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A New GTB-Type Thallium Niobate

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(*Received* 15 *January* 1979; *accepted* 26 *February* 1979)

Abstract

A new compound in the system Tl–Nb–O has been synthesized as single crystals of composition very close to $TlNb_7O_{18}$. It crystallizes in the tetragonal system with $a = b = 27{\cdot}50$ (2), $c = 3{\cdot}94$ (1) Å, space group $P4/mbm$, and $Z = 8$. The structure was refined to $R = 6\%$ for 1089 reflections $[I \geq 3\sigma(I)]$. The excess of cations found by refinement of the structure is not sufficient for charge balance. The suggested formula, $Tl_{7.7}Nb_{54+x}O_{146-y}$, may be a result of the combined effect of the excess of cations and stacking faults involving the O atoms.

Introduction

Synthesis of single crystals in the system Tl–Nb–O led to the formation of several new oxides. One of these, with an interlinked tunnel structure (Gasperin, 1977), proved to have cationic-exchange and ionic-conductivity properties. Another, the subject of this paper, is isotypic with Rb or K niobates, the formulae of which are not well defined. A preliminary study of one of these (Gatehouse, Lloyd & Miskin, 1972) showed an unknown octahedral arrangement and was named GTB (Gatehouse Tungsten Bronze). However, the proposed scheme which gives the formula $Rb_3Nb_{54}O_{146}$ does not lead to charge balance.

It appeared worthwhile to pursue as far as possible the structure of this Tl compound because it often happens that the structural and chemical formulae do not agree for non-stoichiometric niobates.

Synthesis and description

Single crystals were obtained by the flux-growth method. The best results occurred when a mixture of Tl_2CO_3, Nb_2O_5 and B_2O_3 in the proportion 4:2:16 was heated at 1373 K in a Pt crucible. After cooling at a constant rate (6 K h^{-1}) to 773 K, the boron glass formed was extracted with boiling water. The resulting product was homogeneously crystallized, giving colourless needles.

The chemical analysis, with 17·1% Tl, and the measured density (5·0 Mg m^{-3}) correspond to the formula $TlNb_7O_{18}$ with $Z = 8$. However, owing to the large amount of Tl volatilized during the heating, it is not certain that the composition of the single crystal selected is the same as the whole.

Lattice parameters and systematic absences were determined from rotation and Weissenberg photographs. The crystals are rectangular prisms elongated along [001] and flattened in the [110] direction. They crystallize in the tetragonal system with $a = b = 27{\cdot}50$ (2), $c = 3{\cdot}94$ (1) Å and the extinctions (0*kl* only

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present when $k = 2n$) suggest two possible space groups: $P4/mbm$ or $P\bar{4}b2$. However, noncentrosymmetry was not proved by doubling laser frequency.

Experimental

The crystal selected for the measurement of intensities was 630 × 86 × 44 μm. Data collection was made on a Philips diffractometer with a graphite monochromator and, because of the cell size, Cu $K\bar{\alpha}$ radiation. Intensities were measured by the ω–2θ method, with a scan speed of 0·025° s^{-1} between 2 and 67°, yielding 1681 independent reflections. After subtracting the background, the data were corrected for Lorentz–polarization factors.

For absorption corrections, the program *AGNOST*, which uses the de Meulenaer & Tompa (1965) analytical method and takes into account the crystal morphology, was applied at first to several reflections measured in the ψ scan over 180° with a step of 10°. In this manner, it was possible to refine the crystal dimensions and μ. The theoretical value of μ for the formula $TlNb_7O_{18}$ is about 65·0 mm^{-1} but after this refinement μ was between 30·0 and 40·0 mm^{-1}, and the adopted value was 35·0 mm^{-1}. Scattering factors of Tl^+ and Nb^{5+} were corrected for anomalous dispersion.

