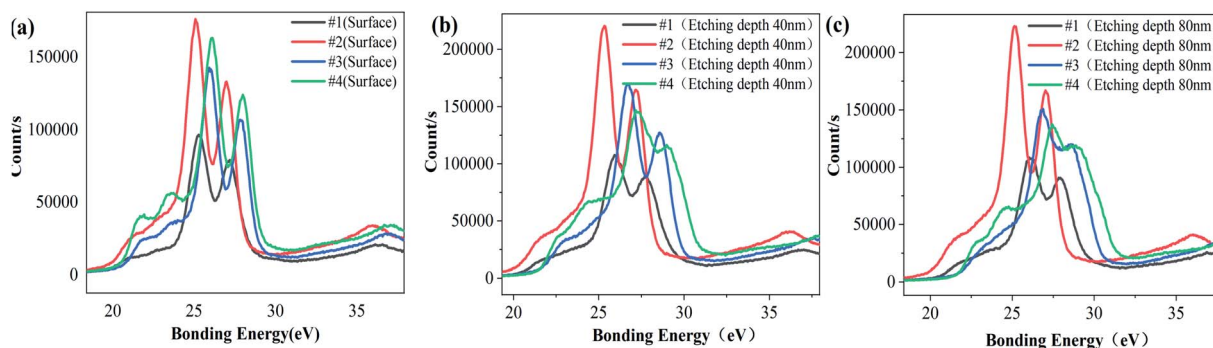


Fig. 4 Comparison of XPS spectra of Ta4F electronic layer with the same depth (a) surface (b) etching depth of 40 nm (c) etching depth of 80 nm.





