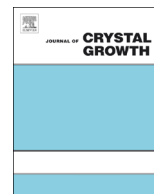




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Journal of Crystal Growth

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# Twin defects in thick stoichiometric lithium tantalate crystals prepared by a vapor transport equilibration method



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## ARTICLE INFO

### Article history:

Received 6 August 2015

Received in revised form

24 September 2015

Accepted 25 September 2015

Communicated by: V. Fratello

Available online 9 October 2015

### Keywords:

A1. Twins

A1. The sintering stress

A2. VTE method

B1. Stoichiometric lithium tantalate

## ABSTRACT

The twins were observed and investigated in vapor transport equilibration (VTE) treated lithium tantalate crystals by burying congruent lithium tantalate crystals (CLT) in a Li-rich polycrystalline powder. Twins and their etched patterns were observed under an optical polarizing microscope, and the geometry of the twins was discussed. Twin composition planes were the  $\{01\bar{1}2\}$  planes. The cause of twinning was analyzed and verified by experiment. The results indicate that the emergence of twins is due to sintering stress, which arises from sintered Li-rich polycrystalline powders at high temperature. 3.2 mm thick stoichiometric lithium tantalate (SLT) crystals without twins were obtained by setting corundum crucibles over the top of the crystals to make crystals free from the sintering stress. In addition, cracks were observed at the intersection of twin bands, and the stress caused by the dislocation pile-up was considered to be the reason for the formation of cracks.

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## 1. Introduction

Lithium tantalate (LiTaO<sub>3</sub>, LT) crystals are an attractive functional material that can be used in extensive applications such as frequency conversion [1], acoustic devices [2], holographic data storage [3] and pyroelectric detectors [4,5]. As a typical non-stoichiometric oxide, high-quality bulk LiTaO<sub>3</sub> crystals can be grown from a congruent melt by the conventional Czochralski method. However, due to lithium deficiency, there are many intrinsic defects in CLT crystals, which hinder their further applications. Compared with CLT crystals, SLT crystals exhibit better properties, including lower coercive field [6,7], a high photo-refractive damage threshold [8,9], a large electro-optical coefficient [10] and high thermal conductivity [11].

Although SLT crystals show more exciting performance than CLT crystals, it is difficult to obtain SLT crystals with high optical quality by the conventional Czochralski method because of the segregation problem associated with growing a non-congruent

composition. At present, several methods have been reported to prepare SLT crystals. Furukawa et al. [12] successfully grew large SLT crystals using the double crucible Czochralski (DCCZ) method with an automatic powder supply system, which requires a complex equipment system and entails high costs. Shumov et al. [13] reported that near stoichiometric LiTaO<sub>3</sub> single crystals were grown by the conventional Czochralski method, but the composition along the growth axis of the boule is inhomogeneous. Undoped and MgO-doped SLT crystals were grown by the zone-leveling Czochralski (ZLCz) technique by Hsu et al. [14]. Besides the above mentioned melt-growth methods, the VTE method [15] is another method to convert single CLT crystals into the near stoichiometric and desired composition within the solid solution phase field by Li<sup>+</sup> diffusion at high temperature. The SLT crystals prepared by a VTE method possess uniform composition along the radial direction [16] and lower coercive fields [6,7] than those obtained by other methods. In addition, compared with other methods, the manufacturing process is much simpler. However, the thickness of SLT crystals prepared by the VTE method is less than 1.2 mm in past research [7,17], and SLT crystals with thickness more than 1.2 mm are necessary for practical applications.

In this paper, to prepare thick SLT crystals by the VTE method, the CLT crystals were buried in Li-rich lithium tantalate polycrystalline powder and the SLT crystals with thickness up to 3.2 mm could be obtained. However, twin defects were observed

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in VTE treated crystals. The objective of the present study was to investigate and eliminate twin defects.

## 2. Experimental procedure

Li-rich lithium tantalate polycrystalline powder was prepared from high purity (99.99%) raw  $\text{Li}_2\text{CO}_3$  and  $\text{Ta}_2\text{O}_5$  powders with a composition of  $\text{Li}/\text{Ta}=60/40$ . The Li-rich polycrystalline powder was loaded into a corundum crucible, and Z-cut CLT crystals were buried in the powder to obtain a high lithium oxide pressure. The crucible was covered with a corundum lid, then heated to 1350 °C and maintained for 250 h before cooling down to room temperature. Other SLT crystals were prepared at temperatures of 1100 °C, 1200 °C, 1270 °C and 1300 °C, respectively.

The compositions of congruent and VTE treated crystals were characterized through the measurement of Curie temperature, which was determined by a differential scanning calorimeter (DSC) (Setaram thermal analyzer, Setsys Evolution) with a heating rate of 10 °C/min. The instrument was calibrated before measuring. Both sides of the VTE treated crystals including twin interlayers were well lapped and polished, then etched in a mixture of HF and  $\text{HNO}_3$  (1:2 in volume) at 100 °C for 30 min. Twins and their etched patterns were observed under an optical polarizing microscope.