Table 1. *Positional parameters* (×10^4) *and isotropic thermal parameters*

Occupancy			x	y	z	B_{eq} (Å^2)
	Nb(1)	2(*d*)	5000 (0)	0 (0)	0 (0)	1·8
	Nb(2)	4(*g*)	1986 (1)	6986 (1)	0 (0)	1·6
	Nb(3)	8(*i*)	2328 (1)	9379 (1)	0 (0)	1·1
	Nb(4)	8(*i*)	3678 (1)	9642 (1)	0 (0)	1·4
	Nb(5)	8(*i*)	664 (1)	7212 (1)	0 (0)	1·5
	Nb(6)	8(*i*)	1583 (1)	8260 (1)	0 (0)	1·3
	Nb(7)	8(*i*)	382 (1)	8390 (1)	0 (0)	1·2
	Nb(8)	8(*i*)	864 (1)	9484 (1)	0 (0)	1·4
0·16	Nb(9)	2(*b*)	0 (0)	0 (0)	5000 (0)	1·4
0·12	Nb(10)	4(*h*)	3840 (12)	8840 (12)	5000 (0)	1·5
	O(1)	2(*c*)	0 (0)	5000 (0)	5000 (0)	4·4
	O(2)	4(*h*)	1976 (32)	6976 (32)	5000 (0)	4·7
	O(3)	8(*j*)	2280 (8)	9377 (8)	5000 (0)	2·9
	O(4)	8(*j*)	3653 (8)	9601 (8)	5000 (0)	2·9
	O(5)	8(*j*)	652 (11)	7215 (11)	5000 (0)	4·4
	O(6)	8(*j*)	1575 (9)	8273 (9)	5000 (0)	3·3
	O(7)	8(*j*)	381 (6)	8397 (6)	5000 (0)	0·8
	O(8)	8(*j*)	791 (6)	9500 (6)	5000 (0)	1·3
	O(9)	4(*g*)	3992 (9)	8992 (9)	0 (0)	1·2
	O(10)	8(*i*)	2082 (6)	8718 (6)	0 (0)	1·6
	O(11)	8(*i*)	2997 (5)	9302 (6)	0 (0)	1·2
	O(12)	8(*i*)	1954 (6)	7684 (6)	0 (0)	2·1
	O(13)	8(*i*)	1044 (5)	8780 (5)	0 (0)	0·4
	O(14)	8(*i*)	208 (5)	9144 (5)	0 (0)	0·3
	O(15)	8(*i*)	1562 (5)	9621 (5)	0 (0)	0·8
	O(16)	8(*i*)	944 (5)	7904 (5)	0 (0)	1·3
	O(17)	8(*i*)	107 (5)	7684 (5)	0 (0)	0·9
	O(18)	8(*i*)	1271 (6)	6932 (6)	0 (0)	2·4
	O(19)	8(*i*)	277 (6)	6652 (6)	0 (0)	1·7
	O(20)	8(*i*)	4283 (6)	9996 (6)	0 (0)	1·2
0·28	Tl(1)	4(*h*)	1084 (4)	6084 (4)	5000 (0)	4·8
0·36	Tl(2)	8(*j*)	776 (2)	5925 (2)	5000 (0)	4·8
0·24	Tl(3)	8(*j*)	3426 (3)	8556 (4)	5000 (0)	2·6
0·06	Tl(4)	8(*j*)	3268 (8)	8632 (14)	5000 (0)	0·9
0·02	Tl(5)	8(*j*)	2608 (15)	8030 (21)	5000 (0)	1·8
0·14	Tl(6)	8(*j*)	2697 (3)	7822 (4)	5000 (0)	2·3

Structure determination and refinement

The Patterson maps of sections perpendicular to [001] show that all the intense peaks are situated on the sections $z = 0$ and $\frac{1}{2}$, which confirms the space group $P4/mbm$.

