

Powder Neutron Diffraction Study of the Nonstoichiometric Solid Solution of Lithium Tantalate $9\text{LiTaO}_3:\text{Ta}_2\text{O}_5$

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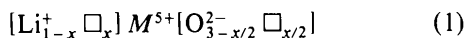
(Received 6 April 1981; accepted 20 October 1981)

Abstract

The nonstoichiometric solid solution $9\text{LiTaO}_3:\text{Ta}_2\text{O}_5$ has been studied with the powder neutron diffraction technique, and the intensity data have been used to refine several structural models with the Rietveld method. The results of these calculations show that the best fit to the experimental observations is obtained with the model for the defective structure proposed by Nassau & Lines [*J. Appl. Phys.* (1970), **41**, 533–537] ($R_n = 4.37$, $R_p = 6.91$, $R_w = 9.34$, $R_e = 5.58$ for 2964 observations). Data have also been collected from stoichiometric LiTaO_3 , and the results of the refinement of this structure ($R_n = 3.64$, $R_p = 6.97$, $R_w = 9.70$, $R_e = 5.63$ for 2725 observations) agree well with those obtained with single-crystal diffraction techniques.

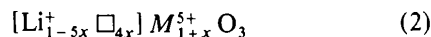
Introduction

Because of their electrical and optical properties, the niobate and the tantalate of lithium, LiNbO_3 and LiTaO_3 , have been intensively studied in recent years (Raeuber, 1977). Both compounds exist over a fairly large nonstoichiometric solid-solution range, extending from about 45 to 50 mol% of Li_2O in $M_2\text{O}_5$.^{*} Some of the most important properties of LiNbO_3 and LiTaO_3 are strongly dependent on the Li/M ratio, and for this reason possible mechanisms of nonstoichiometry in these oxide systems have received considerable attention. The models proposed so far in discussing the deviations from the ideal composition refer to LiNbO_3 . The same considerations, however, should also apply to LiTaO_3 , as well as to the other compounds isostructural with the niobate. Fay, Alford & Dess (1968) proposed, for fully oxidized LiNbO_3 , a structure containing Li^+ and O^{2-} vacancies. This model may be represented with the formula



^{*} Here and in what follows the symbol *M* indicates Nb or Ta.

in which the symbol \square denotes a vacancy. The description of Fay *et al.* contradicts density data as well as lattice-parameter measurements, and for this reason it will not be considered any further in this study. Lerner, Legras & Dumas (1968) have discussed the possibility of Nb substituting for Li with the formation of Li vacancies for charge compensation. This model may be represented with the formula



and is schematically illustrated in Fig. 1. As shown in the figure, the defects consist of rows containing three adjacent metal ions in the *c* direction of the hexagonal unit cell. Nassau & Lines (1970) critically reviewed this structure and concluded that the energy involved in three adjacent metal ions must be considerably higher than that of a stacking-fault arrangement containing only pairs of equal cations in the *c* direction. The model that they propose is illustrated in Fig. 2 for both metal-rich and Li-rich compositions. A highly symmetric defective structure for LiMO_3 has been introduced recently by Raeuber (1977). In this case, as

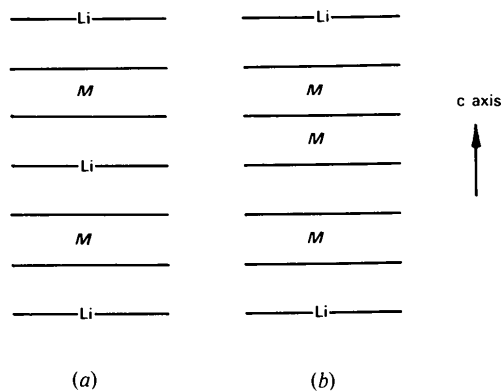


Fig. 1. (a) Stacking sequence of cations in the nondefective structure of LiMO_3 . The horizontal lines indicate the O layers. (b) The defective structure proposed by Lerner *et al.* (1968). The *M* ion which substitutes the lithium ion is shifted along the *c* axis so that it occupies an octahedral site rather than the triangular environment of oxygen ions of the original Li^+ .

illustrated in Fig. 3, the defects extend exactly over one identity period along the *c* axis.

