

STRUCTURAL FEATURES THAT CAUSE DIFFERENT IONIC CONDUCTIVITY IN RbNbWO AND TINbWO

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The compounds RbNbWO₆ and TINbWO₆ belong to a group with idealized chemical formula AB₂O₆. The structural basis is a pyrochloro-like three-dimensional framework built up of BO octahedra occupied by W atoms, the latter being partially replaced by Nb atoms. This results in nonstoichiometry of the composition. Large Rb and Tl cations are positioned in the framework voids which can be statistically occupied.

The crystals of this type are interesting because of their peculiar optical and electric properties. At temperatures below 330 and 360 K such crystals exhibit electrical polarity, while upon heating they undergo a peculiar phase transition of the ferroelectric-ionic superconductor-type. A structural study of both these compounds is of special interest because TINbWO₆ crystals exhibit significantly higher spontaneous polarization in the low-temperature ferroelectric phase as well as higher ionic conductivity in the high-temperature superionic state, as compared to rubidium tungsten-niobate. Ionic conductivity in these compounds is due to univalent Tl and Rb cations which occupy large framework voids being comparatively weakly linked to its atoms and can relatively easily migrate along the channels within the structure.

Experimental neutron diffraction data were obtained at temperatures 423 and 573 K, that exceed the phase transition point, i.e. the samples were studied at two temperatures in the superionic state.

It was established that the frameworks of both compounds have practically identical geometry, while the arrangement of Rb and Tl atoms in equal octahedra differ significantly. As is shown in Figs 1a, b, 2a, b, 3a, b, Rb cation is located at the octahedra centre, while Tl cation is shifted from this centre towards octahedral faces by 0.6 Å and statistically occupies

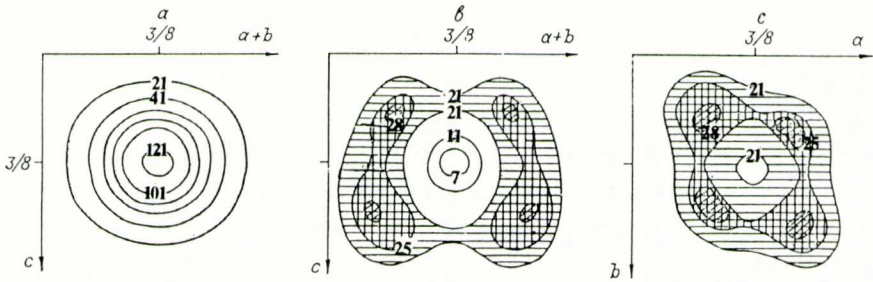


Fig. 1. Difference nuclear density maps in structures of RbNbWO_6 (a-diagonal section) and TiNbWO_6 (b-diagonal, c-coordinate sections). $T = 423 \text{ K}$. Isoline scale is $\rho \cdot 0.1 \text{ \AA}^{-3}$.

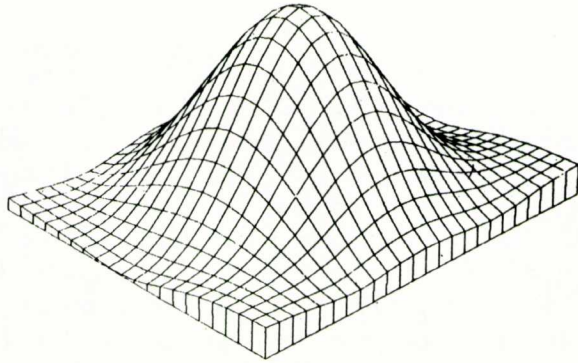


Fig. 2a. Three-dimensional difference density map in the RbNbWO_6 structure.

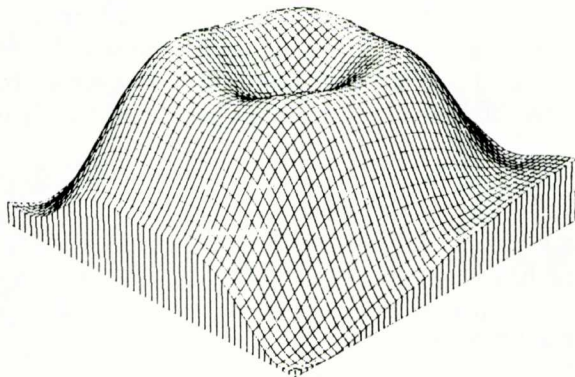


Fig. 2b. Three-dimensional difference density map in the TiNbWO_6 structure.