Because the Patterson maps did not yield atomic positions with sufficient precision for the structure determination (the value of R was always $>0{\cdot}6$), *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977) was used and eight independent Nb atoms were located. Then, as suggested by the length of c, eight O atoms were superposed on the Nb atoms at $z = \frac{1}{2}$. At this stage, a refinement of the structure by block-diagonal least squares with isotropic thermal parameters led to $R = 0{\cdot}30$. Fourier maps followed by difference syntheses gave the positions of 12 O atoms in the plane ($xy0$). Some electronic density clusters in the section $z = \frac{1}{2}$ could only be the result of the statistical distribution of Tl atoms on different sites.

Introduction of the weighting scheme $\omega = 1/\sigma^2$, and refinement of the atomic positions, the multiplicity factors of the statistical atoms and the anisotropic thermal parameters reduced R to its final value of 0·06 for 1089 independent reflections with $I \geq 3\sigma(I)$.* The reflections 002, 003 and 004, affected by extinction, were omitted.

The atomic coordinates and equivalent isotropic temperature factors are given in Table 1. From a consideration of their distances from neighbouring O atoms, and notwithstanding an unusual environment, two residual electron densities have been attributed to excess Nb, listed in Table 1 as Nb(9) and Nb(10).

Description of the structure

The framework of the structure is composed of NbO_6 octahedra sharing corners; this confirms the description given by Gatehouse. It is illustrated in Fig. 1 in projection down **c**.

The bases of the octahedra containing the Nb atoms form polygons with 3, 4, 5, 6 and 7 sides. The centre of the pentagon is occupied by Nb(7) which is thus at the centre of a pentagonal bipyramid.

Fig. 2 shows the framework in the plane ($xy\frac{1}{2}$): the O atoms situated on the Nb atoms define cavities with 3,

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34306 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

4, 6 and 7 sides. Tl$^+$ is statistically distributed over the two largest: Tl(1) and Tl(2) in the hexagonal polygons, Tl(3), Tl(4), Tl(5) and Tl(6) in the heptagons. Their departure from the cavity centre can be explained in two ways: the large distance from the nearest O atoms, and the presence of $6s^2$ electrons of monovalent Tl. The square cavity contains about five electrons, attributed to excess Nb because the distance from an O atom (2·57 Å) seems too short for Tl–O. The triangular cavities are completely empty.

The distances to the atoms surrounding the cations up to 3·5 Å are given in Table 2. The average Nb–O and Tl–O distances are approximately equal to the sum of their ionic radii. Nb(7)–O bonds in the pentagonal bipyramid are slightly longer than those in the octahedra.

The O···O distances range from 2·51 to 2·98 Å, except for those of the pentagon which are shorter (2·40 to 2·52 Å), probably because of the presence of Nb(7).

The temperature factors for Tl(1) and Tl(2) indicate that their positions are not precise enough and their statistical distribution should be increased.

Finally, O(2), O(3), O(4), O(5) and O(6) have rather large temperature factors which can be explained by

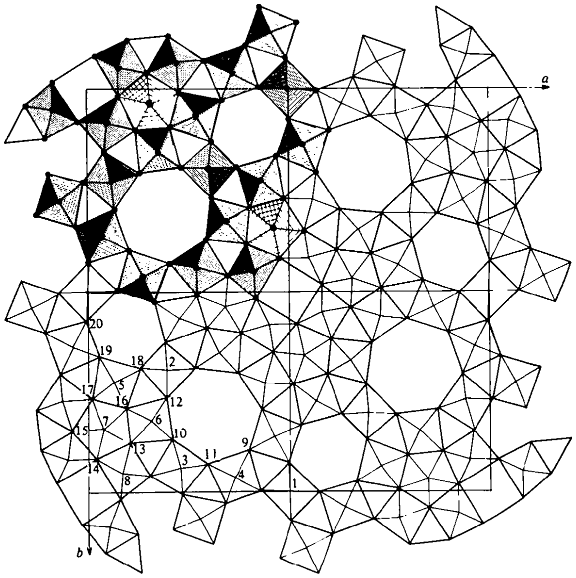

Fig. 1. Arrangement of the octahedra in the plane ($xy0$). The numbers correspond to those in Table 1.

