

## Neutron Powder Diffraction Study of the Intermediate-Temperature Form of Lithium Tantalate

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**Abstract.**  $M\text{-LiTa}_3\text{O}_8$ , monoclinic,  $C2/c$ ,  $a = 9.410$  (1),  $b = 11.521$  (1),  $c = 5.0506$  (5) Å,  $\beta = 91.108$  (5)°,  $Z = 4$ . The location of the lithium ion in the structure has been determined by profile analysis of powder diffraction data.

**Introduction.**  $M\text{-LiTa}_3\text{O}_8$ , stable between 800 and 1100°C, has been identified by Roth, Parker, Brower & Minor (1974) during an investigation of the  $\text{LiTaO}_3\text{-Ta}_2\text{O}_5$  system. Its crystal structure has been previously analyzed by X-ray single-crystal techniques (Gatehouse, Negas & Roth, 1976). The compound was found to be crystallographically similar to the mineral wodginite. However, it was not possible to determine the position of the lithium ion in the structure because of the dominant scattering of the  $\text{Ta}^{5+}$  ions. The  $\text{Li}^+$  ions were, therefore, approximately located in octahedral sites by analogy with related compounds and on the basis of other crystallochemical considerations such as the weak tendency of the  $\text{Ta}^{5+}$  ions to share octahedral edges and the unlikely possibility of face sharing. With this assignment the proposed structure becomes an ordered variant of the  $\alpha\text{-PbO}_2$  structure type with the  $\text{Li}^+$  and  $\text{Ta}^{5+}$  ions more equidistantly ordered than in the structure of  $\text{LiNb}_3\text{O}_8$ . As the values of the neutron

scattering amplitudes of the atoms in the structure do not differ greatly from each other, a neutron diffraction analysis of the title compound was carried out to determine the position of the  $\text{Li}^+$  ion and thus confirm or reject the  $\text{Li-O}$  coordination polyhedra assumed in the X-ray work.

$M\text{-LiTa}_3\text{O}_8$  was prepared by mixing  $\text{LiTaO}_3$  and  $\text{Ta}_2\text{O}_5$  under acetone, drying overnight and then heating the mixture at 1025°C for several hours. The product of this treatment was allowed to cool slowly, then ground and the entire operation repeated until X-ray powder patterns of samples obtained in successive operations showed no change. Equilibrium was assumed to have been obtained after four remixings and after a total of 50.5 h at 1025°C.

Neutron diffraction measurements were made at room temperature on a powder diffractometer of intermediate resolution at the National Bureau of Standards Reactor. The experimental conditions used to take the powder pattern are indicated in Table 1. The refinement of the structure was based on the space group  $C2/c$  and was carried out with the method of total profile analysis proposed by Rietveld (1969). The neutron scattering amplitudes were  $b(\text{Ta}) = 0.70$ ,  $b(\text{O}) = 0.58$ ,  $b(\text{Li}) = -0.215 \times 10^{-12}$  cm (Bacon, 1972). The contribution to the profile from the background was determined at portions of the powder pattern free from diffraction effects, and estimated by linear extrapolation from these regions at high scattering angles, where overlapping is most severe. The initial values of the structural and lattice parameters were those determined in the X-ray study, and those of the profile parameters  $U$ ,  $V$  and  $W$  were calculated theoretically (Caglioti, Paoletti & Ricci, 1958). In the first stage of the analysis the coordinates and temperature factors of all atoms were kept fixed and two refinements of the scale factor and of the lattice and profile parameters were carried out, one with the  $\text{Li}^+$  ion in the position postulated by Gatehouse, Negas & Roth (1976), and one with the  $\text{Li}^+$  ion removed from the structure. The  $R$  factors obtained in the two refinements were 6.1 and 10.6% respectively. This result clearly shows that the location of the  $\text{Li}^+$  ion was postulated correctly in the X-ray work. In the final refinement a total of 30 structural, lattice and profile parameters were refined simultaneously until all shifts were less than 0.30σ.