## 3. Results and discussion

### 3.1. VTE results

The Curie temperature of reacted powder from dried  $\text{Li}_2\text{CO}_3$  and  $\text{Ta}_2\text{O}_5$  with the stoichiometric composition is 695.6 °C. The composition of VTE treated crystals can be estimated from the Curie temperature. To avoid the influence of  $\text{Li}^+$  diffusion from the side faces [18] and of the surface composition [19], samples were cut from the center of VTE treated crystals and a layer with the thickness of about 300  $\mu\text{m}$  was rubbed away from both surfaces of samples.

The results of VTE treated  $\text{LiTaO}_3$  samples are presented in Table 1. The compositions of samples 2–6, 8 and 10 are near stoichiometric, and the thickness is up to 3.2 mm. Some twin defects are found in samples 2–8, and cracks are observed at the intersection of twin bands. The width of twin interlayers with parallel boundaries ranges from 50  $\mu\text{m}$  to 100  $\mu\text{m}$  on the (0001) face in crystals treated at 1350 °C (samples 2–4). The width of twin interlayer in crystals treated at low temperature is narrower than that at the high. Some narrow wedge-shaped twins are also observed in SLT crystals prepared at 1270 °C and 1200 °C (samples 5–8), besides twins with parallel boundaries. The wedge-shaped twins start from an edge of the sample and end at some distance from the edge. No twins are found in crystals treated at 1100 °C

(samples 9 and 10), but cracking is observed in sample 9 because of inhomogeneous composition in the crystals.

### 3.2. Twin defects

Fig. 1(a) shows unpolished SLT crystals under an optical microscope. After polishing, VTE treated crystals including a twin interlayer were etched in a mixture of HF and  $\text{HNO}_3$ , and the etching patterns were observed under an optical microscope. As observed in Fig. 1(b), etching rates between twins and the host crystal are different. The photomicrograph of twins (Fig. 2) under a polarizing microscope indicates the lattice orientations in twins and host crystals are different. The phenomena mentioned above agree with the results reported by Vere and Park [20,21] in lithium niobate.

Furthermore, twins are parallel to the line connecting two of the three growth ridges (i.e. X direction). The cross-section was cut perpendicular to the X axis. It is found that traces of the twinning interlayer on the face of  $\{2\bar{1}\bar{1}0\}$  have an angle of 57° with the {0001} plane through measuring the thickness of the crystal and the length of boundaries on the  $\{2\bar{1}\bar{1}0\}$  plane (Fig. 3). According to the geometric features, twin composition planes are  $\{01\bar{1}2\}$  planes. Twins in the  $\{01\bar{1}2\}$  planes were found in SLT crystals prepared by the double crucible method [22] and conventional Czochralski technique [13], and observed when  $\text{LiTaO}_3$  crystals were loaded along the [0001] direction at room temperature [23]. Moreover, twins in other planes are not reported in  $\text{LiTaO}_3$  crystals.

### 3.3. Cracks

As observed in Fig. 4, the cracks happen when one twin interlayer intersects with another, and no cracks are observed at the twin boundaries, where one twin interlayer does not intersect with another. Fig. 1(b) indicates that the polarization state of twins is different from that of the host crystals [20]. The polarization directions of twins and host crystals are not antiparallel. According to the structure of lithium tantalate and geometry of twins, the included angle between the  $-Z$  direction of host crystal and the  $+Z$  direction of the twin is  $65^\circ 52'$ .

Vere [20] reported that electrostatic forces within the intersecting region of two twin bands led to crack nucleation. Park [21] thought that cracks were due to the stress that arose from opposite lattice distortions because of different polarization directions between twins and host crystals. However, for  $\text{LiTaO}_3$  crystals, the VTE processing temperature is far above the ferroelectric–paraelectric phase transition temperature. Crack nucleation at twin intersections may occur at temperatures above the phase transition point, while no spontaneous polarization is in crystals. According to the pole mechanism of twin formation proposed by Cottrell and Bilby [24], twins grow by the movement of a twinning dislocation through successive twinning planes. The locomotive imperfect dislocations accumulate when encountering the twin

**Table 1**  
The results of VTE treated  $\text{LiTaO}_3$  crystals.

Samples	Thickness (mm)	Curie temperature (°C)	Twins
1. Congruent $\text{LiTaO}_3$	–	603.4	Free
2. $\text{LiTaO}_3$ treated at 1350 °C for 250 h	3.2	694.1	Observable
3. $\text{LiTaO}_3$ treated at 1350 °C for 250 h	2.2	694.8	Observable
4. $\text{LiTaO}_3$ treated at 1350 °C for 250 h	1.5	695.7	Observable
5. $\text{LiTaO}_3$ treated at 1270 °C for 250 h	1.5	694.9	Observable
6. $\text{LiTaO}_3$ treated at 1270 °C for 250 h	1.0	694.9	Observable
7. $\text{LiTaO}_3$ treated at 1200 °C for 250 h	1.5	689.1	Observable
8. $\text{LiTaO}_3$ treated at 1200 °C for 250 h	1.0	694.9	Observable
9. $\text{LiTaO}_3$ treated at 1100 °C for 250 h	1.0	648.6	Free
10. $\text{LiTaO}_3$ treated at 1100 °C for 250 h	0.3	695.0	Free

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