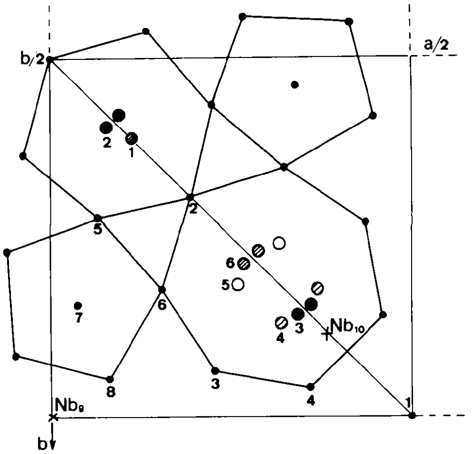

Fig. 2. Arrangement in the plane ($xy\frac{1}{2}$). The numbers correspond to those in Table 1. ● Oxygen atoms. ○ Thallium atoms. The degree of shading of the circles is proportional to the electron density.

Table 2. *Cation–anion distances* (Å) (*precision* 0·02 Å)

Nb(1)–O(1)	1·97 (×2)	Nb(8)–O(15)	1·95
Nb(1)–O(20)	1·97 (×4)	Nb(8)–O(8)	1·98 (×2)
⟨Nb(1)–O⟩	1·97	Nb(8)–O(14)	1·99
		Nb(8)–O(13)	2·00
Nb(2)–O(12)	1·92 (×2)	Nb(8)–O(14)	2·03
Nb(2)–O(2)	1·97 (×2)	⟨Nb(8)–O⟩	1·99
Nb(2)–O(18)	1·97 (×2)		
⟨Nb(2)–O⟩	1·95	Nb(9)–O(8)	2·57 (×4)
Nb(3)–O(11)	1·85	Nb(10)–O(9)	2·06 (×2)
Nb(3)–O(10)	1·94	Nb(10)–O(4)	2·15 (×2)
Nb(3)–O(3)	1·97 (×2)	⟨Nb(10)–O⟩	2·11
Nb(3)–O(17)	2·00		
Nb(3)–O(15)	2·21	Tl(1)–O(18)	3·09 (×4)
⟨Nb(3)–O⟩	1·99	Tl(1)–O(5)	3·29 (×2)
		Tl(1)–O(19)	3·35 (×4)
Nb(4)–O(20)	1·93	Tl(1)–O(2)	3·47
Nb(4)–O(19)	1·97	⟨Tl(1)–O⟩	3·26
Nb(4)–O(4)	1·97 (×2)		
Nb(4)–O(9)	1·98	Tl(2)–O(20)	2·97 (×2)
Nb(4)–O(11)	2·09	Tl(2)–O(19)	3·12 (×2)
⟨Nb(4)–O⟩	1·99	Tl(2)–O(20)	3·23 (×2)
		Tl(2)–O(1)	3·32
Nb(5)–O(18)	1·84	Tl(2)–O(4)	3·43
Nb(5)–O(19)	1·87	⟨Tl(2)–O⟩	3·17
Nb(5)–O(5)	1·97 (×2)		
Nb(5)–O(17)	2·00	Tl(3)–O(9)	2·78 (×2)
Nb(5)–O(16)	2·05	Tl(3)–O(4)	2·94
⟨Nb(5)–O⟩	1·95	Tl(3)–O(11)	3·08 (×2)
		Tl(3)–O(4)	3·24
Nb(6)–O(10)	1·87	Tl(3)–O(11)	3·47 (×2)
Nb(6)–O(12)	1·88	⟨Tl(3)–O⟩	3·11
Nb(6)–O(6)	1·97 (×2)		
Nb(6)–O(16)	2·01	Tl(4)–O(11)	2·80 (×2)
Nb(6)–O(13)	2·06	Tl(4)–O(4)	2·87
⟨Nb(6)–O⟩	1·96	Tl(4)–O(9)	2·97 (×2)
		Tl(4)–O(3)	3·40
Nb(7)–O(7)	1·97 (×2)	⟨Tl(4)–O⟩	2·97
Nb(7)–O(16)	2·04		
Nb(7)–O(17)	2·08	Tl(5)–O(12)	2·83 (×2)
Nb(7)–O(15)	2·09	Tl(5)–O(6)	2·91
Nb(7)–O(13)	2·11	Tl(5)–O(10)	3·09 (×2)
Nb(7)–O(14)	2·12	Tl(5)–O(2)	3·38
⟨Nb(7)–O⟩	2·06	⟨Tl(5)–O⟩	3·02
		Tl(6)–O(12)	2·86 (×2)
		Tl(6)–O(2)	3·06
		Tl(6)–O(12)	3·09 (×2)
		Tl(6)–O(6)	3·32
		⟨Tl(6)–O⟩	3·05

