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Structural Studies of the Solid Electrolyte High-$LiTa_3O_8$

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The high temperature modification of $LiTa_3O_8$ has been studied by X-ray single-crystal and neutron powder diffraction techniques. The orthorhombic unit cell ($Z=4$) has the dimensions $a=16.705(2)$, $b=3.836(1)$, $c=8.928(1)$ Å. A structural model has been proposed based on the space group *Pmma* (No. 51) and refined by least squares to $R(F)=0.045$ on the basis of 1206 independent X-ray reflections. A mechanism of the isotropic electrical conductivity of the compound is discussed in relation to the proposed structure and the slight disorder which may be attributed to it.

The last ten years have witnessed a steadily growing interest in the study of solid electrolytes for their potential use as battery and energy storage materials. General reviews of the field have been given by many authors (*cf.* Refs. 1, 2). As part of a project on energy-related research, investigations of solid electrolyte compounds have been started at the Arrhenius Laboratory. The present paper reports on the high temperature form of the trimorphic compound $LiTa_3O_8$, referred to hereafter as high-$LiTa_3O_8$. This compound is structurally related to $LiNb_6O_{15}F$.[3,4] High-$LiTa_3O_8$ has been shown to be a solid electrolyte with moderately good conduction properties: at 500 K the conductivity of a pellet is about 10^{-2} ohm^{-1}m^{-1} with an activation energy of 0.78 eV.[5] Measurements on large single crystals prepared at the Arrhenius Laboratory have shown the electrical conductivity to be isotropic rather than anisotropic.[6] The purpose of the present work has been to elucidate the essential structural features of high-$LiTa_3O_8$ and relate these to the conduction properties of the material.

EXPERIMENTAL

Preparation. High-$LiTa_3O_8$ was prepared by mixing absolutely dry Li_2CO_3 (Merck, *pro analysi*) and Ta_2O_5 (Fluka, 99.9 %) in the molar ratio 1:3. The mixture was slowly heated in a platinum crucible, placed in an iridium-wound electric furnace, until it melted at about 1900 K. Large, slightly pink crystals up to a few cubic millimeters in volume can be obtained by very slow crystallization from the melt. The high temperature modification of $LiTa_3O_8$ thus obtained is metastable at room temperature.

Preliminary X-ray studies. X-Ray powder photographs of the sample were taken with a Guinier-Hägg type focusing camera using strictly monochromatized Cu$K\alpha_1$ radiation ($\lambda=1.54050$ Å) and with potassium chloride as an internal standard ($a=6.29294$ Å).[7] The unit cell parameters were refined by least squares. Of 76 powder reflections, 72 could be indexed; four very weak lines originated from a slight impurity of $LiTaO_3$. The dimensions of the orthorhombic unit cell at 298 K are: $a=16.705(2)$, $b=3.836(1)$, $c=8.928(1)$ Å, and $V=572.1$ Å^3. The density was determined experimentally by the apparent loss of weight in benzene. It was found to be 7.81 ± 0.05 g cm^{-3} which compares favourably with the theoretical value of 7.86 g cm^{-3} ($Z=4$).

Comparison of the unit cell dimensions and visual inspection of the Guinier photographs for high-$LiTa_3O_8$ and $LiNb_6O_{15}F$ (*Pmma* symmetry[3]) clearly indicated that their crystal structures must be closely related. Refinement of the Guinier powder profile of high-$LiTa_3O_8$ utilizing the Rietveld technique[8,9] and with $LiNb_6O_{15}F$ structural parameters as a start gave an $R(F)$ value of 0.082. This also indicates a close resemblance between the two structures.

Weissenberg photographs were recorded about the *a* and *b* axes. Orthorhombic symmetry was confirmed, and no evidence of superstructure could be

detected. The only systematic extinctions were $hk0$ reflections for $h=2n+1$, suggesting as possible space groups *Pmma*, *Pm2a*, and $P2_1ma$.