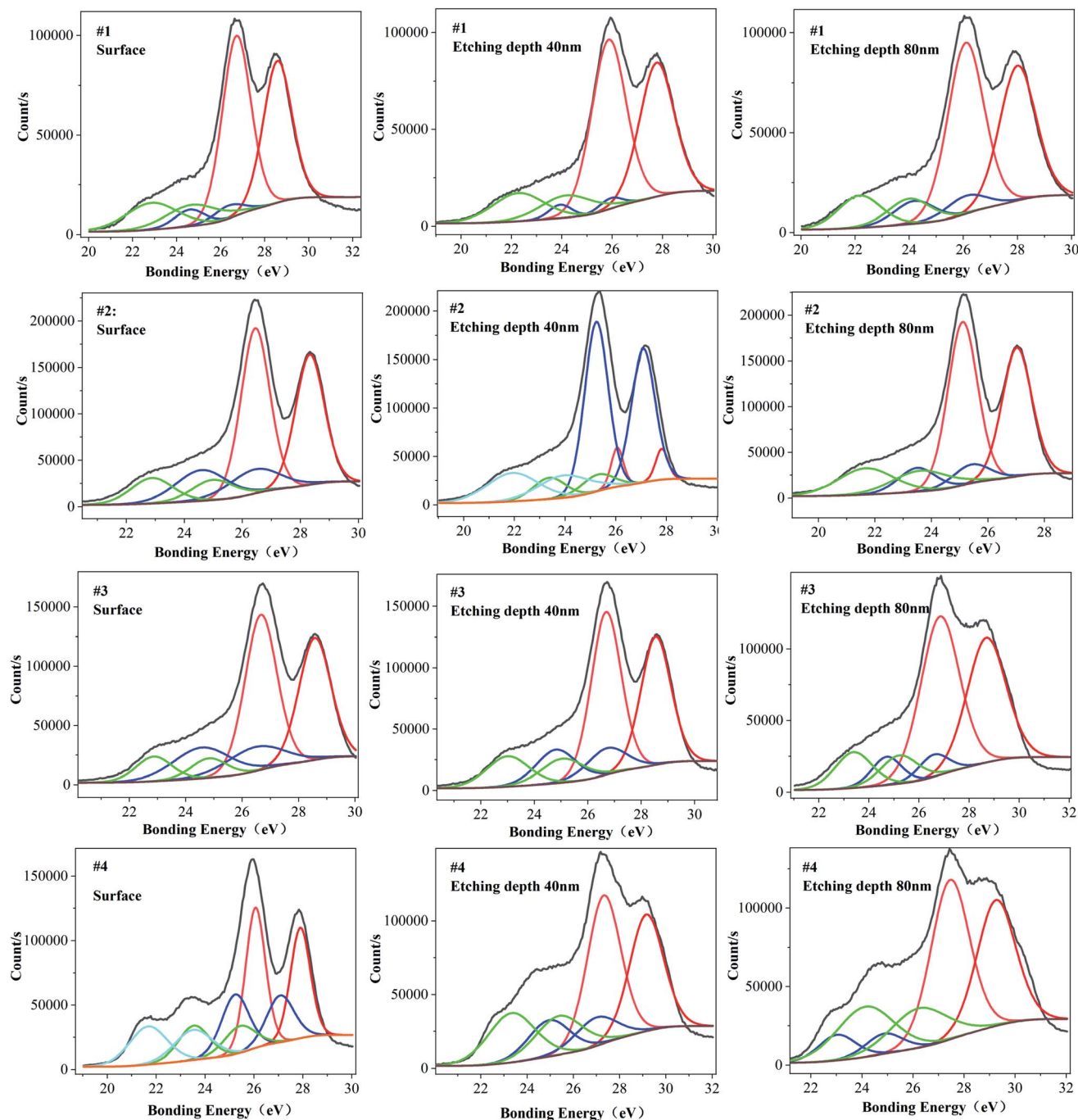


Fig. 5 Peak splitting fitting of Ta<sub>4</sub>F electron layer.

on the internal O atomic content. The relative atomic proportion of O decreases in the wafer, thus, the relative Li content of VTE-treated LT crystals increases.

Fig. 3 is the XPS energy spectrum of the Ta<sub>4f</sub> electron layer at different depths for each sample. It can be seen from Fig. 3 that the peak binding energy of Ta<sub>4f</sub> electron layer in samples #1, #3 and #4 is higher than that of the surface, and the peak binding energy of Ta<sub>4f</sub> electron layer on sample #2's surface is equal to that of the inner layer. The valence state of Ta is related to the binding energy of Ta<sub>4f</sub> electron layer. According to this analysis, it

can be concluded that the valence states of Ta in the surface and inner layer for samples #1, #3 and #4 are different, and for sample 2 they are the same. Table 3 and Fig. 4 show the corresponding binding energy values and comparison diagrams of Ta<sub>4f</sub> electron layer peaks of samples #1–4. It is clear that the double peak binding energy of the Ta<sub>4f</sub> electron layer of samples #3 and #4 is higher than that of samples #1 and #2. The double peak binding energy of Ta<sub>4f</sub> in sample #2 is the lowest among the four samples, *i.e.*, with increasing Li the peak binding energy of the Ta<sub>4f</sub> electron layer first decreases and then increases.



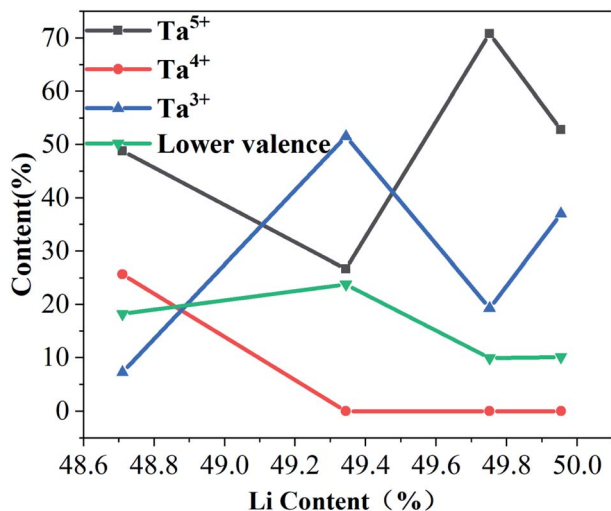


Fig. 6 Proportion of Ta valence state with different Li content in LT crystal.