their discontinuous bonding with the Tl atoms. The effect of this bonding is naturally less perceptible on O(9), O(10), O(11), O(12), O(18), O(19) and O(20) located in the (*xy*0) plane.

Discussion

The refinement suggests the formula $Tl_{7.7}Nb_{54.8}O_{146}$, which represents an electrical imbalance of about ten charges.

Since the difference syntheses do not show any excess of cations, we have carried out a refinement on the occupancy factor of O atoms with the highest temperature factors: O(2) and O(5). It shows that the O(2) site is occupied to 72% and O(5) to 81%, but the temperature factors do not drop and refinement does not improve. Thus no conclusions are possible.

To check whether or not fluoride impurities, always present with Nb, are the cause of the charge imbalance, a quantitative analysis for fluorine was made by fast γ-ray spectrometry (Borderie, Pinault & Barrandon, 1977) of the crystal studied and of the Nb_2O_5 used for the synthesis. It shows the atomic ratio $[F]/[O] = 0{\cdot}028$ in Nb_2O_5 and ten times less in the crystal, consistent with the temperature of crystal formation. This small quantity of fluorine is not sufficient to lead to the charge imbalance. If this colourless, transparent oxide is electrically neutral, one can conclude that the charge imbalance is a combined effect of stacking faults of O atoms and an excess of cations, leading to the formula $Tl_{7.7}Nb_{54+x}O_{146-y}$.

The last problem is: why are the absorption coefficients given in *International Tables for X-ray Crystallography* (1974) almost twice as large as the observed values? It is possible that a systematic error occurred during the measurement of the intensities. We propose to continue the studies of absorption, with more favourable conditions, on another isotypic structure which should enable us to refine the model proposed here.

The non-stoichiometric tetragonal GTB niobates of monovalent ions, with $a \simeq 27{\cdot}5$, $c \simeq 3{\cdot}9$ Å, are built up from octahedra joined at corners which define tunnels with 4, 6 and 7 sides partially occupied by monovalent ions. This arrangement, first described by Gatehouse for a Rb niobate of unknown composition, is not observed in any other oxide. It seems to be stable enough to accommodate an excess of negative charge neutralized by a surplus of cations and probably by some vacancies of anions generating stacking faults.

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On the Stereochemistry of Valence Bonds and the Structures of XeO_3, XeF_4 and XeF_2

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(*Received* 23 *January* 1979; *accepted* 6 *March* 1979)

Abstract

In the stereochemistry of valence bonds the difference in nucleus–lone pair and nucleus–bonding pair attraction is used to explain certain coordination geometry, and to predict the structures of simple molecules. The results are applied to the crystal structures of some Xe compounds.

In their theory of the stereochemistry of valence bonds, Sidgwick & Powell (1940) assumed that bonding pairs and lone pairs of electrons were of equal importance and distributed themselves to minimize interelectron repulsion. For example, three pairs are arranged to form a triangle, four a tetrahedron, five a trigonal prism and six an octahedron. The theory has proved successful, but could not account for the deviations from the tetrahedral angle that exist in NH_3 and H_2O.

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