Anharmonic thermal vibration in a crystal of lithium(I) tantalum(V) trioxide, LiTaO_3

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Abstract

The electron-density distribution in a crystal of LiTaO_3 has been investigated with the single-crystal X-ray diffraction method. The crystal has the cell dimensions $a = 5.15329(7)$ and $c = 13.7806(5)$ Å with the space group $R\bar{3}c$ and $Z = 6$. Residual electron densities due to anharmonic thermal vibration were observed around the Ta^{5+} ion. Refinement with anharmonic thermal parameters improved the coincidence of the observed and calculated structure factors significantly. The C_{333} (the coefficient of Δz^3) value of Ta^{5+} is most significant among the third and fourth order anharmonic potential parameters. It has revealed that significant errors are sometimes introduced into positional parameters if contributions of odd order terms of anharmonic potentials are ignored.

Introduction

The ferroelectric crystal of LiTaO_3 is isomorphous with LiNbO_3 , having a structure closely related to those of corundum and ilmenite (Megaw, 1973). The absolute structure was determined with the X-ray diffraction method at 297 K by Abrahams and Bernstein (1967), and also with the neutron diffraction method by Abrahams, Hamilton and Sequeira (1967). The temperature dependence of the atomic parameters in the ferroelectric phase ($R\bar{3}c$) and the paraelectric structure ($R\bar{3}c$) at 940 K was investigated by Abrahams, Buehler, Hamilton and Laplaca (1973), and it was revealed that as temperature approaches T_c (907 K) the oxygen atom approaches the position (x , $1/3$, $1/12$) in the hexagonal cell. Graham (1976) detected the pressure dependence of the piezoelectric polarization, and the ionic displacement with applied electric fields was directly observed with the X-ray diffraction technique by Fujimoto (1982).

It is of interest to obtain electron-density distributions in crystals of LiTaO_3 in relation to the ionic displacement and polarization. In this study, the electron-density distribution and anharmonic thermal vibrations of atoms in LiTaO_3 was investigated with the single-crystal X-ray diffraction method at room temperature.

Experimental

A crystal shaped into a sphere of 0.123 mm in diameter was used for intensity collection. The cell parameters were determined from 2θ values of 81 reflections higher than 76° , measured on a Rigaku automated four-circle diffractometer (AFC-5UD) with $\text{Mo K}\alpha_1$ radiation ($0.70926 \text{ \AA}$). The crystal data are given in Table 1. Intensity measurements were performed on the diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation ($0.71073 \text{ \AA}$) in a quarter of the reciprocal space up to 150° in 2θ ($\sin \theta / \lambda = 1.359$). In addition a total of 204 strong reflections were measured in the full reciprocal space for anisotropic extinction corrections. When $\sigma(|F_o|)/|F_o|$ was

TABLE 1. Crystal data of LiTaO_3 at 23°C

space group	R3c
a($\text{\AA}$)	5.15329(7)
c($\text{\AA}$)	13.7806(5)
Z	6
D_x (g cm^{-3})	7.416
μ for $\text{MoK}\alpha$ (cm^{-1})	510.98*

* Calculated from the mass attenuation coefficients given in International Tables for X-ray Crystallography (1974).

TABLE 2. Experimental conditions

Diameter of specimen (mm)	0.123
Radiation	$\text{MoK}\alpha$
Monochromator	Graphite
Max of 2θ ($^\circ$)	150
Ranges of indices	$-14 \leq h \leq 14, 0 \leq k \leq 14, 0 \leq l \leq 37$
Scan width ($^\circ$)	$1.50 + 0.5 \tan \theta$ where $0 < 2\theta \leq 90$ $1.35 + 0.5 \tan \theta$ where $90 < 2\theta \leq 150$
Scan technique	$\omega - 2\theta$
Scan speed	4° min^{-1} in 2θ
Max. number of repetition	10
Criterion to terminate repetition	$\sigma(F)/ F \leq 0.01$
Number of measured reflections	2373
Number of used reflections	1463
Number of independent reflections	519

larger than 0.01, the measurement was repeated up to 10 times, where $\sigma(|F_o|)$ is the standard deviation of the structure amplitude $|F_o|$ due to the counting statistics. The reflections with $|F_o| < 3\sigma(|F_o|)$ were omitted from the data set used in the subsequent calculations. Experimental conditions in intensity measurements and a number of reflections are given in Table 2.