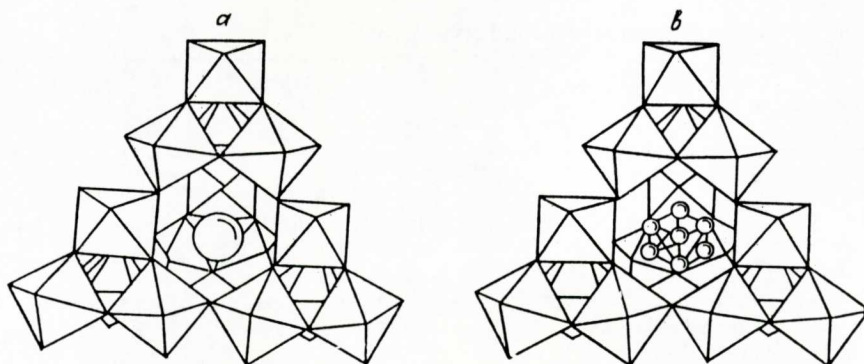


Fig. 3

eight sites that correspond to two crystallographically independent sites in the $Fd\bar{3}m$ space group. Such a situation is unusual for classical crystal chemistry of inorganic compounds.

It was found that at 573 K there is a significant deviation of thermal atomic vibrations of Rb ions from the harmonic law. Difference map of Rb cation probability distribution obtained by removal of the harmonic component indicates preferable Rb ion shifts towards the 'windows' bordering octahedral sites (Fig. 4). Appropriate sections of this map are similar to maps of statistical Tl ion distribution in $TlNbWO_6$.

Cationic diffusion paths during the ionic transport in the studied structures are different. The difference in the conductivity is due to the character of Rb and Tl ion arrangement in the structures.

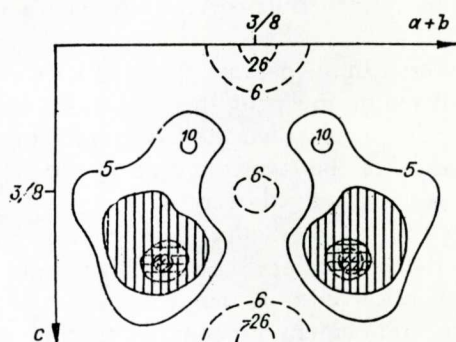


Fig. 4. Diagonal section of zero nuclear density synthesis of $RbNbWO_6$ structure. Contributions of atoms in harmonic approximation are subtracted. Isoline level scale $\rho = 0.02 \text{ \AA}^{-3}$.

Table 1. Neutron diffractions data and crystals data.

Parameter	RbNbWO ₆		TiNbWO ₆	
	423 K	573 K	423 K	573 K
	<i>Fd 3m</i>		<i>Fd 3m</i>	
<i>a</i> , Å	10.382	10.392	10.396	10.401
ϕ , cm	0.30		0.40	
μ , cm ⁻¹	0.020		0.014	
($\sin \Theta/\lambda$) _{max} , Å ⁻¹	0.78	0.78	0.78	0.78
Number of observed reflections	1150	597	676	682
Number of independent reflections	85	86	97	99
Number of equivalent reflections	24	12	12	12
R averaged, of equivalent reflections, %	3.01	2.30	2.35	2.51

Remarkable overlapping of density peaks naturally results in a rather high degree of the correlation between the occupancies of 32 and 32' sites of Tl₁ and Tl₂ atoms and their thermal parameters obtained after least-squares refinement of the structural model, Tl atoms being statistically positioned at two independent sites. It is impossible to determine unambiguously the most probable values of the strongly correlating parameters during the LSM refinement because, in fact, there is no evident global minimum of the discrepancy function R for these parameters. In our case, the coefficients of correlation between the occupancies and the thermal parameters of Tl₁ and Tl₂ atoms were 0.95. Our attempts to refine these parameters led to different solutions, depending on the choice of the initial approximation and the refinement procedure, R-factor being practically the same: R = 1,55%.

In this case the scatter in the parameters essentially exceeded the standard deviations calculated by inverting the matrix of normal equations.

In order to solve the problem we applied compulsory scanning of occupancies. the procedure of the refinement of all the parameters was repeated several times at various fixed occupancies $q_1 = 1/8 + \Delta q$ and $q_2 = 1/8 - \Delta q$ in the range of possible changes of q from $-1/8$ to $+1/8$. In the region of minimum R-factor values was 0.01. It should be noted that a strong correlation was observed only between q occupancies and thermal parameters. In all the refinement procedures all the other parameters, including the redaction coefficient and the extinction parameter, remained stable, to an accuracy not worse than 0.1% for the whole of low R-factor values.

Table 2. Position and isotropic thermal atomic parameters and main interatomic distances (T = 573 K).