Single-crystal data (X-ray diffractometer data). A small prismatic single crystal with the approximate dimensions $0.03\times0.14\times0.05$ mm^3 was used for recording the single-crystal data. These were collected with a Siemens automatic four-circle diffractometer (graphite monochromator, Mo$K\alpha$ radiation, $\theta-2\theta$ scan with $\theta_{max}\approx35°$). Of about 1300 measured reflections, 1206 had $\sigma(I)/I<0.5$ and were regarded as significantly observed. These were corrected for Lorentz, polarization, and absorption effects ($\mu=603$ cm^{-1}; transmission factors in the range 0.066 – 0.161).

STRUCTURE INVESTIGATIONS (X-RAY SINGLE-CRYSTAL DATA)

The layers $h0l$, $h1l$, $h2l$, *etc.*, were very similar, indicating that practically all atoms are situated in one plane perpendicular to the short b axis. A Patterson synthesis confirmed that all tantalum atoms could be placed in or near the $y=0$ plane. The centric space group *Pmma* (*cf.* $LiNb_6O_{15}F$ [3]) was chosen to begin the refinements. Only the tantalum atoms were included in the first stages. Hughes' weighting function [10] was always used. The atomic scattering factors used were those for Ta^{5+} and O^{2-} including the real and imaginary anomalous dispersion terms.[11,12] The conventional R factor, defined as $R(F)=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|$, dropped to 0.104 when the tantalum atoms, all at $y=0$, were refined with isotropic temperature factors. The temperature factor was noted to be about three times larger for Ta(4) [*cf.* below] than for the other tantalums. After three cycles of refinement with anisotropic temperature factors, the R value fell to 0.081. Ta(4) now acquired a large amplitude in the direction of the b axis. Moreover, the standard deviations obtained were anomalously large.

At this stage, the possibility of a lower, non-centric symmetry was considered. Statistical tests based on the normalized structure factors were undecisive as to the question of the existence of a centre of symmetry. Neither could a Giebe-Scheibe piezoelectric tester produce definite results in this respect. Therefore refinements were also made in the two feasible non-centric space groups *Pm2a* and $P2_1ma$ with Ta(4) shifted slightly from its former position. No significant improvement could be observed, however ($R=0.090$ with isotropic and 0.076 with anisotropic tantalums, respectively, for space group *Pm2a*). Returning to *Pmma*, the Ta(4) atoms were then "split" to lie disordered on either side of the mirror plane at $y=0$. This refinement, with all atoms vibrating isotropically (still no oxygens included), with an R value of 0.078 and very reasonable standard deviations, was a significant improvement on earlier refinements.

The subsequent difference Fourier synthesis revealed almost all oxygen atoms situated in (or near) the $y=0$ plane, and close to the corresponding positions in $LiNb_6O_{15}F$.[3] The oxygen atoms in the $y=1/2$ plane were, however, much more difficult to identify. A large number of refinements were made, also with "split" (disordered) oxygen atoms, but with no greater improvements. Although some of the oxygen atoms may well be disordered, the authors prefer at this stage to report a structural model (*cf.* Fig. 1) in which only Ta(4) is disordered and all other atoms lie at $y=0$ or $y=1/2$. Also, only isotropic temperature factors are used henceforward. This model gave an R value of 0.054, which was further improved to 0.045 on the inclusion of an isotropic extinction parameter ($g=0.073\pm0.006$)[13] in the refinement. The atomic and thermal parameters are given in Table 1. A general survey of the computer programs has been published earlier.[14] The structure factor list can be obtained on request from the Arrhenius Laboratory (The Secretariat, Inorganic Chemistry).

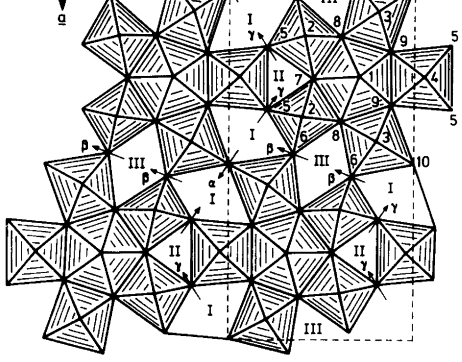

Fig. 1. Projection of the crystal structure of high-$LiTa_3O_8$ along the b axis. Numbers 1 – 4 refer to tantalum (at $y\approx0$) and oxygen (at $y=1/2$) atoms. Numbers 5 – 10 refer to oxygen atoms at $y=0$. Tunnels I – III are parallel to the b axis. Migration paths α, β, and γ are also indicated.

