

to differences in the hydrogen bond systems. Since the N...Cl bond is situated in the mirror plane at $x = 1/4$ (and $x = 3/4$) it cannot influence the **a** parameter. For similar reasons the O...Cl bond cannot influence the **b** parameter. Therefore both types of hydrogen bonds might be shortened on deuteration and this could explain the difference in the stabilities of IDAC and DIDAC.

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Note on the Crystal Structure of a Mixed Nb-Zr-Oxide

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In our studies on the ZrO_2 - Nb_2O_5 system¹ we have observed a phase with the approximate composition $(Nb,Zr)O_{2.46}$. Powder data (Table 1) show that this is identical with that first found by Trunov *et al.*,² who suggested the formula $ZrO_2 \cdot (5-7)Nb_2O_5$. The same phase has later been studied by Allpress and Roth³ who thought it to be a polymorph of $Nb_{24}ZrO_{62}$ which they called β - $Nb_{24}ZrO_{62}$. Stephenson *et al.*⁴ have also investigated the phase, formulating it as $ZrO_2 \cdot 16Nb_2O_5$ and proposing a structure.

Since we failed to prepare the phase " $(Nb,Zr)O_{2.46}$ " in a pure form, we are unable to give accurate data on its composition. Weissenberg photographs $h0l-h3l$ have been taken from single crystals of the oxide and the relative intensities of the reflections measured visually. The Patterson projection $P(u,p,w)$ as well as the Harker sections $(u,0,w)$ and $(u,\frac{1}{2},w)$ have been

calculated and these clearly show " $(Nb,Zr)O_{2.46}$ " to be closely related to other monoclinic niobium-rich oxides with $b = 3.82 \text{ \AA}$ (cf. $H-Nb_2O_5$), but with a more complicated crystal structure. The Patterson projection indicates that the structure is built up of blocks with ReO_3 -structure extending infinitely in the y -direction and 3 or 4 MeO_6 -octahedra in each of two directions in the xz plane. The best explanation of the Patterson distributions is that each unit cell contains two 4×4 , two 4×3 , two 3×4 , and two 3×3 blocks. The blocks are fitted together in a way analogous to that in $H-Nb_2O_5$ and leave space for some tetrahedrally surrounded metal atoms (probably two). We have calculated structure factors for several proposed structures built up from the blocks mentioned above, using the metal positions derived from known structures. For the best of these models the agreement between observed and calculated structure amplitudes was satisfactory except for some of the weaker reflexions. We have also made similar calculations based on the crystal structure proposed by Stephenson *et al.* These give approximately the same agreement as that for the best of our models.

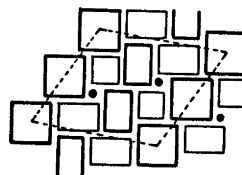


Fig. 1. Idealized projection of the most favoured of our proposed structures for " $(Nb,Zr)O_{2.46}$ ". The full circles represent metal atoms in tetrahedral positions.

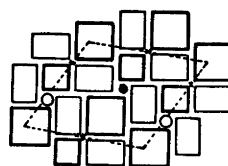


Fig. 2. Idealized projection of the structure of $ZrO_2 \cdot 16Nb_2O_5$ proposed by Stephenson *et al.* The filled circle represents a metal atom in a tetrahedral position, the open circles are empty positions and intersecting shear planes are marked with a cross.

The main difference between our (Fig. 1) and Stephenson's (Fig. 2) proposals is that the latter introduces two new forms of block junctions and that the former employs only known block junctions. In Stephenson's model, corners of

Table 1. Crystallographic data for "(Zr,Nb)O_{2.46}".

Unit cell dimensions: $a = 39.82 \pm 0.02 \text{ \AA}$; $b = 3.829 \pm 0.002 \text{ \AA}$; $c = 35.34 \pm 0.02 \text{ \AA}$, and $\beta = 116.46 \pm 0.05^\circ$.

Systematically absent reflexions: None.

Possible space group: *P2*.

Powder data. $\text{CuK}\alpha_1$ radiation. $a(\text{CuK}\alpha_1) = 1.54051 \text{ \AA}$.

<i>I</i> obs	$\sin^2\theta \times 10^5$ obs	<i>d</i> obs	<i>h k l</i>	$\sin^2\theta \times 10^5$ calc	<i>d</i> calc
m	374	12.60	{ 3 0 $\bar{2}$	376	12.56
			{ 1 0 2	378	12.53
vw	435	11.71	{ 2 0 $\bar{3}$	439	11.63
			{ 1 0 $\bar{3}$	439	11.63
vw	528	10.60	{ 3 0 $\bar{3}$	532	10.56
			{ 0 0 3	533	10.55
			{ 2 0 2	611	9.854
vw	619	9.790	{ 4 0 $\bar{1}$	619	9.790
			{ 3 0 1	620	9.782
			{ 4 0 $\bar{3}$	718	9.090
vw	717	9.097	{ 1 0 3	721	9.071
			{ 3 0 $\bar{2}$	939	7.949
vw	941	7.940	{ 4 0 $\bar{4}$	945	7.924
			{ 5 0 $\bar{3}$	997	7.714
			{ 2 0 3	1001	7.699
vw	1167	7.130	{ 5 0 0	1167	7.130
vw	1359	6.607	{ 4 0 2	1359	6.607
vw	1840	5.678	{ 4 0 3	1843	5.874
vw	1920	5.559	{ 7 0 $\bar{4}$	1924	5.553
vw	2119	5.291	{ 6 0 $\bar{6}$	2127	5.281
			{ 7 0 $\bar{5}$	2129	5.279
			{ 8 0 4	2436	4.935
vs	2438	4.933	{ 4 0 $\bar{4}$	2446	4.925
			{ 7 0 $\bar{6}$	2450	4.921
vw	2873	4.544	{ 8 0 $\bar{6}$	2871	4.546
vw	3053	4.408	{ 9 0 $\bar{3}$	3050	4.410
vw	3990	3.856	{ 10 0 $\bar{6}$	3990	3.856
			{ 4 0 6	4006	3.848
			{ 1 1 0	4093	3.807
w	4099	3.805	{ 1 1 $\bar{1}$	4105	3.802
			{ 0 1 1	4106	3.801
			{ 2 1 0	4233	3.744
vs	4239	3.741	{ 1 1 $\bar{2}$	4236	3.742
			{ 9 0 1	4264	3.730
			{ 2 1 $\bar{2}$	4283	3.722
s	4274	3.726	{ 6 0 5	4569	3.604
m	4568	3.604	{ 5 0 6	4707	3.550
vs	4705	3.551	{ 10 0 $\bar{8}$	4711	3.549
w	4758	3.531	{ 4 1 $\bar{3}$	4764	3.529
w	4941	3.465	{ 11 0 7	4944	3.464

some of the adjacent blocks are characterized either by an empty tetrahedral position or by the sharing of an octahedral edge, thereby leading to intersecting shear planes.

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