Integrated intensities were corrected for the Lorentz and polarization factors, and absorption corrections were carried out, utilizing the values of the absorption correction factor A^* for spherical crystals given in *International Tables for X-Ray Crystallography Vol. II* (1967). For each reflection, the mean path length, $T = (dA^*/d\mu)/A^*$, was calculated for the correction of the secondary extinction effect, where μ is the linear absorption coefficient.

Refinement

Two kinds of refinements were tried: the conventional structure refinement (harmonic thermal vibrations) with anisotropic extinction corrections and the refinement with anharmonic potential parameters for the Ta⁵⁺ ion. The atomic scattering factors for Li⁺ and Ta⁵⁺ ions and dispersion correction factors were taken from *International Tables for X-Ray Crystallography Vol. IV* (1974). For the scattering factors of O²⁻ ion, those given by Tokonami (1965) were used.

a) Refinement with harmonic thermal parameters

The refinement was started from the values of positional parameters given by Abrahams and Bernstein (1967), utilizing the full-matrix least-squares program *LINKT*, which includes subroutines for extinction correction after Becker and Coppens (1974a, b, 1975) and for refinement of anharmonic potential parameters after the method of Tanaka and Maruno (1983). Because of the small scattering factors, anisotropic temperature parameters were undeterminable for the Li⁺ ion. The Gaussian mosaic-spread distribution was assumed for the extinction correction. Since the LiTaO₃ structure has no center of symmetry (R3c), violation of Friedel's law due to anomalous dispersion must be considered. Therefore, the refinements were carried out on two sets of atomic arrangements which are enantiomorphous with each other. The first setting gave the R ($(\sum ||F_o| - |F_c||) / \sum |F_o|$) and R_w ($(\sum (|F_o| - |F_c|)^2 / \sum |F_o|^2)^{1/2}$) values of 0.0166 and 0.0218 on the type-I anisotropic extinction corrections, respectively, and 0.0125 and 0.0149 on the type-II extinction corrections, respectively. On the other hand, the second setting gave the R and R_w values of 0.0192 and 0.0240 on the type-I extinction corrections and 0.0152 and 0.0185 on the type-II extinction corrections. Therefore, the result of the first set of atomic arrangements with the type-II extinction corrections was adopted as the correct one in this study. At this stage, the difference Fourier map was synthesized

after averaging equivalent reflections. A section of the map parallel to $(01\bar{1}0)$, just cut through the centers of Li and Ta atoms, and passing near the O atom is shown in Fig. 1.

FIG. 1. The section of the difference Fourier map parallel to $(01\bar{1}0)$ and containing the Li^+ and Ta^{5+} ions after the conventional crystal structure refinement. The O^{2-} ion lies near this section, the site projected on this plane being denoted with a cross. Contours are at intervals of $0.50\text{e}\text{\AA}^{-3}$. Negative and zero contours are in broken and dashed-dotted lines, respectively.

FIG. 2. The section of the difference Fourier map on the same plane as in Fig. 1 after the refinement with anharmonic potential parameters. Contours are at intervals of $0.50\text{e}\text{\AA}^{-3}$. Negative and zero contours are in broken and dashed-dotted lines, respectively.

b) Refinement assuming anharmonic thermal vibration for the Ta⁵⁺ ion.