Table 1. Fractional atomic coordinates and isotropic temperature factors for high-$LiTa_3O_8$ described in *Pmma* ($Z=4$). X-Ray as well as neutron-determined values are given, the latter in *italics*. In the neutron powder diffraction refinement, the tantalum positions were fixed at their X-ray determined values, and overall temperature factors were used (see the text).

Atom	Position	x	y	z	B (Å^2)
Li(I)[a]	4(*j*)	–	–	–	–
		0.087(4)	1/2	*0.049(7)*	
Li(II)[a]	4(*j*)	–	–	–	–
		0.171(4)	1/2	*0.238(8)*	
Li(III)[a]	4(*j*)	–	–	–	–
		−0.019(4)	1/2	*0.391(8)*	
Ta(1)	2(*e*)	1/4	0	0.6871(1)	0.57(2)
Ta(2)	4(*i*)	0.1328(1)	0	0.3921(1)	0.55(1)
Ta(3)	4(*i*)	0.0601(1)	0	0.8109(1)	0.53(2)
Ta(4)[b]	4(*k*)	1/4	0.0387(3)	0.0532(1)	0.52(2)
O(1)	2(*f*)	1/4	1/2	0.688(2)	0.8 (2)
		1/4	1/2	*0.685(4)*	
O(2)	4(*j*)	0.130(1)	1/2	0.400(3)	3.4 (4)
		0.115(1)	1/2	*0.411(2)*	
O(3)	4(*j*)	0.061(2)	1/2	0.825(3)	4.0 (5)
		0.056(2)	1/2	*0.809(3)*	
O(4)	2(*f*)	1/4	1/2	0.057(5)	3.6 (6)
		1/4	1/2	*0.073(4)*	
O(5)	4(*i*)	0.162(2)	0	0.185(3)	3.3 (4)
		0.164(1)	0	*0.196(2)*	
O(6)	4(*i*)	0.019(2)	0	0.344(3)	2.6 (4)
		0.013(1)	0	*0.345(3)*	
O(7)	2(*e*)	1/4	0	0.450(2)	1.3 (3)
		1/4	0	*0.464(3)*	
O(8)	4(*i*)	0.133(1)	0	0.620(1)	0.8 (2)
		0.133(1)	0	*0.627(2)*	
O(9)	4(*i*)	0.176(1)	0	0.877(2)	1.3 (2)
		0.175(1)	0	*0.889(2)*	
O(10)	2(*a*)	0	0	0	0.8 (2)
		0	*0*	*0*	

[a] The occupancies for the lithiums are less than unity (compare text). [b] Ta(4) has an occupancy of 0.5.

NEUTRON DIFFRACTION STUDIES

The large difference in X-ray scattering power for tantalum and lithium meant that all efforts to locate the lithium ions in the difference Fourier maps would be fruitless. The situation for neutron scattering is, however, more favourable. The scattering amplitudes b (in *cm*) are -0.194×10^{-12} for lithium, 0.70×10^{-12} for tantalum, and 0.575×10^{-12} for oxygen.[15] Neutron powder diffraction data have been collected at the Studsvik R2 reactor from 2 cm^3 of powdered high-$LiTa_3O_8$ ($\lambda=1.56$ Å with a flux of 10^6 neutrons cm^{-2} s^{-1}; $3\leq\theta\leq42°$ with $\Delta(\theta)=0.04°$). The Rietveld full-profile refinement procedure[8] was then used, fixing the tantalums from the X-ray study and refining the oxygens only. This gave a final $R(I)$ factor of 0.160 with overall temperature factors B(Ta) = 1.0(2) and B(O) = 1.2(1) Å^2. This is poorer agreement than expected and can presumably be attributed to disorder in the structure, as discussed above. The largest negative peaks [b(Li) is negative] in the difference Fourier map appeared in the $y=1/2$ plane (see Fig. 2). These peaks suggest that the lithium ions occupy the structural tunnels, labelled I – III in Fig. 1, although this is a very simplified model.

