Relationship between the structure and optical properties of lithium tantalate at the zero-birefringence point

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Abstract

The structure of lithium tantalate between room temperature and 445 K has been investigated using neutron diffraction. It is found that the displacement of the Ta atom from the centre of the O octahedra and the tilt of the octahedra both decrease with increasing temperature. The measured structures form the basis of a range of density functional theory calculations utilising the WIEN2k code, with a focus on calculating the optical properties. The results show that the birefringence of LT mainly depends on the Ta displacement and the octahedral tilt, with the linear change in these as a function of temperature producing the change in birefringence with temperature, which results in them becoming zero-birefringent.

Introduction:

Lithium tantalate (LT) is an important material for electro-optic devices and with lithium niobate (LN) it forms a solid solution $LiNb_{1-x}Ta_xO_3$ (LNT), which has been of interest for its room temperature zero-birefringence [1–5]. It is well known that LT can be made with a range of Li concentrations, with compositions ranging from 45 mol% Li_2O to 50 mol% Li_2O [6,7]. The birefringence has been investigated as a function of temperature[2] between 48 and 50 mol% Li_2O using vapour transport equilibrium (VTE) treated crystals, giving the temperature of the zero-birefringence point of stoichiometric LT as 373 K [2]. The birefringence of LNT

crystals has also been investigated and for congruent LNT crystals, a composition of 93-96 mol% Ta is zero birefringent at room temperature [1,3,8].

LN and LT are isostructural and ferroelectric, with space group *R3c*. They both undergo a high-temperature phase transition to the paraelectric space group *R-3c*. A set of parameters for rhombohedral perovskite structures such as LN and LT was introduced by Megaw to parameterise the structure using the cation positions, octahedral distortion and octahedral tilt [9]. The position of the Nb/Ta atom is given by its displacement (*t*) along the c-axis from the centre of the oxygen octahedra, the Li position is given by its displacement (*s*) from the O plane at z = 1/4 and the O position by the octahedral distortion (*d*) and tilt (*e*). The parameter *e* is related to the octahedral tilt ω by

$$\tan\omega = 4\sqrt{3}e\ . \qquad (1)$$

The change in these parameters with increasing temperature was calculated for LN by Megaw using the powder XRD measurements of Abrahams et al[10]; the octahedral tilt decreases with increasing temperature, resulting in an increase in the volume of the octahedra and an increase in the *a* lattice parameter [11]. The curve in the *c* lattice parameter as a function of temperature is explained by the decrease in the Nb displacement with increasing temperature. Above the Curie point, in the paraelectric phase the Nb/Ta displacement and the octahedral distortion disappear, but the octahedral tilt remains.

A number of single-particle DFT calculations on LT have been performed with a focus on calculating the band gap; Cabuk et al calculated a band gap of 3.86 eV using the local-density approximation (LDA) and Riefer et al calculated a band gap of 3.71 eV using the generalised gradient approximation (GGA) [12,13]. It has been suggested for LN that DFT calculations should be performed focusing on the well known physical properties, such as the refractive index [14]. Riefer et al made a series of calculations on LNT focusing on the optical properties and the calculated values agreed closely with the measured values of Wood et al [3]. These calculations included self-energy effects and electron-hole interactions, which increased the calculated band gap of LT to 5.65 eV.

The present study aims at a better understanding between the structure and optical properties by using experimentally-determined structures as the basis for single-particle DFT calculations. These measurements have been made between room temperature and 445 K with the expected zero-birefringence point of LT at 373 K.

Experimental details:

The LT sample was prepared by a solid-state reaction between Li_2CO_3 (99.99 %) and Ta_2O_5 (99.85 %), with the Li in Li_2CO_3 enriched to 99.9 % ^{7}Li. The starting materials were ball-milled in isopropanol, sealed in a platinum crucible and sintered for 140 hours at 1160 °C.

High-temperature X-ray diffraction (XRD) measurements were performed using a PANalytical MPD diffractometer equipped with an Anton Paar HTK1200 sample furnace. Measurements between 20 and 135° in 2θ were made every 20 K between room temperature and 1090 K.

Powder neutron diffraction data were collected every 15 K between room temperature and 445 K on the high-resolution D2B diffractometer at the Institut Laue-Langevin, Grenoble, France. A large sealed vanadium can containing 15 g of powder was used for the experiments. The wavelength of the neutron beam was 1.594 Å and the detector for the D2B diffractometer consists of 128 ^{3}He counting tubes, spaced 1.25 ° apart. A full diffraction pattern between 5 and 165 ° in 2θ was recorded after moving the detector through 25 0.05 ° steps, and each scan was repeated 10 times to improve the counting statistics. Rietveld refinements of the neutron and XRD data were performed using Topas Academic [15].