Because the prominent residual densities were observed around the Ta⁵⁺ ion in the difference Fourier map after the ordinary structure refinement (Fig. 1), the further refinement was carried out including the parameters of anharmonic thermal vibration for the Ta⁵⁺ ion. The generalized Willis' method (Willis, 1969; Tanaka and Marumo, 1983) was used in this refinement. Since the point symmetry of the Ta⁵⁺ site is 3 in the crystal of LiTaO₃, the potentials are expressed in the following form, if only the lowest odd (third) and even (fourth) anharmonic terms are taken into account,

$$\begin{aligned}
 V(u) = & V_0 + \frac{1}{2} [b_1(u_1^2 + u_2^2) + b_3u_3^2] \\
 & + c_{111}(u_1^3 - 3u_1u_2^2) + c_{222}(u_2^3 - 3u_2u_1^2) + c_{333}u_3^3 \\
 & + c_{311}(u_1^2u_3 - u_2^2u_3) + q_{1111}(u_1^4 + u_1^2u_2^2 + u_2^4) \\
 & + q_{3333}u_3^4 + q_{1133}(u_1^2u_3^2 + u_2^2u_3^2) + q_{1131}(u_1^3u_3 - 3u_1u_2^2u_3) \\
 & + q_{2233}(u_2^3u_3 - 3u_2^2u_1u_3),
 \end{aligned}$$

TABLE 3. Positional and thermal parameters of the respective atoms and extinction parameters of LiTaO₃.

Positional parameters						
atom	x	y	z			
Li	0	0	0.2909(7)			
Ta*	0	0	0			
O	0.0495(4)	0.3425(4)	0.0749(6)			

Thermal parameters(Å ²)						
atom	U ₁₁ (or B)	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Li	0.21(2)					
Ta	0.00492(2)	= U ₁₁	0.00356(3)	= U ₁₁ /2	0	0
O	0.0066(4)	0.0059(4)	0.0055(4)	0.0028(3)	-0.0016(3)	-0.0026(4)

Extinction parameters (10 ⁻⁴ cm)			
G ₁₁	14.0(11)	G ₁₂	-2.0(3)
G ₂₂	3.0(3)	G ₁₃	8.3(11)
G ₃₃	13.6(13)	G ₂₃	1.9(4)

The form of the anisotropic temperature factor is defined as

$$\exp \{ -2\pi^2 [(h^2 + k^2)a^{*2}U_{11} + l^2c^{*2}U_{33} + \frac{1}{2}hka^{*2}U_{11}] \}$$

* Origin is chosen at the Ta site.

TABLE 4. Harmonic ($10^{-19}\text{J}\text{\AA}^{-2}$), third order anharmonic ($10^{-19}\text{J}\text{\AA}^{-3}$) and fourth order anharmonic ($10^{-19}\text{J}\text{\AA}^{-4}$) potential parameters for Ta atom at 296 K, with e.s.d.'s in parentheses. Thermal parameter U_{ij} is related to b_i as $U_{ij} = kT/b_i$, where k is the Boltzmann constant and T is temperature (K).

b_1	b_3			
8.313(6)	11.47(9)			
c_{111}	c_{222}	c_{311}	c_{333}	
9.9(125)	-16.2(68)	11.5(38)	-111.7(199)	
q_{1111}	q_{1133}	q_{3333}	q_{1131}	q_{2223}
-43.5(89)	402.6(791)	-573.0(1642)	14.0(2841)	516.5(2863)