The XPS spectrum was fitted using Thermo Avantage software. Using a Shirley background, a peak width less than 2.7 eV, and bimodal fitting, the area ratio of Ta4f<sub>7/2</sub> to Ta4f<sub>5/2</sub> is calculated as 4 : 3, and the peak spacing between Ta4f<sub>7/2</sub> and Ta4f<sub>5/2</sub> is 1.8–2.1 eV.<sup>28</sup> From the paper of Sun De-hui, we obtained that the binding energy of Ta4f<sub>7/2</sub> (corresponding to Ta<sup>5+</sup>)

is 27.6 eV, and the binding energy of Ta4f<sub>7/2</sub> (corresponding to Ta<sub>Li</sub><sup>4+</sup>) is 25.6 eV.<sup>29</sup> When Ta is in the environment of oxygen atoms, the binding energies are 26.05 eV for Ta<sup>5+</sup>, 24.5–24.7 eV for the binding energy of Ta<sup>4+</sup>/Ta<sup>3+</sup>, and 23.1–23.3 for Ta<sup>2+</sup>.<sup>28</sup> From the NIST XPS database, the binding energy of the Ta4f<sub>7/2</sub> electron layer of Ta<sub>4</sub>C<sub>3</sub> is 23.11 eV.<sup>30</sup> From analysis of the above results, we consider that the binding energy of Ta<sup>5+</sup> is greater than 26.05 eV, the binding energy of Ta<sup>4+</sup> is between 25.4–26.05 eV, the binding energy of Ta<sup>3+</sup> is 23.11–25.4 eV, and the lower valence Ta ion has binding energy lower than 23.11 eV.

Fig. 5 shows the fitting of the electron peaks of the Ta<sub>4f</sub> layer. From the fitting of the binding energy corresponding to the double peak, LT crystals contain Ta not only as Ta<sup>5+</sup>, but also in other valence states.<sup>31</sup> The electron binding energy of the Ta<sub>4f</sub> layer corresponds to the different valence states of Ta. The proportion of different Ta valence states of Ta is fitted according to the peak area, and this proportion is shown in Fig. 6.<sup>29</sup> It can be seen from Fig. 6 that with increasing Li concentration the proportion of Ta<sup>5+</sup> first decreases, then increases and finally decreases again. When the Li concentration is 49.751%, the proportion of Ta<sup>5+</sup> appears maximised, and the proportion of Ta<sup>5+</sup> is the highest at this time. Ta<sup>4+</sup> decreases gradually with increasing Li concentration. When Li concentration reaches 49.344%, Ta<sup>4+</sup> disappears completely. The proportion of Ta<sup>3+</sup> follows the opposite trend to that of Ta<sup>5+</sup>; with increasing Li concentration, Ta<sup>3+</sup> first increases, then decreases, and finally increases again. The proportion of Ta in other valence states