Due to a lack of sufficient experimental data, it has not been possible to decide which of these models is present in the structures of nonstoichiometric niobate and tantalate. In order to take advantage of the favorable values of the scattering lengths of the atomic species present in the compounds, we have, therefore, decided to make an attempt to solve the defective structures of these phases by neutron diffraction. To avoid the complication that might arise with the possible reduction of Nb^{5+} to Nb^{4+} , in our study we

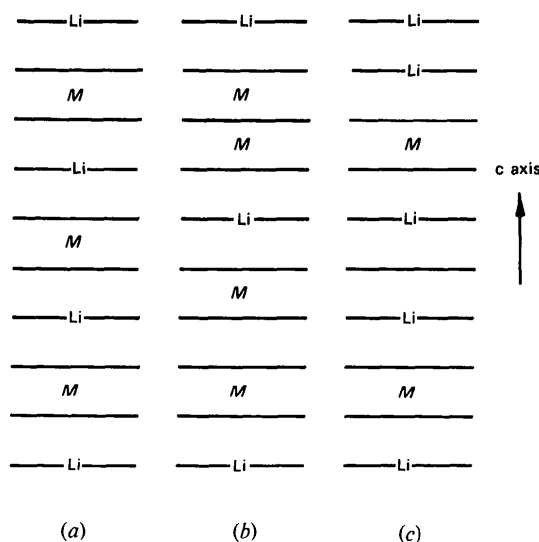


Fig. 2. The stacking-fault model proposed by Nassau & Lines (1970) showing the three-cation fault. (b) M^{5+} -rich compositions. (c) Li^+ -rich compositions. The reference nondefective structure is shown in (a).

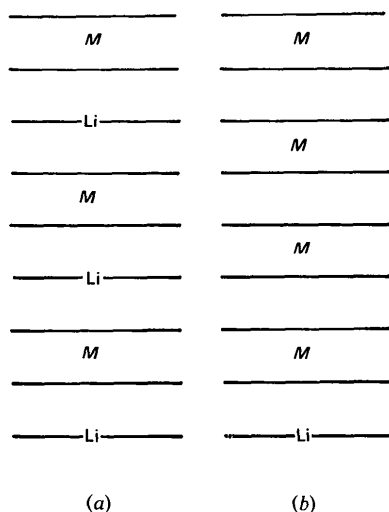


Fig. 3. (a) Nondefective reference structure of LiMO_3 . (b) Symmetric nonpolar stacking disorder proposed by Raeuber (1977).

decided to use LiTaO_3 rather than LiNbO_3 . In order to introduce the largest possible number of defects in the structure and still be in the solid-solubility range of Ta_2O_5 in LiTaO_3 , the composition $9\text{LiTaO}_3:\text{Ta}_2\text{O}_5$ was selected. Finally, we decided to use the powder method in association with the Rietveld (1969) procedure of profile refinement so that the difficulties associated with the growth of large, homogeneous, and well characterized single crystals could be avoided.

Experimental

The sample of stoichiometric LiTaO_3 was prepared by heating the commercially available material at 1820 K in a Pt crucible for 18 h. The nonstoichiometric phase was prepared by mixing the same commercially available LiTaO_3 with Ta_2O_5 (99.9% purity) in the molar ratio of 9:1 and by heating the mixture in a Pt crucible at 1270 K for 19 h. The product of this treatment was ground and heated at 1820 K for 18 h, and this operation was repeated twice. In all cases, the X-ray powder patterns of the final products used in the neutron experiments showed no extra lines indicating the presence of a second phase.*

The neutron diffraction data for both compositions were collected at room temperature with a five-detector diffractometer at the National Bureau of Standards Reactor (Prince & Santoro, 1980), using the experimental conditions summarized in Table 1. The powder patterns of the compounds contain numerous isolated peaks as well as resolved clusters. Since the neutron diffraction peak shapes are not necessarily Gaussian (Santoro & Prince, 1980), several single reflections, distributed over the entire angular range of 2θ , were checked by fitting them to Gaussian distributions with the least-squares method. These calculations gave an

* The X-ray powder patterns were measured with a high-angle diffractometer utilizing a graphite monochromator. With this instrument we can detect, in favorable circumstances, about 1% of a second phase.

Table 1. *Experimental conditions used to measure the powder patterns of stoichiometric and nonstoichiometric LiTaO_3*

Monochromatic beam: reflection 220 of a Cu monochromator with mosaic spread of $\sim 15'$ arc
Wavelength: 1.542 (1) Å
Horizontal divergences: 10, 20, and $10'$ arc for the in-pile, monochromatic-beam, and diffracted-beam collimators, respectively
Sample container: vanadium can of ~ 10 mm diameter
Angular ranges scanned by each of the five detectors: 10–40, 30–60, 50–80, 70–100, 90–120°; step: 0.05°
Number of independent Bragg reflections: 55 for both compounds
Number of observations used in the profile refinements: 2725 for stoichiometric LiTaO_3 and 2964 for the nonstoichiometric composition

average value of 1.35 for the goodness of fit χ , *i.e.* a value quite adequate for most structure refinements.