where u_1 , u_2 and u_3 are the components of the deviation of the atom from the equilibrium position along rectangular coordinates defined as follows; the u_3 axis lies along the threefold axis, u_1 in the plane determined by u_3 and the Ta-O bond which is closest to the (01 $\bar{1}$ 0) plane, and u_2 is perpendicular to u_1 and u_3 . For Li^+ and O^{2-} ions, anharmonicity of the thermal vibrations was ignored because of their small scattering factors compared to those of Ta^{5+} ion. The least-squares calculations were carried out by changing the anharmonic potential parameters c_{ijk} and q_{ijkl} together with other parameters except the harmonic thermal parameters of the Ta^{5+} ion, and reduced the R and R_w values to 0.0110 and 0.0139, respectively. A section of the difference Fourier map through Li and Ta atoms calculated after this refinement is shown in Fig. 2. In the final cycle of the least-squares calculation, the maximum of the ratio Δ/σ was 0.013, where Δ and σ are the magnitude of shift and the standard deviation, respectively. The final positional and anisotropic thermal parameters (an isotropic thermal parameter for Li^+) are listed in Table 3 together with the extinction correction parameters, and the harmonic and anharmonic potential parameters for the Ta^{5+} ion are tabulated in Table 4.

Results and discussion

Fig. 3 shows the LiO_6 and TaO_6 octahedra in the structure, and interatomic distances and bond angles are tabulated in Table 5. In accordance with the difference in the ionic radius between Li^+ (0.90 $\text{\AA}$; Shannon, 1976) and Ta^{5+} (0.78 $\text{\AA}$) ion, the mean Li-O distance (2.162 $\text{\AA}$) is longer than the mean Ta-O bond distance (1.985 $\text{\AA}$). The O-O distances on the shared face is shortest among the edges of the octahedra.

FIG. 3. LiO_6 and TaO_6 octahedra in LiTaO_3 . Figures are atomic distances in Å.

FIG. 4. The section of the difference Fourier map on the same plane as in Fig. 1 synthesized after the conventional crystal structure refinement with phases obtained with anharmonic potential-parameter refinement. Contours are at intervals of $50.0 \text{ e}\text{\AA}^{-3}$.

Owing to the electrostatic repulsion, the Li^+ and Ta^{5+} ions are largely shifted from the centers of the respective coordination octahedra towards the vacant octahedral sites along the threefold axis as in other ilmenite- and corundum-type crystals. In the LiO_6 octahedron, the distance between the Li^+ ion and the shared face is $1.6163 \text{ \AA}$, whereas that between Li^+ and the opposite face is $0.6804 \text{ \AA}$. In the TaO_6 octahedron, the corresponding distances are $1.2561 \text{ \AA}$ and $1.0318 \text{ \AA}$, respectively. The ratio of the distance between the cation and the shared face to that between the cation and the opposite face is much larger in the LiO_6 octahedron (2.376) than in the TaO_6 octahedron (1.226). Effects of the cation shifts also appear in the cation-oxygen distances, that is, the distances from the cations to the O^{2-} ions on the shared face are much shorter than those to the

TABLE 5. Atomic distances (Å) and bond angles (°) in LiTaO₃.

Atomic distances(Å)			
Ta-O ⁱ	2.022(5)	O ⁱ -O ⁱⁱ	2.731(3)
Ta-O ^{iv}	1.948(4)	O ⁱ -O ^{iv}	2.793(9)
Ta-O (mean)	1.985	O ⁱ -O ^v	2.824(9)
		O ⁱ -O ^{vii}	2.792(9)
Li-O ⁱ	2.258(9)	O ⁱ -O ^{vi}	3.039(9)
Li-O ^{vii}	2.065(4)	O ^{iv} -O ^v	2.862(2)
Li-O (mean)	2.162	O ^{vii} -O ^{viii}	3.377(2)
Ta-Ta	3.759(0)	Ta-Li	2.881(10)
Li-Li	3.759(0)		3.032(2)
			3.433(5)
Angles(°)			
O ⁱ -Ta-O ⁱⁱ	85.0(2)	O ⁱ -Li-O ⁱⁱ	74.4(4)
O ⁱ -Ta-O ^{iv}	89.4(2)	O ⁱ -Li-O ^{vii}	80.3(2)
O ⁱ -Ta-O ^v	90.7(2)	O ⁱ -Li-O ^{vi}	89.2(2)
O ^{iv} -Ta-O ^v	95.5(2)	O ^{vii} -Li-O ^{viii}	111.0(3)
Ta-O ⁱ -Li	84.4(2)	Li-Ta-O ⁱ	51.3(3)
O ⁱ -Li-Ta	44.3(2)		