Table 1. *Experimental conditions used to measure the powder pattern of  $M\text{-LiTa}_3\text{O}_8$*

Monochromatic beam: reflection 220 of a Cu monochromator
Mean neutron wavelength: 1.358 (1) Å
Take-off angle: 63.8°
Monochromator mosaic spread: 20' arc
Horizontal divergences
(a) In-pile collimator $\alpha_1 = 21'$ arc
(b) Monochromatic beam collimator $\alpha_2 = 24'$ arc
(c) Diffracted beam collimator $\alpha_3 = 23'$ arc
Theoretical values of full width at half maximum (fwhm) parameters*
$U = 0.72$ , $V = -0.47$ , $W = 0.24$ deg <sup>2</sup>
Sample container: vanadium can of ~1 cm diameter
$2\theta_{\text{initial}} = 9.0^\circ$ , $2\theta_{\text{final}} = 78.0^\circ$ , step = 0.1°
Number of independent Bragg reflections: 247
Number of observations above background: 641

\* The parameters  $U$ ,  $V$  and  $W$  appear in the expression  $H^2 = U \tan^2 \theta + V \tan \theta + W$ , where  $H$  is the fwhm of a reflection with Bragg angle  $\theta$ . Their theoretical values are calculated with the expressions given by Caglioti, Paoletti & Ricci (1958).

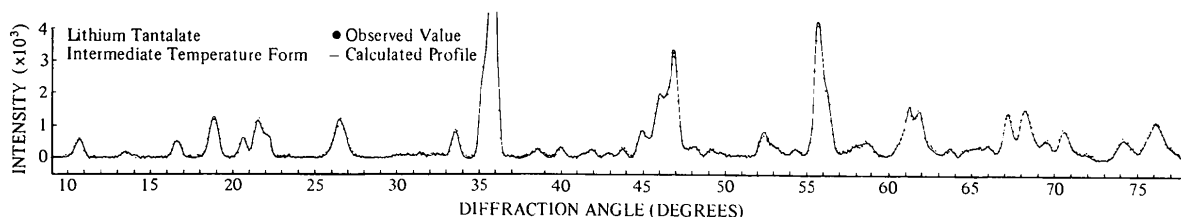


Fig. 1. Comparison of the calculated and observed neutron diffraction profiles for  $M\text{-LiTa}_3\text{O}_8$ .

Table 2. Results of the total profile refinement of the structure of  $M\text{-LiTa}_3\text{O}_8$

Numbers in parentheses are standard deviations in the last decimal figure.  $U = 1.6$  (1),  $V = -1.2$  (1),  $W = 0.44$  (2)  $\text{deg}^2$ .

	Position in $C2/c$	$x$	$y$	$z$	$B$ ( $\text{\AA}^2$ )*
Ta(1)	8(f)	0.2419 (6)	0.0868 (4)	0.2485 (13)	0.28 (5)
Ta(2)	4(e)	0.0	0.3328 (6)	0.25	0.28 (5)
O(1)	8(f)	0.3536 (5)	0.4512 (5)	0.4386 (11)	0.31 (4)
O(2)	8(f)	0.3843 (5)	0.1795 (6)	0.4246 (10)	0.31 (4)
O(3)	8(f)	0.1331 (5)	0.4364 (4)	0.0826 (12)	0.31 (4)
O(4)	8(f)	0.1178 (5)	0.1962 (4)	0.1062 (11)	0.31 (4)
Li	4(e)	0.0	0.8453 (20)	0.25	1.3 (4)

$$R = 100[\sum I/(obs) - I/(calc)]/\sum I/(obs) = 2.9\%$$

$$R_p = 100[\sum |y(obs) - y(calc)|/\sum y(obs)] = 5.4\%$$

$$R_w = 100\{\sum w[y(obs) - y(calc)]^2/\sum wy^2(obs)\}^{1/2} = 6.8\%$$

$$R_e = 100[(N - P + C)/\sum wy^2(obs)]^{1/2} = 5.3\%$$

In the above formulas  $N$  is the number of statistically independent observations,  $P$  the number of parameters refined,  $C$  the number of constraints,  $I$  the integrated intensities,  $y(obs)$  and  $y(calc)$  the profile intensities and  $w$  the weights associated with the data points  $y(obs)$ .