In the final refined model, the tantalum positions were again fixed at their X-ray determined values, while the lithium and oxygen positions were refined (*cf.* Table 1). For simplicity, the four lithium ions

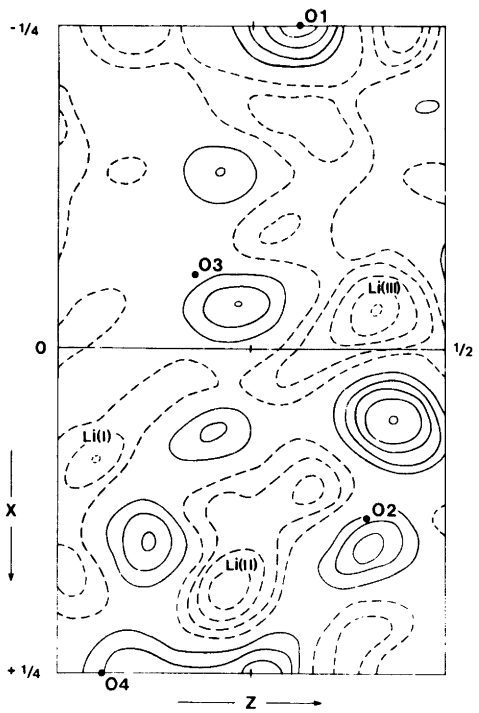

Fig. 2. Neutron difference Fourier map at the section $y=1/2$ (see text).

per unit cell were assumed to be uniformly distributed among three 4(*j*) positions so that there is one "half" lithium at $y=1/2$ in each tunnel, *i.e.* the occupancy factors for Li(I)–Li(III) are 0.5, 0.25 and 0.25, respectively. The overall isotropic temperature factors refined to $B(\mathrm{Li})=-8.7(6)$, $B(\mathrm{Ta})=1.0(2)$, and $B(\mathrm{O})=1.0(1)$ Å^2. Scale factor, zero-point, cell parameters and half-width parameters[8] were also refined. The final agreement factors were: $R_I=0.127$, $R_p=0.180$, and $R_{pw}=0.193$.

It can be noted from Table 1 that the e.s.d.'s for the neutrondetermined oxygen positions are comparable with those from the X-ray study. It may be significant that poor agreement is found for O(4) and O(7). Their *y*-values successfully refined in a later trial refinement, but they acquired anomalously large individual temperature factors. The *R* values, though, improved significantly (0.093, 0.161, and 0.172). This reinforces earlier suspicions that at least certain of the atoms are disordered or do not conform to the centrosymmetric space group *Pmma*. The negative temperature factor for lithium may again be some artefact of an oversimplified model.

STRUCTURAL CONSIDERATIONS AND IONIC CONDUCTIVITY

The structure of high-$LiTa_3O_8$ comprises a polygonal network built up of pentagonal Ta(1)O_7 bipyramids each surrounded through edge-sharing by five TaO_6 octahedra to form a kind of "five-pointed" star (*cf.* Fig. 1). It may also be regarded as a layer structure with its layers in the $y=0$ plane, and held together through the O(1)–O(4) atoms between the layers. Ta(4) is situated 0.15 Å out of the $y=0$ plane on a 50 % disordered site. From packing considerations it would seem likely that the Ta(4)O_6 octahedra arrange themselves in rows parallel to the *b* axis such that each individual row is ordered [*i.e.* Ta(4) is displaced from the $y=0$ plane in the *same* way *within* a row], and that the disordering occurs *between* rows. The physical meaning of the Ta(4) displacement is not clear as regards the lithium ion transport in the structure. The pentagonal bipyramids and octahedra are fairly regular. Some interatomic distances have been listed in Table 2.