DFT calculations using the full-potential linear augmented plane-wave method (FP-LAPW), were carried out using the WIEN2k code [16]. The GGA introduced by Perdew, Burke and Ernzerhof was utilised for these calculations, with muffin-tin radii of 1.69, 1.89 and 1.63 a_0 for the Li, Ta and O atoms, respectively [17]. The effect of the number of k-points and the $R_{MT}K_{MAX}$ on the convergence of the calculations was investigated and 1000 k-points with an $R_{MT}K_{MAX}$ of 7 was subsequently used throughout, ensuring complete convergence with a reasonable time required for each calculation.

Results and discussion:

The lattice parameters from Rietveld refinements of the XRD measurements show a discontinuity at the Curie point. Figure 1 shows the variation in the *c* and *a* lattice parameters and the residual of a linear fit to the *a* lattice parameter as a function of temperature. The c lattice parameter and the residual of the linear fit to the *a* lattice parameter have been fitted with second- and fourth-order polynomials above and below the Curie point, respectively. The crossing point of these fitted curves gives a Curie point for the LT powder of 927(3) K,

which according to a study of the Curie point as a function of the Li concentration in LT [18], gives a composition of 49.7 (1) mol% Li_2O.

The change in the atomic positions, represented by the Megaw parameters were calculated using Rietveld refinements of the neutron diffraction data measured between room temperature and 445 K. The Rietveld refinement of the diffraction data recorded at 300 K is shown in figure 2. The calculated Megaw parameters from this refinement are given in table 1, along with the previously determined values by Megaw using single-crystal XRD measurements on an SLT crystal by Abrahams and Bernstein at 297 K [9,19]. The refined lattice parameters for all the neutron measurements are included in table 2 along with the wRp, Rp and GOF of the refinements.

The calculated Megaw parameters are plotted as a function of temperature in figure 3. The Ta displacement and tilt angle both decrease with increasing temperature, similar to LN. The Li displacement also decreases with increasing temperature. A trend in the octahedral distortion cannot be determined because the errors in the calculated values are of the same order as the change in value across the temperature range investigated.

DFT calculations were performed on the structures given by the linear fits to the Ta displacement, Li displacement, octahedral distortion and octahedral tilt, which were calculated from the Rietveld refinements of the neutron diffraction measurements. A series of calculations were also performed only allowing the Li displacement, Ta displacement, octahedral tilt or lattice parameters to vary. The octahedral distortion was kept fixed at the room-temperature value for these calculations. The calculated band gap varied from 3.91 eV at 300 K to 3.86 eV at 445 K.

The refractive indices were determined using the method developed by Ambrosch-Draxl and Sofo, which is included in the WIEN2k package [20]. The resulting birefringence when all the properties were allowed to vary and when each was varied separately is plotted in figure 4. The calculated room-temperature birefringence is -0.030(2) which does not agree with the expected value of -0.005(1).[5] The calculated value is dependent on the band gap and is affected by its underestimation when using the GGA[21]. The birefringence increases with increasing temperature when all the atomic positions are varied and the zero-birefringence point can be estimated by correcting the calculated room-temperature birefringence to the previously measured value of -0.005(1). This gives a zero-birefringence temperature of

363(10) K, which agrees with the experimentally measured value of 373 K and confirms that the calculated change in the birefringence with temperature is reliable.

The change in the birefringence when only the Ta atoms are allowed to move is very similar to the response when all the atomic positions are varied, suggesting that the dominant effect on the optical properties on LT is the position of the Ta atom within the O octahedra. The changes in the octahedral tilt and Li displacement both result in a small increase in the birefringence with temperature which is equal to the decrease given by the change in the lattice parameters. A trough at 368 K is visible in the calculated data when the Li displacement is changed, which is not seen in the other calculated values and is presumably an artefact caused by allowing only one atom to move.

Conclusions:

The structural changes as a function of temperature have been confirmed to be the same as for those of LN; the Ta displacement and the octahedral tilt both decrease with increasing temperature. The use of neutron diffraction in this study has also shown a decrease in the Li displacement with increasing temperature. The results of the DFT calculations show that the displacement of the Ta from the centre of the O octahedra has the largest effect on the optical properties of LT. Changes in the Li displacement, octahedral tilt and lattice parameters all have a small effect on the calculated birefringence. The structure remains polar through the zero-birefringence point, with the small changes in the Ta displacement and octahedral tilt determining the change in the birefringence. These results also highlight the need for accurate structures when calculating the optical properties of LN and LT using DFT calculations.

Table Captions:

Comparison between the calculated Megaw parameters for LT at 300 K from this study and those determined by Megaw using the single-crystal XRD measurements of Abrahams and Bernstein at 297 K [9,19].