\* All sites occupied by the same atomic species were constrained to have a common temperature factor.

The results of this refinement are given in Table 2 and the observed and calculated profiles are shown in Fig. 1.

**Discussion.** A comparison of the results obtained in this study with those obtained with X-ray single-crystal methods shows that almost all the atomic coordinates of the Ta and O ions agree well [within three times the standard deviations  $\sigma$ , except for the  $y$  coordinate of the Ta(2) ion which differs in the two cases by  $5\sigma$ ]. The position postulated for the  $\text{Li}^+$  ion differs, however, by about  $20\sigma$  from that found experimentally. Selected interatomic distances involving the  $\text{Li}^+$  ion have therefore been recalculated and are shown in Table 3. The values reported in this table are to be considered more reliable than those obtained in the X-ray work.

The thermal parameters shown in Table 2 agree with in the stated errors with those reported in the X-ray work [average  $B(\text{Ta}) = 0.26$ , average  $B(\text{O}) = 0.59 \text{\AA}^2$ ]. However, the values of  $B$  for the O atoms obtained

Table 3. Selected interatomic distances with their standard deviations in parentheses

Li-Ta(1)	3.45 (1) $\text{\AA}$
Li-Ta(2)	3.25 (1)
Li-O(1)	2.09 (2)
Li-O(2)	2.37 (2)
Li-O(4)	2.148 (8)

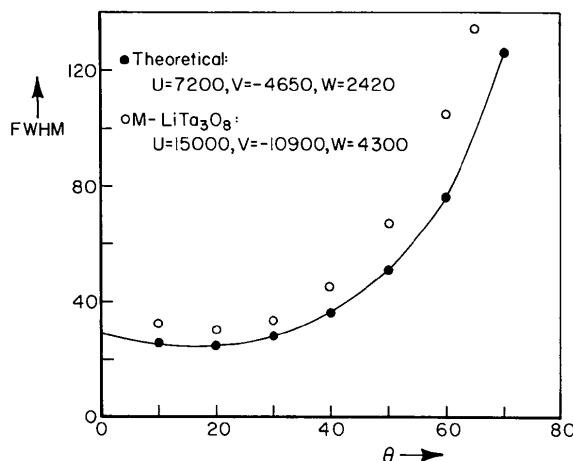


Fig. 2. Comparison between observed and calculated full widths at half maximum. (In this figure the values of  $U$ ,  $V$  and  $W$  are expressed in  $10^4 \times \text{deg}^2$  units.)

in this study are relatively low and not significantly different from those of the metal atoms. This result is very likely due to the uncertainty in the choice of the background level due to the severe overlapping of the diffracted peaks. In fact, an improper estimate of the background has little effect on the positional parameters of the atoms but affects their thermal parameters significantly.

The lattice constants obtained in the present study agree well with those determined with X-ray single-crystal and powder techniques (Gatehouse, Negas & Roth, 1976). However, due to the uncertainty with which the neutron wavelength is known, the X-ray parameters should be preferred over those derived in the neutron refinement.\*

\* The cell-dimension errors given in the *Abstract* do not include the error in the neutron wavelength.

The values of the profile parameters  $U$ ,  $V$  and  $W$  obtained after refinement (Table 2) are significantly higher than those calculated theoretically (Table 1). The effect of such differences on the full widths at half maximum (fwhm) is illustrated in Fig. 2. This type of discrepancy between theoretical predictions and experimental results has been observed previously (Caglioti & Ricci, 1962) and could be attributed to a number of causes, including crystallite size broadening of the diffracted peaks. However, crystallites of distinct crystal habits (such as lath-like, needle-like, *etc.*) and of dimensions sufficiently small to produce line broadening would affect the widths of some diffraction peaks much more than those of others, changing radically the relationship between the fwhm  $H$  and the diffraction angle  $\theta$  and thus making the application of Rietveld's method impossible. On the other hand, it is possible to show that crystallites of spherical or approximately spherical shape do not alter the form of the function  $H(\theta)$  and the value of the parameter  $V$  but change the values of

the parameters  $U$  and  $W$  by equal increments. Since we have for our case  $|V_{\text{calc}}| < |V_{\text{exp}}|$  (see Tables 1 and 2), it must be concluded that the differences between the observed and calculated values of  $U$ ,  $V$  and  $W$  cannot be attributed to crystallite size effects but rather to inappropriate or incomplete assumptions in the original theory.