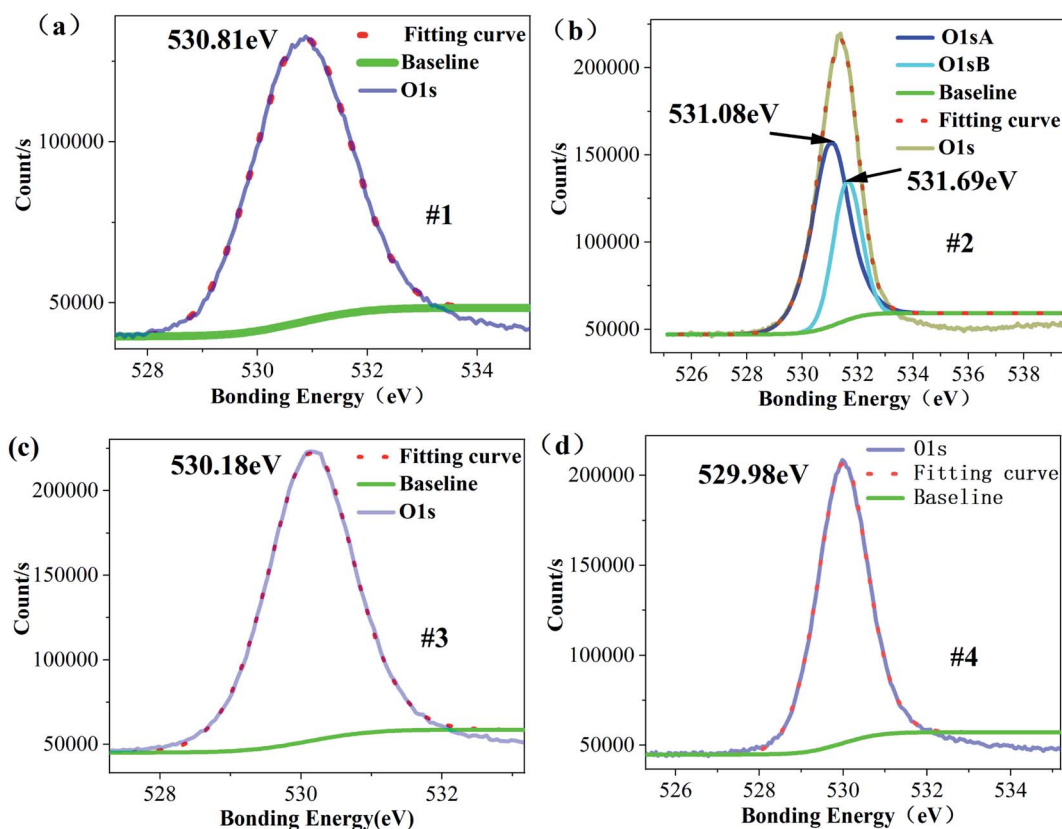


Fig. 7 XPS energy spectrum peak splitting fitting of electrons in O1s layer (a) #1 (b) #2 (c) #3 (d) #4.



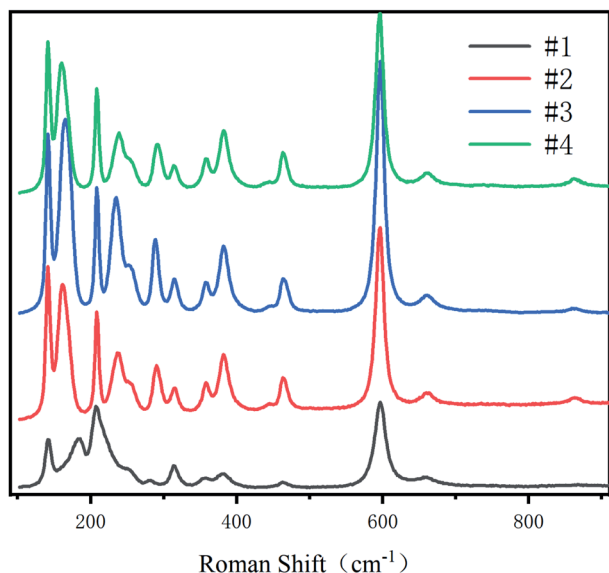
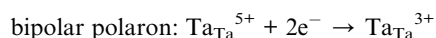
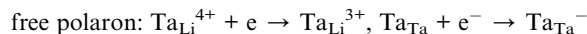


Fig. 8 Raman spectrum.

first increases, then decreases and remains unchanged. Therefore, the concentration of Li in NSLT crystals has an influence on the proportion of Ta valence states.

From valence state analysis of the Ta<sub>4f</sub> electron layer of NSLT crystals, only the V<sub>Li</sub> and Ta<sub>Li</sub> defect model could not explain the emergence of Ta<sup>3+</sup> and other Ta valence states. Therefore, our analysis follows the following three principles: (1) ensure charge balance; (2) when the number of defects in LT crystal increases, the crystal density increases; and (3) there is an Li deficiency in CLT crystals.<sup>19</sup> The lack of Li ions in the crystal will lead to the imbalance of positive and negative charges, which leads to the occurrence of defects in the V<sub>Li</sub> and Ta<sub>Li</sub> range. Some electrons in the crystal are attracted by Ta<sub>Li</sub><sup>4+</sup> defects or Ta<sub>Ta</sub><sup>5+</sup> to form polarons, and the polarized Ta will shift, that is, lattice relaxation will occur. The mechanism of polariton formation is described in Schirmer's paper.<sup>32,33</sup> The free polarons, bipolar polarons and bound polarons, proposed by Maaider *et al.*, and Nb<sub>Li</sub> defects are equivalent to Nb<sub>V</sub> + V<sub>Li</sub> (Nb<sub>Li</sub> defect shifts to the nearby octahedral oxygen site).<sup>20</sup> Krampf *et al.* calculated that, according to the first principle, LT crystals also contain polarons, bipolar and bound polarons.<sup>34</sup> We propose a new defect model of Ta<sub>Li</sub> + V<sub>Li</sub> + polarons:



Among these, Ta<sub>Li</sub><sup>3+</sup> and Ta<sub>Ta</sub><sup>-</sup> form bound polarons (Ta<sub>Ta</sub><sup>-</sup> Ta<sub>Li</sub><sup>3+</sup>)<sup>23,35</sup>. CLT crystals contain V<sub>Li</sub>, Ta<sub>Li</sub><sup>4+</sup>, V<sub>Li</sub> + Ta<sub>V</sub>, bound polarons (Ta<sub>Ta</sub><sup>-</sup> Ta<sub>Li</sub><sup>3+</sup>)<sup>2+</sup> and Ta<sub>Li</sub><sup>3+</sup>, showing that CLT crystals can simultaneously contain Ta<sup>5+</sup>, Ta<sup>4+</sup>, Ta<sup>3+</sup> and lower-valence Ta. When the Li concentration increases to 49.344%, V<sub>Li</sub> and a small proportion of Ta<sub>Li</sub><sup>4+</sup> defects disappear due to the entry of Li, resulting in the disappearance of most Ta<sup>4+</sup> in the XPS spectrum of the Ta<sub>4f</sub> electron layer. However, due to the entry of a large number of Li ions, the number of cations also increases. According to the principle of charge balance, the total price state of Ta ions decreases. Fig. 7 shows the XPS energy spectrum of the O1s electron layer. From this spectrum, the peak corresponding to its binding energy is divided into two peaks, and the peak binding energy is increased to varying degrees. This occurs because the binding energy corresponding to the XPS energy peak increases after the loss of electrons during the oxidation reaction, and the binding energy of electrons obtained in the reduction reaction decreases, indicating that O<sup>2-</sup> ions have lost some electrons. Since Ta<sub>Li</sub><sup>4+</sup> defects absorb electrons more easily, these defects absorb an electron and become Ta<sub>Li</sub><sup>3+</sup>. When the Li ion concentration reaches 49.751%, the binding energy of O decreases; that is, several electrons are gathered by O atoms. At this point, a proportion of Ta<sub>Li</sub><sup>3+</sup> becomes Ta<sub>Li</sub><sup>4+</sup> defects again, and a small portion of bound polarons disappear and become Ta<sub>Li</sub><sup>4+</sup> defects and Ta<sub>Ta</sub><sup>5+</sup> once more. As the Li content further increases, the Ta<sub>Li</sub><sup>4+</sup> defects are replaced by Li again, resulting in a large number of Ta<sup>5+</sup> ions. When the Li content continues to increase, the O binding energy decreases, indicating that the octahedral O obtains some electrons. However, the decrease is small, indicating that the electrons available from octahedral O are close to saturation. At this point, the Ta<sup>5+</sup> content decreases and Ta<sup>3+</sup> content increases, while that of lower-valence Ta does not significantly change. This implies that Ta<sub>Ta</sub> is more likely to absorb one electron to form a bound polaron with an adjacent Ta<sub>Li</sub><sup>3+</sup>, or absorb two electrons to become Ta<sup>3+</sup>.

To summarise, with increasing Li content in LT wafers, Li vacancy defects and Ta<sub>Li</sub><sup>4+</sup> defects essentially disappear. However, when Li : Ta = 1 : 1, a large amount of Ta<sub>Ta</sub><sup>3+</sup> species

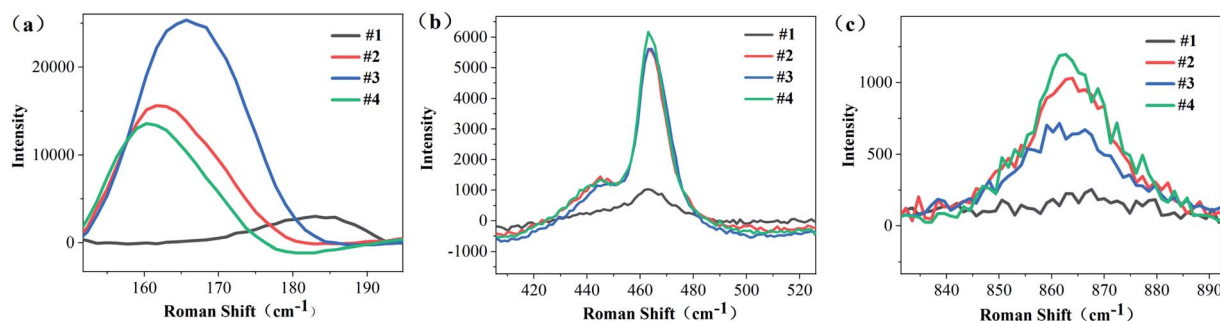


Fig. 9 Raman spectral magnification (a) 160 cm<sup>-1</sup> (b) 460 cm<sup>-1</sup> (c) 867 cm<sup>-1</sup>.