Atom	Parameters	RbNbWO ₆		TiNbWO ₆	
		423 K	573 K	423 K	573 K
	$x = y = z$	0	0	0	0
Nb, W	$B_{\text{OKB}} (\text{\AA}^2)$	1.85	1.94	1.78	1.85
	$B_{11} = B_{22} = B_{33}$	0.0041	0.0045 (1)	0.0040	0.0043 (1)
	$B_{12} = B_{13} = B_{23}$	-0.0012	-0.0009 (1)	-0.0010	-0.0008 (1)
O	x	0.3123	0.3121 (1)	0.3120	0.3120 (1)
	$y = z$	0.125	0.125	0.125	0.125
	B_{OKB}	1.25	1.90	1.31	1.70
	B_{11}	0.0027	0.0037 (1)	0.0029	0.0039 (1)
	$B_{22} = B_{33}$	0.0030	0.0040 (1)	0.0031	0.0040 (1)
	B_{23}	0.0011	0.0016 (1)	0.0013	0.0016 (1)
Rb	$x = y = z$	0.375	0.375		
	B_{H30}	6.5	7.6 (1)		
	$C^{123} \cdot 10^3$		0.004 (1)		
	$D^{1111} \cdot 10^4$		-0.0055 (6)		
	$D^{1122} \cdot 10^4$		-0.0012 (4)		
Ti ₁	$x = y = z$			0.412	0.412 (3)
	B_{OKB}			5.2	5.5
	$B_{11} = B_{22} = B_{33}$			0.012	0.013 (2)
	$B_{12} = B_{23} = B_{13}$			-0.0014	-0.0012 (8)
Ti ₂	$x = y = z$			0.348	0.347 (7)
	B_{OKB}			5.2	5.6
	$B_{11} = B_{22} = B_{33}$			0.012	0.013 (2)
	$B_{12} = B_{23} = B_{13}$			-0.0018	-0.0012 (8)
	$R_w, \%$	1.9	1.3	1.9	1.6
	$R, \%$	1.6	1.1	1.5	1.5

The results of the above refinement procedure of the structural model with compulsory occupancy scanning at 573 K are shown in Fig. 5. As for T = 423 K the difference consists only in the fact that the plateau size of minimum values is less by some .q interval. The use of the standard procedure of least-squares refinement for unambiguous determination of the

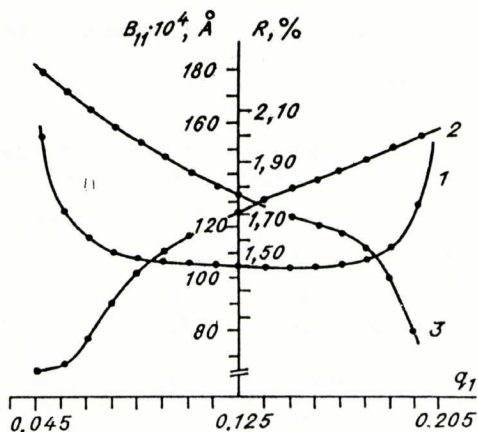


Fig. 5. Dependence of R-factor (curve 1) and thermal parameters B_{11} for Tl_1 (curve 2) and Tl_2 atoms (curve 3) on the occupancy q_1 of site by Tl_1 atom; $q_2 = 1/8 - q_1$; $T = 543$ K.

structure parameters and the estimation of their confidence intervals in this case were, in fact, impossible. Additional information is needed. This can be crystal-chemical, physical or some other information. In our case we have chosen the solution that leads to equal $Beqv.$ for Tl_1 and Tl_2 atoms. If we ignore this circumstance, the least-squares technique in an automated regime will lead randomly to one of possible solutions, and the calculated deviations of the correlating parameters will yield significantly lowered values of their confidence intervals.

From the obtained thermal parameters for a double-site model of $TlNbWO_6$ we calculated probability density functions (PDF) $P(x)$ of Tl_1 and Tl_2 atom displacements from their equilibrium sites. We also obtained distributions of single-atom potentials near these sites (Fig. 6a, b, c).

The character of the distortion of a harmonic PDF by anharmonic corrections for $RbNbWO_6$, obtained as a result of the refinement, also indicates preferable Rb atom shifts towards the above "windows" of conductivity (Fig. 7) during the thermal motion.

The Tl ion displacement from 8(b) to 32(e) site is due to specific features of the electronic structure of these ions, such as a lone electron pair.

A comparison of thermal atomic vibrations at $T = 423$ and 573 K suggests that the phase transition leading to loss of conductivity as the temperature falls, results from the displacements of the main framework cations from three-fold symmetry axes (Table 3).