The neutron data were analyzed with the Rietveld (1969) method, modified by Prince (1980), to process

the intensities from the five counters of the diffractometer simultaneously. The background was assumed to be a straight line with a finite slope and was refined for each channel together with the profile and structural

Table 2. *Results of the refinements of nonstoichiometric and stoichiometric LiTaO_3*

Numbers in parentheses are standard deviations on the last decimal figure. The letter *C* indicates that the corresponding parameter was constrained during refinement. The first three models were refined in space group *R3*, the others in *R3c*. *n* is the occupancy factor.

	Model of Lerner <i>et al.</i> (1968)	Model of Nassau & Lines (1970)	Model of Raeuber (1977)	Defects ignored	Stoichiometric LiTaO_3	Abrahams, Hamilton & Sequeira (1967)
Ta(1) <i>x</i>	0	0	0	0	0	0
<i>y</i>	0	0	0	0	0	0
<i>z</i>	0	0	0	0	0	0
<i>B</i> (\AA^2)	0.53 (3)	0.54 (3)	0.53 (3)	0.43 (3)	0.16 (3)	0.32 (7)
<i>n</i>	0.33	0.33	0.33	0.33	0.33	
Ta(2) <i>x</i>	0	0	0			
<i>y</i>	0	0	0			
<i>z</i>	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$			
<i>B</i> (\AA^2)	0.53 <i>C</i>	0.54 <i>C</i>	0.53 <i>C</i>			
<i>n</i>	0.33	0.33	0.33			
Ta(3) <i>x</i>	0	0	0			
<i>y</i>	0	0	0			
<i>z</i>	0.280 (4)	0.273 (5)	$\frac{1}{3}$			
<i>B</i> (\AA^2)	0.53 <i>C</i>	0.54 <i>C</i>	0.53 <i>C</i>			
<i>n</i>	0.02	0.01	0.01			
Ta(4) <i>x</i>		0	0			
<i>y</i>		0	0			
<i>z</i>		0.773	$\frac{2}{3}$			
<i>B</i> (\AA^2)		0.54 <i>C</i>	0.53 <i>C</i>			
<i>n</i>		0.01	0.01			
O(1) <i>x</i>	0.0494 (2)	0.0498 (2)	0.0496 (3)	0.0493 (3)	0.0492 (3)	0.0498 (6)
<i>y</i>	0.3401 (4)	0.3407 (4)	0.3403 (4)	0.3403 (4)	0.3430 (4)	0.3436 (4)
<i>z</i>	0.0720 (2)	0.0720 (2)	0.0721 (2)	0.0724 (2)	0.0693 (2)	0.0688 (4)
<i>B</i> (\AA^2)	0.44 (2)	0.45 (2)	0.48 (2)	0.38 (2)	0.22 (2)	0.52 (6)
<i>n</i>	1.0	1.0	1.0	1.0	1.0	
O(2) <i>x</i>	0.6599 <i>C</i>	0.6593 <i>C</i>	0.6597 <i>C</i>			
<i>y</i>	0.9506 <i>C</i>	0.9502 <i>C</i>	0.9504 <i>C</i>			
<i>z</i>	0.5720 <i>C</i>	0.5720 <i>C</i>	0.5721 <i>C</i>			
<i>B</i> (\AA^2)	0.44 <i>C</i>	0.45 <i>C</i>	0.48 <i>C</i>			
<i>n</i>	1.0	1.0	1.0			
Li(1) <i>x</i>	0	0	0	0	0	0
<i>y</i>	0	0	0	0	0	0
<i>z</i>	0.2783 (6)	0.2765 (5)	0.2808 (5)	0.2799 (4)	0.2803 (3)	0.278 (2)
<i>B</i> (\AA^2)	2.3 (2)	2.0 (2)	3.3 (2)	5.2 (2)	1.9 (1)	1.2 (2)
<i>n</i>	0.27	0.2756	0.28	0.33	0.33	
Li(2) <i>x</i>	0	0	0			
<i>y</i>	0	0	0			
<i>z</i>	0.7783 <i>C</i>	0.7765 <i>C</i>	0.7808 <i>C</i>			
<i>B</i> (\AA^2)	2.3 <i>C</i>	2.0 <i>C</i>	3.3 <i>C</i>			
<i>z</i>	0.29	0.2756	0.28			
Li(3) <i>x</i>		0				
<i>y</i>		0				
<i>z</i>		0.62 (1)				
<i>B</i> (\AA^2)		2.0 <i>C</i>				
<i>n</i>		0.01				
R_n	4.88	4.37	5.09	5.59	3.64	3.88 based on F
R_p	7.03	6.91	7.10	7.26	6.97	6.04 based on F^2
R_w	9.50	9.34	9.61	9.75	9.70	
R_e	5.58	5.58	5.58	5.58	5.63	
χ	1.70	1.67	1.72	1.75	1.72	