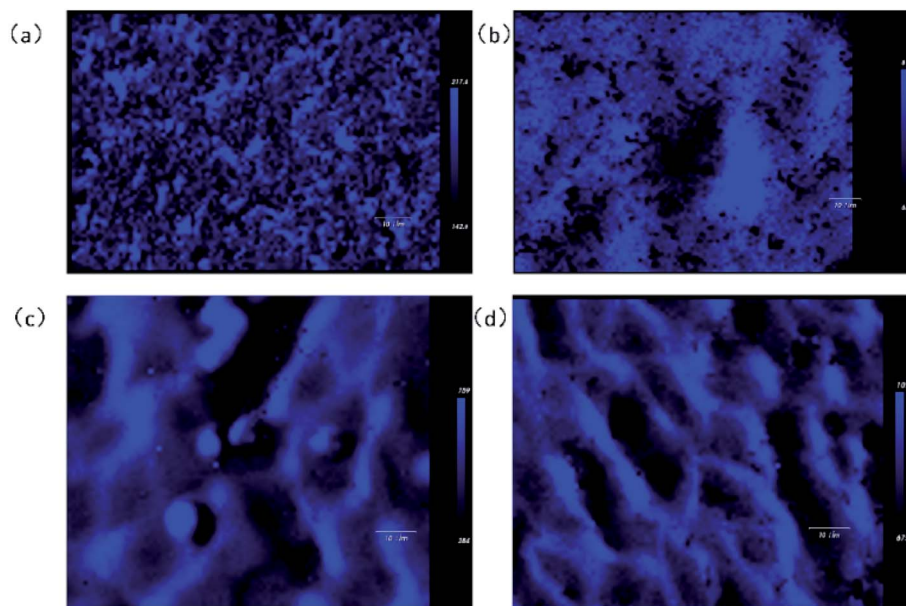


Fig. 10 Raman peak intensity imaging.

appears. When the Curie temperature is 677.23 °C and the Li content is 49.751%, the LT wafer contains the highest amount of Ta<sup>5+</sup> ions and there is no Ta<sup>4+</sup> in the wafer. The lattice structure of NSLT wafer tends to be perfect at this time; therefore, it is inferred that the performance of NSLT is also optimised at this time.

### 3.3 Raman spectroscopic analysis

Raman spectrum can characterize defects in the crystal. As can be seen from Fig. 8, #2, #3 and #4 have 13 Raman peaks, but #1 has only 11 Raman peaks # 1 sample has a Raman peak at

181 cm<sup>-1</sup>, but with the diffusion of Li ions, this peak is blue shifted. The peaks of #2, #3 and #4 samples are blue shifted to 163 cm<sup>-1</sup>, 166 cm<sup>-1</sup> and 162 cm<sup>-1</sup> respectively. And there is a companion peak at 460 cm<sup>-1</sup>, which has never appeared in the Raman spectra of NSLT crystals in other papers.

Because the Raman spectra of LT crystals with different Li contents have different baseline and the Raman peaks are not smooth, origin is used to process the Raman spectra. First, the baseline is subtracted from the original Raman spectrum; Secondly, the Raman peaks subtracted from the baseline were smoothed by savitzky Golay method; Finally, the Raman spectra were fitted with (Gaussian Lorentzian cross product) gaussian