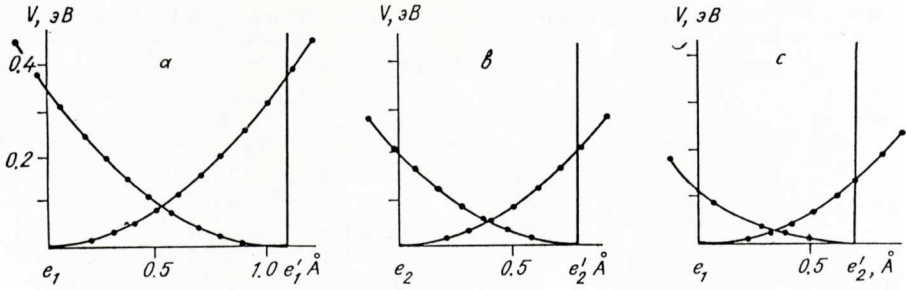


Fig. 6. Single-atom potential of Tl atoms in the TiNbWO_6 structure. Directions: $\text{Tl}_1 - \text{Tl}_2$ (a), $\text{Tl}_2 - \text{Tl}'_2$ (b), $\text{Tl}_1 - \text{Tl}'_2$ (c).

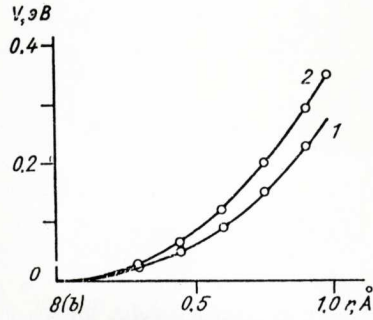


Fig. 7. Behaviour of single-atom potential of Rb atom in the RbNbWO_6 structure, along the directions $\text{III}(1)$ and $\text{III}(2)$ $T = 573 \text{ K}$.

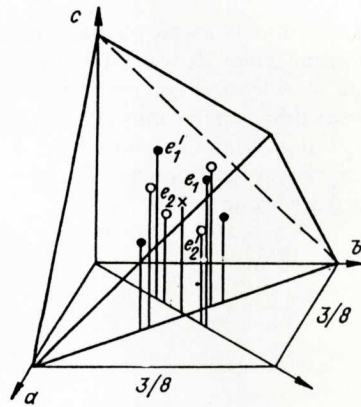


Fig. 8. Mutual arrangement of Tl ions occupying statistically 32 e_1 and 32 e_2 sites near the $8b$ ($3/8, 3/8, 3/8$) site denoted by a cross. Distances: $e_1 - e_1' = 1.09 \text{ \AA}$, $e_2 - e_2' = 0.78 \text{ \AA}$, $e_1 - e_2' = 0.68 \text{ \AA}$. Tetrahedral vertices are 16 d sites.

Table 3. Ellipsoids of thermal vibration of basis atom in RbNbWO₆ and TiNbWO₆.

Atom and point symmetry	<i>i</i> = 1, 2, 3	RbNbWO ₆		TiNbWO ₆	
		423 K	574 K	423 K	573 K
(Nb, W)	1	0.100 (3)	0.120 (3)	0.106 (3)	0.120 (3)
$\bar{3}m$	2, 3	0.174 (1)	0.173 (1)	0.168 (1)	0.167 (1)
O	1	0.102 (2)	0.115 (2)	0.100 (1)	0.113 (1)
	2	0.122 (2)	0.142 (2)	0.126 (1)	0.146 (1)
$2mm$	3	0.149 (1)	0.176 (1)	0.155 (1)	0.176 (1)
Rb					
$\bar{4}2m$	1, 2, 3	0.287 (3)	0.308 (3)		
Tl ₁	1			0.22 (2)	0.24 (2)
$3m$	2, 3			0.27 (1)	0.28 (1)
Tl ₂	1			0.21 (1)	0.24 (2)
$3m$	2, 3			0.28 (1)	0.28 (1)

ABSTRACT

At temperatures below 330 and 260 K RbNbWO₆ and TiNbWO₆ exhibit electric polarity, while upon heating they undergo a peculiar phase transition of the ferroelectric-ionic superconductor-type. TiNbWO₆ crystals exhibit significantly higher spontaneous polarization in the low-temperature ferroelectric phase as well as higher ionic conductivity in the high-temperature superionic state, as compared to rubidium tungsten-niobate.

Experimental neutron diffraction data were obtained at temperatures 422 and 572 K, that exceed the phase transition point. It was established that the frameworks of both compounds have practically identical geometry, while the arrangement of Rb and Tl atoms in equal octahedra differ significantly. Pb cation is located at the octahedra centre, while Tl cation is shifted from this centre towards octahedral faces by 0.6 Å and statistically occupies eight sites that correspond to two crystallographically independent sites in the F_dam space group.