Atom	Occup.	z		Occup.	z		Occup.	z
	M		SD	M		SD	M	
Ta4				M	0.01	0.77	D	
Li2	Li	0.29	0.77	SD	Li	0.28	0.75	S
Li3				Li	0.01	0.62	D	
Ta2	M	0.33	0.50	SD	M	0.33	0.50	S
Ta3	M	0.02	0.28	D	M	0.01	0.27	D
Li1	Li	0.27	0.27	S	Li	0.28	0.26	S
Ta1	M	0.33	0.00	SD	M	0.33	0.00	SD
	Li		SD	Li		SD	Li	SD

Fig. 4. The 'average' defective structures analyzed in the present study: (a) model proposed by Lerner *et al.* (1968); (b) model proposed by Nassau & Lines (1970); (c) model proposed by Raeuber (1977). The letters *S* and *D* indicate whether the corresponding atom is present in the stoichiometric or in the defective structure. The approximate values of the occupancies and of the *z* coordinates of each metal atom are also indicated. As in the previous figures, the heavy horizontal lines indicate the layers formed by the O atoms. The labeling of the atoms is the same as that given in Table 2.

parameters. The initial values of the profile parameters *U*, *V*, and *W* were calculated with the formulas derived by Caglioti, Paoletti & Ricci (1958). The 'average' structures corresponding to each of the models considered in this study were obtained by mixing, in the appropriate proportions and in accordance with the prepared composition, the stoichiometric structure with the atomic distributions illustrated in Figs. 1, 2, and 3. The schematic atomic configurations, the occupancy factors, and the approximate *z* coordinates of the metal atoms of each of the defective structures generated in this way are shown in Fig. 4. The initial values of the positional parameters of the O atoms and of the isotropic temperature factors were those given by Abrahams, Hamilton & Sequeira (1967). The neutron scattering amplitudes used in the calculations were $b(\text{O}) = 5.8$, $b(\text{Ta}) = 7.0$, and $b(\text{Li}) = -2.14$ fm (Bacon, 1972). All parameters were allowed to vary simultaneously until the residual R_w was reduced by less than one part in a thousand by one cycle of refinement (for the definition of R_w and the other *R* factors commonly used in profile-analysis studies, see, *e.g.*, Hewat, 1974). The results of all refinements are given in Table 2.*

* Tables of observed profile intensities for stoichiometric and nonstoichiometric LiTaO_3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36493 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England, or directly from the authors.

Discussion

It has been pointed out (Cheetham & Taylor, 1977) that a choice between alternative models is difficult in the case of profile analysis if there is uncertainty in the estimation of background intensities and if the shape of the diffraction peaks is not properly described. We may exclude the possibility that these two systematic errors play a significant role in the present analysis. In fact, as we have indicated previously, the validity of the Gaussian approximation for our diffraction experiments was tested and was found satisfactory before refinement. In addition, the background parameters were included in all of our calculations as refinable variables, and there was no correlation coefficient larger than 0.25 between the background and the other parameters. Under these conditions, it is probably safe to assume that the background intensities have not introduced any significant bias.

In order to choose between the models of Lerner *et al.* (1968) and Nassau & Lines (1970), we wish to test the hypothesis that the two models give equally good descriptions of the structure. This hypothesis is analyzed in an accompanying paper by Prince (1982) who concludes that the hypothesis can be rejected at the 5% level of significance and that the model of Nassau & Lines gives a better fit to the data.

It is possible to reject the model proposed by Raeuber (1977) with the same procedure. We may, therefore, conclude that the stacking-fault arrangement of the cations discussed by Nassau & Lines (1970) fits our experimental data better than any of the models proposed to explain the deviations from the ideal composition in LiNbO_3 and LiTaO_3 so far, and we will consider this model in all of our subsequent discussions.