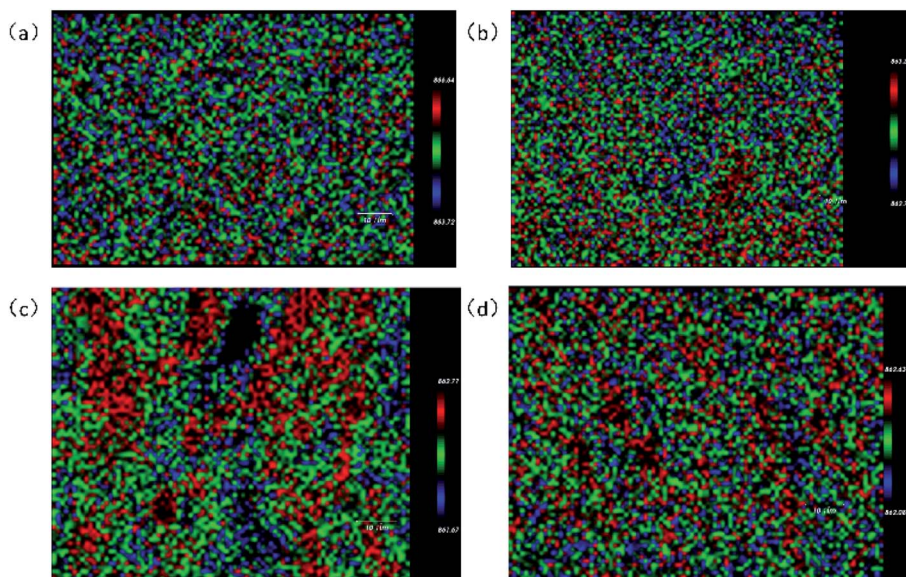


Fig. 11 Raman peak location imaging.





lorentcross,<sup>36,37</sup> and the Raman peaks near  $160\text{ cm}^{-1}$ ,  $460\text{ cm}^{-1}$  and  $867\text{ cm}^{-1}$  of LT crystal were observed in Fig. 9.

The substitution of Ta for Li reduces the translational property of the lattice, resulting in a large range of the wave vector  $k$  of the scattered rope in the Brillouin region, and the wide distribution of  $K$  leads to the increase of the Raman linewidth.<sup>38</sup> From Fig. 10(a), it can be obtained that the CLT crystal has a Raman peak at  $181\text{ cm}^{-1}$ . However, as Li increases, this Raman peak is frequency shifted and the Raman half-peak width becomes smaller. It is obvious from Fig. 10(b) that there is a companion peak at  $460\text{ cm}^{-1}$  in the Raman band, and this peak is associated with O ions, which proves that O ions change during the increase of Li content, leading to the companion peak in the Raman peak.<sup>39</sup> When the wafer is a CLT crystal, the Raman shift is  $460\text{ cm}^{-1}$  without this companion peak. With the increase of Li content, this companion peak appears and increases with the increase of Li content. Since Li and O form a weak Li–O bond, we consider this companion peak as the characteristic Raman peak of Li–O in this paper.<sup>40</sup> This companion peak also demonstrates that the defect structure of the crystal changes with the diffusion of Li into it. Figure 10(c) shows the Raman peak near  $863\text{ cm}^{-1}$ . This peak characterizes the intrinsic defects within the LT crystal, with Raman half-peak widths of 65.95, 22.5, 22.47, and  $24.62$  for #1, #2, #3, and #4, respectively.<sup>41</sup> The half-peak width of this peak did not tend to decrease all the time with increasing Li content, so this peak was subjected to Raman imaging to further investigate this peak.

### 3.4 Raman imaging

In order to observe the atomic and stress distribution of NSLT crystals, the  $863\text{ cm}^{-1}$  peak was observed by Raman imaging to observe the intrinsic defects and structure.

From Fig. 10, it can be seen that the peak intensity of CLT is 217.4, while that of NSLT is 1071, with the diffusion of Li ions entering. From the analysis of peak intensity distribution, with the increase of Li content, the peak intensity distribution gradually converges and eventually presents a grid distribution, that is, the stress distribution is better concentrated, which also proves that the increase of Li content leads to the decrease of defects. The Peak Position Map also re-demonstrates that Li diffusion can lead to changes in local structure. From Fig. 11, we can see that with the increase of Li content, the red pixel points in the graph increase significantly, and the clustering of different pixel points occurs, especially in Fig. 11c.

The peak intensity of Raman imaging demonstrates that the diffusion of Li leads to defect reduction and better ordering of atoms, but there are also some stress concentrations. From the peak position map of Raman imaging, it can be seen that the distribution of atoms in LT crystals is not very uniform, and the local disorder in LT crystals becomes more obvious with the diffusion of Li ions.

## 4 Conclusions

NSLT crystals with different Li contents was prepared by VTE method. The effects of different Li content on the internal

structure of LT wafers and on the mechanism of defect formation were discussed. The Curie temperature of LT wafers treated by VTE increased significantly, and the Curie temperature is positively correlated with the Li content in the LT crystals. Therefore, the Li content increased in LT crystals treated by VTE.