Symmetry codes

none x, y, z i: $2/3-i, 1/3+y, 1/2+i$ ii: $2/3+x, 1/3+i, 1/2+j$ iii: $2/3-y, 1/3-x, 1/2+j$ iv: $-i, -x, z$ v: $-y, i, z$ vi: $1/3-y, 2/3-x, 1/2+k$ vii: $1/3+x, 1/3+i, 1/2+k$ viii: $1/3-i, 2/3+y, 1/2+k$ ($i=x-y, j=1/3+z, k=2/3+z$)

O²⁻ ions on the opposite faces both in the TaO₆ and LiO₆ octahedra.

In the difference Fourier map after the conventional structure refinement, the Ta⁵⁺ ion lies in a saddle region with the depth -0.94 eÅ^{-3} , and there are large negative peaks on both sides of Ta⁵⁺ along the threefold axis. The one on the side of the shared face is at 0.41 Å apart from Ta⁵⁺ with the depth -4.24 eÅ^{-3} , and the other at 0.42 Å with the depth -4.21 eÅ^{-3} . Positive peaks are observed at distances of 0.47 and 0.48 Å from Ta⁵⁺ on the line perpendicular to the threefold axis and passing through the Ta⁵⁺ site, having the heights of 1.54 eÅ^{-3} and 1.49 eÅ^{-3} .

After the refinement with anharmonic potential parameters, the residual electron densities were markedly reduced around the Ta⁵⁺ ion (Fig. 2). The negative peak on the threefold axis on the side of the shared face is reduced to -0.65 eÅ^{-3} and that on the opposite side to -0.73 eÅ^{-3} . Positive peaks observed around Ta⁵⁺ in Fig. 1 are also reduced significantly. A large part of residual electron densities around Ta⁵⁺ ion after

the conventional refinement is, therefore, supposed to be due to anharmonicity of the thermal vibration of the Ta^{5+} ion. In fact, the refinement with anharmonic potential parameters reduced the R and R_w factors significantly.

The anharmonic potential parameters of c_{222} , c_{311} , c_{333} , q_{1111} , q_{1133} , q_{3333} and q_{2223} have larger absolute values than the respective standard deviations (Table 4). Among them, c_{333} has the most prominent value in accordance with existence of the large residual peaks on the threefold axis in Fig. 1. However, the parameter c_{333} should cause an asymmetrical electron-density distribution for the relevant atom, since it is the coefficient of u_3^3 . In Fig. 1 the residual densities are distributed approximately centrosymmetrically around the Ta^{5+} ion, contradicting this expectation. Therefore, the positional parameters were compared before and after the refinements with the anharmonic potential parameters. The positional parameters before the anharmonic refinement are; Li(0, 0, 0.2861), Ta(0, 0, 0) and O(0.0497, 0.3427, 0.0701). Since there is no definite position on the threefold axis to be chosen as the origin of coordinates, Ta was fixed at the origin in all the refinements. The x and y values of O are in good agreements with those in Table 3, though the z coordinates of Li and O atoms are shifted by 0.048 (0.066 Å) after the anharmonic potential-parameter refinement. In other words, the Ta atom was shifted by -0.0048 after the refinement relative to the Li and O atoms. Since the contribution of the third order anharmonic vibrations was ignored, the inaccurate z parameter resulted for Ta after the refinement with the harmonic vibration model. The difference Fourier map was synthesized, on the basis of the positional parameters after the anharmonic refinement and the thermal parameters obtained by the harmonic refinement (Fig. 4). There are quite large, asymmetric residual densities around the Ta atom, indicating a significance of the third order anharmonic vibration of Ta. This anharmonic vibration is supposed to have a relation to the phase transition of this crystal at 907K from $R3c$ to $R\bar{3}c$.

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