Figure captions:

Figure 1: The a) *c* lattice parameter, b) *a* lattice parameter and c) residual of a linear fit to the *a* lattice parameter as a function of temperature. The *c* lattice parameter and residual of the

linear fit to the *a* lattice parameter have been fitted with fourth- and second-order polynomials above and below the Curie point, respectively.

Figure 2: Rietveld refinement of diffraction measurement at 300 K.

Figure 3: The a) Ta displacement, b) Li displacement, c) octahedral distortion and d) octahedral tilt angle as a function of temperature. Linear fits to the data are given by the black lines.

Figure 4: Calculated birefringence values as function of temperature when all parameters vary, are given by the triangles. The values when only the Ta displacement, Li displacement, octahedral tilt or lattice parameters are allowed to vary, are given by the diamonds, triangles, circles and crosses, respectively. Linear fits to the data are given by the lines.

Temperature (K)	a = b (Å)	c (Å)	wRp	Rp	GOF
300	5.1538(2)	13.776(1)	0.057	0.045	1.32
315	5.1550(2)	13.777(1)	0.058	0.045	1.35
330	5.1563(2)	13.776(1)	0.057	0.044	1.32
345	5.1575(2)	13.777(1)	0.057	0.045	1.32
360	5.1588(2)	13.777(1)	0.056	0.044	1.30
375	5.1601(2)	13.777(1)	0.057	0.045	1.32
390	5.1615(2)	13.778(1)	0.057	0.045	1.34
405	5.1629(2)	13.777(1)	0.055	0.044	1.30
425	5.1647(2)	13.778(1)	0.057	0.045	1.34
445	5.1665(2)	13.778(1)	0.058	0.046	1.36

Table 1

	Ta displacement (Å)	Li displacement (Å)	Octahedral distortion	Octahedral tilt (°)
Abrahams	0.20(1)	0.60(2)	-0.0026(2)	22.9(1)
This work	0.195(1)	0.601(4)	-0.0025(1)	22.97(1)