Table 2. Some interatomic distances (Å) within the lithium-oxygen and tantalum-oxygen polyhedra of high-$LiTa_3O_8$. The X-ray coordinates have been used except for the lithium atoms (*cf.* Table 1).

Central atom X	Coord. number	Average distance ⟨X–O⟩	Shortest X–O dist.	Longest X–O dist.
Li(I)	9	2.59(4)	X–O(3): 2.05(7)	X–O(9): 2.87(5)
Li(II)	4	1.92(4)	X–O(2): 1.62(7)	X–O(4): 2.08(7)
Li(III)	7	2.39(4)	X–O(3): 2.05(7)	X–O(8): 2.70(5)
Ta(1)	7	2.04(2)	X–O(1): 1.92(1)	X–O(7): 2.12(2)
Ta(2)	6	1.96(2)	X–O(5): 1.91(2)	X–O(8): 2.04(1)
Ta(3)	6	1.97(2)	X–O(6): 1.91(3)	X–O(8): 2.09(1)
Ta(4)	6	1.94(2)	X–O(4): 1.77(1)	X–O(4'): 2.07(1)

It is clear from the two crystallographic studies that some of the atoms are disordered, or ordered within a lower symmetry space group. Their positions, as given in Table 1, should thus be regarded as "average" positions with respect to the space group *Pmma*. This is true, in particular, of the lithium ions and the oxygen atoms at the extremities of the stars referred to above.

Measurements on high-$LiTa_3O_8$ have shown that the electrical conductivity is isotropic rather than anisotropic.[6] This is in good accordance with the structure (Fig. 1). The lithium ions, which are responsible for the electrical conductivity, reside in sites corresponding to the widest parts of the tunnels I – III. The distribution of charge carriers is supposed to be uniform so that there is 0.5 Li^+ ion in each tunnel (for $0 \leq y \leq 1$). Actually an occupancy smaller than unity is a necessary requirement if the basic conduction mechanism is a lithium "jump" from one position to a neighbouring empty position. Different possible "migration paths" have been indicated in Fig. 1. The obvious ones are along the tunnels I – III for ion transport parallel to the *b* axis. The alternative paths (α, β, and γ) are approximately at $y = 1/2$ and lead ions from one tunnel to another. Each of these six paths contains a "bottleneck". These occur along the tunnels at $y \approx 0$, and between the tunnels at $y \approx 1/2$.

To ascertain the more probable paths of migration, the largest solid sphere which can pass through a bottleneck has been computed for the six different paths. The atomic parameters used are those listed in Table 1 (X-ray data); $r(O^{2-})$ is 1.40 Å. The results show that lithium transport is most unlikely along the tunnels II and III since the lithium radius (~0.6 Å) is about double the "radius" of the II and III bottlenecks at $y = 0$. All four remaining bottlenecks allow the passage of a solid sphere of radius 0.5 – 0.6 Å. This gives structural support to the observed three-dimensional electrical conductivity. In such considerations, however, it must be remembered, firstly, that atoms behave as elastic rather than as solid spheres. Moreover, the thermal motion of the atoms is considerably larger at temperatures where the conductivity is higher. Finally, and most important: the suspected disorder among certain of the oxygen atoms tends to widen the bottlenecks, since these are defined to a large extent by the probably somewhat disordered oxygens at the extremities of the five-pointed stars.

The rest-positions for the lithium ions together with the suggested migration paths constitute a highly simplified picture of the ionic conduction mechanism in high-$LiTa_3O_8$, but one which is in agreement with experiments. [Other structural studies made by Werner and Marinder[16] based on X-ray powder profile refinements support the present structural proposal.] It is evident, however, that much work remains in elucidating the structure completely. One is here reminded of the structural complexity of the much-studied solid electrolyte beta-alumina [*cf. Refs.* 2, 17 – 20]. Efforts to grow single crystals of high-$LiTa_3O_8$ large enough for a neutron diffraction study are currently being made at the Arrhenius Laboratory.

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