The comparison of the atomic coordinates for stoichiometric and defective LiTaO_3 can be made best if we describe the structure in the manner proposed by Megaw (1968), *i.e.* with

$$\begin{aligned} M & \text{ at } 0, 0, w \\ O & \text{ at } u, \frac{1}{3} + v, \frac{1}{12} \\ Li & \text{ at } 0, 0, \frac{1}{3} + w'. \end{aligned}$$

From Table 2 we have, for pure LiTaO_3 , $u_1 = 0.0492$ (3), $v_1 = 0.0097$ (4), $w_1 = 0.0140$ (2), and $w'_1 = -0.0390$ (3). For $9\text{LiTaO}_3:\text{Ta}_2\text{O}_5$, the corresponding values are $u_2 = 0.0498$ (2), $v_2 = 0.0074$ (4), $w_2 = 0.0113$ (2), and $w'_2 = -0.0455$ (5), and the values of the shifts over the pooled errors σ are, therefore, $|\Delta u|/\sigma_1 = 1.7$, $|\Delta v|/\sigma_2 = 4.0$, $|\Delta w|/\sigma_3 = 9.6$, and $|\Delta w|/\sigma_4 = 11.2$. It has been pointed out (Megaw, 1968) that, when $v = w = 0.0$ and $w' = -\frac{1}{12}$, the structure becomes centrosymmetric with space group $R\bar{3}c$. Assuming that there are no inadequacies with the theoretical models of the two structures, we must conclude that the structure of $9\text{LiTaO}_3:\text{Ta}_2\text{O}_5$ approximates a centrosymmetric arrangement more closely

Table 3. *Lattice parameters for stoichiometric and nonstoichiometric LiTaO_3*

Figures in parentheses are standard deviations in the last decimal places.

	LiTaO_3		$9\text{LiTaO}_3:\text{Ta}_2\text{O}_5$		Abrahams & Bernstein (1967)	
	Neutrons	X-rays	Neutrons	X-rays	Ta/Li = 0.95	Ta/Li = 1.00
a (Å)	5.14730 (10)	5.15110 (10)	5.15760 (10)	5.16030 (10)	5.15359 (1)	5.15428 (1)
c (Å)	13.76640 (20)	13.77730 (30)	13.78420 (20)	13.79700 (40)	13.78070 (1)	13.78351 (2)

than the structure of stoichiometric LiTaO_3 . It has been suggested (Megaw, 1968) that at the Curie point the symmetry of LiNbO_3 (and, by analogy, that of LiTaO_3) is that of space group $R\bar{3}c$. The structural results obtained in the present study, therefore, suggest that the Curie temperature of the nonstoichiometric compound should be lower than that of stoichiometric LiTaO_3 . This conclusion is in full agreement with the observation that the Curie temperature of LiTaO_3 decreases as the mol% of tantalum oxide in the melt increases (Ballman, Levinstein, Capio & Brown, 1967).

The data obtained from the nonstoichiometric phase were also used to refine a structural model without defects, and the results of these calculations are shown in Table 2 in the column under the heading 'Defects ignored'. All the parameters calculated in this refinement agree quite closely with those obtained for stoichiometric LiTaO_3 , with the exception of the isotropic temperature factor of the lithium ion, which is unusually high (5.2 \AA^2). Close agreement also exists between the results obtained for pure LiTaO_3 in this study (second column before the last in Table 2) and those reported by Abrahams, Hamilton & Sequeira (1967) for the single-crystal neutron refinement in which only isotropic temperature factors were considered (first column before the last in Table 2).

The lattice-parameter determinations are summarized in Table 3 where our results are compared with those of Abrahams & Bernstein (1967). The values of a and c obtained from the profile refinements of the neutron data are systematically lower than the corresponding ones determined from X-ray powder patterns. Almost certainly this discrepancy is caused by slightly underestimating the neutron wavelength. In fact, a value λ (neutrons) = 1.543 \AA (instead of $\lambda = 1.542 \text{ \AA}$ used in the calculations) would improve the agreement between the two sets of values considerably. The parameters determined by Abrahams & Bernstein (1967) lie between those derived in the present study for LiTaO_3 and for $9\text{LiTaO}_3:\text{Ta}_2\text{O}_5$. A possible explanation for such systematic differences may be

found in the composition of the samples used in the experiments. In fact, the ratios Ta/Li of 0.95 and 1.00 quoted by Abrahams & Bernstein (1967) refer to the composition in the melt. From the phase diagram of $\text{Li}_2\text{O}-\text{Ta}_2\text{O}_5$ (Roth, 1975), one finds that the ratio Ta/Li of these crystals should be slightly larger than that of the liquid.

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