#### References

- BACON, G. E. (1972). *Acta Cryst.* **A28**, 357.  
 CAGLIOTI, G., PAOLETTI, A. & RICCI, F. P. (1958). *Nucl. Instrum.* **3**, 223–228.  
 CAGLIOTI, G. & RICCI, F. P. (1962). *Nucl. Instrum. Methods*, **15**, 155–163.  
 GATEHOUSE, B. M., NEGAS, T. & ROTH, R. S. (1976). *J. Solid State Chem.* **18**, 1–7.  
 RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.  
 ROTH, R. S., PARKER, H. S., BROWER, W. S. & MINOR, D. (1974). Report NASA CR-134599.

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### Triammonium Orthoarsenate Trihydrate

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**Abstract.**  $(\text{NH}_4)_3\text{AsO}_4 \cdot 3\text{H}_2\text{O}$ , monoclinic,  $P2_1/c$ ,  $a = 6.818$  (7),  $b = 6.364$  (5),  $c = 22.811$  (21) Å,  $\beta = 93.74$  (6)° (Syntex  $P\bar{1}$  autodiffractometer),  $Z = 4$ ,  $V = 987.7$  Å<sup>3</sup>, FW 247.08,  $D_c = 1.66$ ,  $D_m = 1.61$  g cm<sup>-3</sup> (by flotation at ~4°C). The crystals were grown at ~4°C in a sealed flask by neutralizing concentrated  $\text{H}_3\text{AsO}_4$  solution with KOH followed by addition of a large excess of  $\text{NH}_4\text{OH}$  solution. The crystal is isostructural with the corresponding phosphate,  $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ . The averaged As–O bond length is 1.685 Å. The compound loses  $\text{NH}_3$  gradually on exposure to the atmosphere at room temperature and finally converts to  $(\text{NH}_4)_2\text{HASO}_4$ .

**Introduction.** Crystals of  $(\text{NH}_4)_3\text{AsO}_4 \cdot 3\text{H}_2\text{O}$  (TAA) are transparent and plate-like. The crystal to be studied was sealed in a Lindemann-glass capillary. The intensity data of 1127 independent reflexions ( $>3\sigma$ ,  $\sin \theta/\lambda < 0.56$  Å<sup>-1</sup>) were collected on a Syntex  $P\bar{1}$  autodiffractometer using Cu  $K\alpha$  (Ni) radiation. The intensities were converted to  $F_o$  values after applying Lorentz–polarization, absorption and time-decay corrections. Intensity data from azimuthal rotation about the two strong

reflexions, 200 and 400, were used for the absorption correction (North, Phillips & Mathews, 1968). The linear absorption coefficient for Cu  $K\alpha$  radiation is 50.9 cm<sup>-1</sup>. Time-decay corrections were made from intensity data of three check reflexions remeasured periodically. Total deterioration of the check reflexions ranged from 8.5 to 9.5%.

The cell-dimension data and space group indicate that TAA is isomorphous with the corresponding phosphate,  $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$  (TAP) (Mootz & Wunderlich, 1970). This was confirmed from Patterson and Fourier syntheses. The non-H coordinates of TAP [except the split O(7) atom] were then used for the initial refinement of the TAA structure by the full-matrix least-squares method; this gave an  $R$  value of 0.14. The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $F_c$  and  $F_o$  are the calculated and observed structure factors, respectively, and  $w$  is the weight. The weighting scheme of Stout & Jensen (1968) was used. A difference Fourier map (DFM) calculation at this stage indicated O(7) could be disordered. Nonetheless, the refinement using anisotropic thermal parameters and assuming a split O(7) atom similar to that in TAP gave no better