Table 2

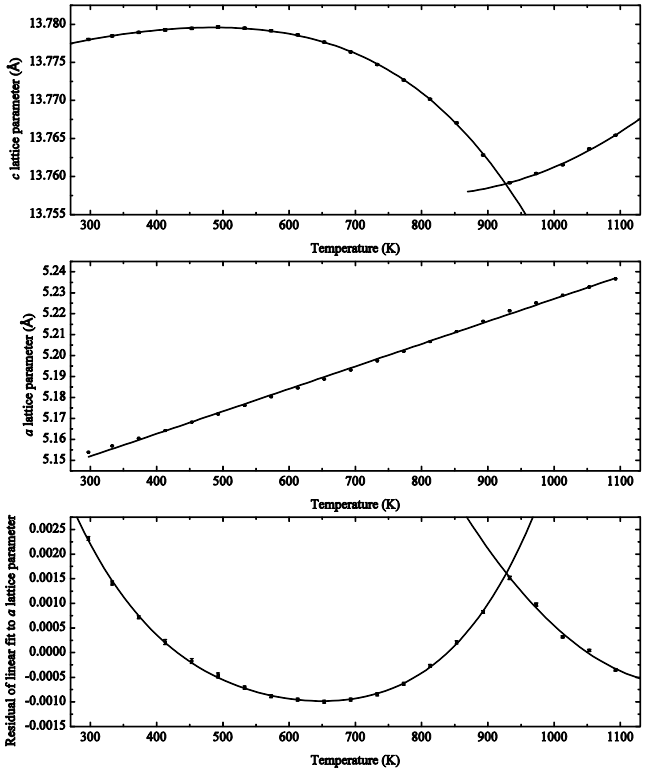

Figure 1

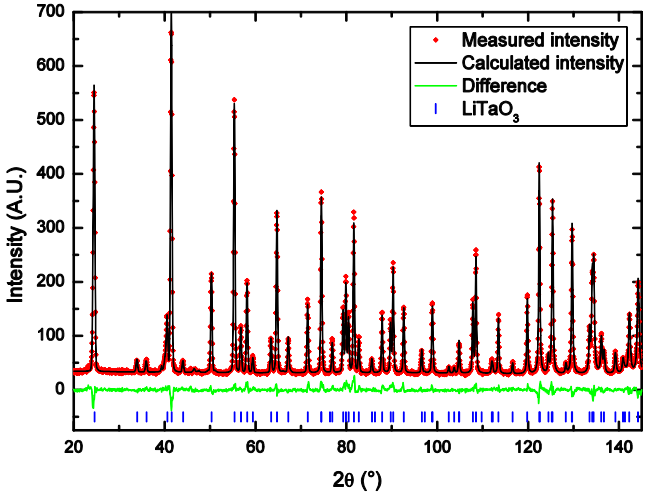

Figure 2

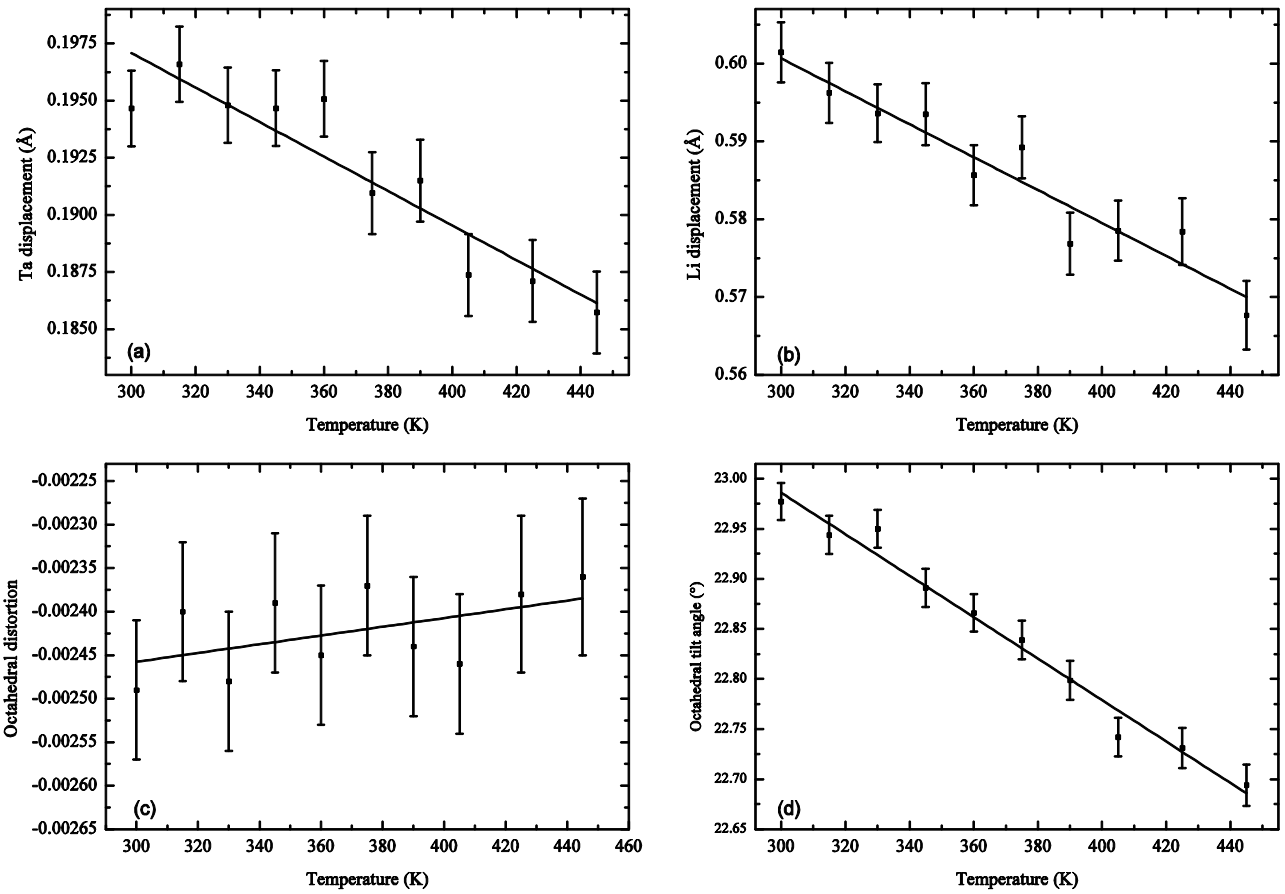

Figure 3

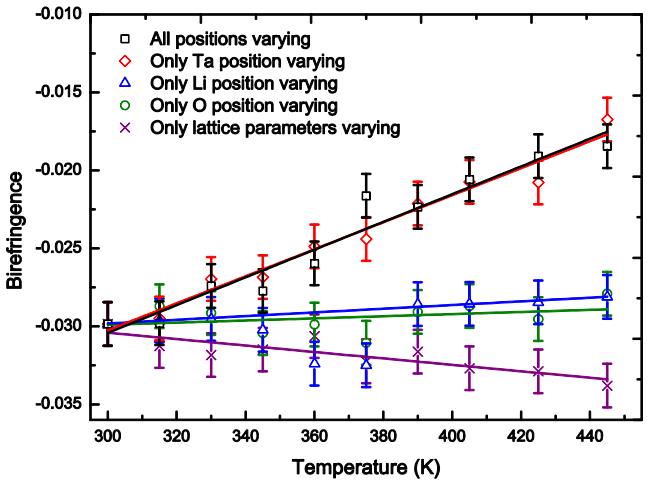

Figure 4

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