From the XPS spectrum of NSLT crystals, it was concluded that the crystal contains Ta in various valence states. The entry of Li ions leads to a large increase of cations in the crystal, which changes the gain and loss of electrons and the peak binding energies of Ta and O. LT crystals contain  $\text{Ta}^{5+}$ ,  $\text{Ta}^{4+}$ ,  $\text{Ta}^{3+}$  and lower-valence Ta.  $\text{Ta}^{4+}$  appears due to the occurrence of a Ta inversion defect, and a portion of  $\text{Ta}^{4+}$  ions absorb one electron to form  $\text{Ta}^{3+}$ . The absorption of electrons leads to the shift of the  $\text{Ta}^{3+}$  position and the formation of a bound polaron with  $\text{Ta}_{\text{Ta}}^{4+}$  which absorbs one electron, resulting in the emergence of lower-valence Ta. When the Li content increases, the  $V_{\text{Li}}$  vacancies and a small portion of  $\text{Ta}_{\text{Li}}^{4+}$  disappears, and another portion of  $\text{Ta}_{\text{Li}}^{4+}$  absorbs an electron to become  $\text{Ta}_{\text{Li}}^{3+}$ . Due to the injection of a large number of cations, part of  $\text{Ta}_{\text{Ta}}^{5+}$  absorbs an electron and becomes  $\text{Ta}_{\text{Ta}}^{4+}$ , forming a bound polaron  $(\text{Ta}_{\text{Ta}}^{5+}\text{Ta}_{\text{Li}}^{3+})^{2+}$  with  $\text{Ta}_{\text{Li}}^{3+}$ . At this time, the relative proportion of  $\text{Ta}^{5+}$  decreases,  $\text{Ta}^{4+}$  disappears completely, and the proportion of  $\text{Ta}^{3+}$  and lower-valence Ta increases. When the Li content increases to 49.751%, O absorbs some electrons. A portion each of  $\text{Ta}_{\text{Li}}^{3+}$ ,  $\text{Ta}_{\text{Ta}}^{4+}$  and  $\text{Ta}_{\text{Li}}^{3+}$  in the form of bound polarons  $(\text{Ta}_{\text{Ta}}^{5+}\text{Ta}_{\text{Li}}^{3+})^{2+}$  disappear, and Li returns to the original octahedral O site.  $\text{Ta}_{\text{Li}}^{4+}$  changes back to  $\text{Ta}^{5+}$ , but a small part of  $\text{Ta}_{\text{Li}}^{3+}$  and  $(\text{Ta}_{\text{Ta}}^{5+}\text{Ta}_{\text{Li}}^{3+})^{2+}$  remain. When the Li content increases to 49.947%, part of  $\text{Ta}_{\text{Ta}}^{5+}$  absorbs two electrons and becomes  $\text{Ta}_{\text{Ta}}^{3+}$ . This leads to a decrease in  $\text{Ta}^{5+}$  and an increase in  $\text{Ta}^{3+}$ , while the proportion of lower-valence Ta remains unchanged. Local distortions on the wafer surface and local structural disorder affecting the valence state of Ta are also seen from Raman spectra and Raman imaging. From the above analysis, the mixed defect model of polarons, Li vacancies and Ta inversions is more suitable to describe the Ta valence changes.

The results show that when the content of Li is 49.751%, this is the inflection point with regards to the proportion of  $\text{Ta}^{5+}$ . Compared with other tested samples, the lattice of this NSLT crystal is closest to the perfect lattice, and so it is speculated that the physical properties of the NSLT crystal are optimised at this Li content. In future work, we will continue to explore the best inflection point of  $\text{Ta}^{5+}$  content in NSLT crystals. Exploring the optimal performance of Li concentration in NSLT crystals is a prospective work for its future applications, such as optical resonators based on NSLT crystals, surface acoustic wave filters, and so on. There are still some questions to be answered in this work, including whether  $\text{Ta}^{3+}$  exists as  $\text{Ta}_{\text{Ta}}^{3+}$  or  $\text{Ta}_{\text{Li}}^{3+}$  when the Li content is 49.751%, and whether or not  $\text{Ta}_{\text{Ta}}^{5+}$  is more inclined to absorb two electrons to form  $\text{Ta}_{\text{Ta}}^{3+}$ . Answering these questions will also require us to further study and clarify the defect mechanism of NSLT crystals.

## Author contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were



performed by Xuefeng Xiao, Qingyan Xu and Shuaijie Liang. The first draft of the manuscript was written by Xuefeng Xiao and Qingyan Xu and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

## Conflicts of interest

There are no conflicts to declare.

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