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VM_9O_{25} (M = Nb, Ta), a Combination of Tetrahedral VO_4 and Octahedral MO_6 Units

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Crystals of VM_9O_{25} (M = Nb, Ta) have been grown by a self-flux method. The crystal structures have been determined from X-ray single crystal diffraction data. Both compounds are isostructural and crystallize in the tetragonal PNb_9O_{25} structure type, $I\bar{4}$, with unit-cell parameters a = 15.690(2) Å, c = 3.8172(9) Å, Vol. = 939.7(3) Å^3, for M = Nb; and a = 15.665(6), c = 3.821(3), Vol. = 937.6(9) for M = Ta; and Z = 2. The crystal structure of tridimensional VM_9O_{25} is formed by a singular combination of two VO_4 tetrahedra and eighteen MO_6 octahedra per unit-cell. The presence of oxygen nonstoichiometry in VNb_9O_{25} is studied.

Introduction

Oxides of the cations with d^1 electronic configuration like tetravalent V, Nb, and Ta are of particular interest to test whether the superconducting properties of single-hole divalent Cu (d^9) oxides are electron-hole symmetric or not. For this reason the authors have begun to study the oxides of pentavalent V and Nb or Ta and their reduction products. The crystal structures shown by the oxides of pentavalent V and Nb or Ta had not been established. On the other hand, the authors observed that solid-state reactions of V_2O_5 and Nb_2O_5 or Ta_2O_5 in various V : M molar ratios (from 1 : 2 to 1 : 9) led to the same phase, and that this appeared isomorphous with PNb_9O_{25} (*1*). By both reasons they proposed to establish the composition of this phase by single-crystal X-ray diffraction. The present work aims to this object. Simultaneously it describes the structure shown by the mentioned phase. The crystal structure of these compounds of pentavalent V and Nb or Ta is the first established for one oxide of two different d elements from the fifth group.

Experimental Section

Crystal growth. VNb_9O_{25} single crystals were grown from a mixture of reagent grade V_2O_5 and Nb_2O_5 in molar ratio V : Nb = 9 : 1 (i.e., a very large excess of V_2O_5), which was heated at 1050°C for 3 hr and cooled to 900°C at a rate of 2°C hr^{-1}. For VTa_9O_{25} a mixture of analitical grade V_2O_5 and Ta_2O_5 in the molar ratio V : Ta = 1 : 1 was heated at 1200°C for 24 hr and cooled to 768°C at

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TABLE I

CRYSTAL AND REFINEMENT DATA FOR VM_9O_{25}

M:	Nb	Ta
Formula weight	1287	2079.4
Crystal system	Tetragonal	Tetragonal
Space group	$I\bar{4}$ (no. 82)	$I\bar{4}$ (No. 82)
a, b (Å)	15.690(2)	15.665(6)
c (Å)	3.8172(9)	3.821(3)
Volume (Å^3)	939.7(3)	937.6(9)
Z	2	2
F (000)	1184.	1760.
ρ (calc) (g cm^{-3})	4.5	7.4
Temp (°C)	22	22
μ (cm^{-1})	56.3	522.5
Cryst dimens (mm)	0.05 × 0.05 × 0.2	0.02 × 0.02 × 0.1
Diffractometer	Enraf–Nonius CAD4	Enraf–Nonius CAD4
Radiation	graphite-monochromated MoKα (λ = 0.71069 Å)	graphite-monochromated MoKα (λ = 0.71069 Å)
Scan technique	$\Omega/2\theta$	$\Omega/2\theta$
Data collected	(0,0,0) to (22,22,5)	(0,0,0) to (22,22,5)
Unique data	798	874
Unique data (I) $\geq 3\sigma$ (I)	650	618
Std rflns	3/39	3/39
RF (%)	4.4	4.0
R_wF (%)	4.5	3.3
Average shift/error	0.08	0.13

the same rate. In both cases the crystals were extracted mechanically.

Data collection. Both VM_9O_{25}(M = Nb, Ta) crystals were mounted in a kappa diffractometer. The cell dimensions were refined by least-squares fitting the 2θ values of 25 reflections. A summary of the fundamental crystal data is given in Table I. The I cell was established in both cases from the systematic extinctions, and the measurement of the intensities of the equivalent reflections showed tetragonal symmetry. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for V, Nb and Ta atoms were taken from the "International Tables for X-Ray Crystallography" (*2*). The space group $I\bar{4}$ was obtained as leading to the best refinement after trying, among others, $I4/m$.

Structure determination. In both structures the heavy atoms were located from a three-dimensional Patterson map. The positions of the oxygen atoms were obtained from Fourier syntheses. Empirical absorption corrections (*3*) were applied at the end of the isotropic refinements. The maximum and minimum absorption factors were 1.299 and 0.90, respectively for VNb_9O_{25}, and 1.08 and 0.94 respectively for VTa_9O_{25}. Mixed full-matrix least-squares refinements minimizing $\Sigma\, w\,(|F_o| - |F_c|)^2$ with isotropic temperature factors for the oxygen atoms and weights (*4*) $w = 1/(a + b|F_o|)^2$ were $a = 9.27$, $b = -0.09$ if $|F_o| < 66$ and $a = 2.55$, $b = 0.02$ if $|F_o| > 66$, led to $R = 0.044$ for M = Nb; and $a = 16.70$, $b = -0.10$ if $0 < |F_o| < 130$ and $a = 2.57$, $b = 0.02$ if $130 < |F_o| < 1200$, led to $R = 0.033$ for M = Ta. Most of the calculations were carried out with the X-RAY 80 system (*5*).

TABLE II

ATOMIC PARAMETERS FOR VM_9O_{25} (M = Nb AND Ta)

Atom	x	y	z	U_{eq}
Nb(1)	0.0000(0)	0.0000(0)	0.0000(0)	22(1)
Nb(2)	0.2189(1)	0.1052(1)	−0.0022(10)	7(1)
Nb(3)	0.6749(1)	0.1179(1)	0.0001(10)	8(1)
V	0.0000(0)	0.5000(0)	0.2500(0)	10(1)
O(1)	0.4868(5)	0.2189(4)	0.5085(81)	9(2)
O(2)	0.9503(5)	0.1160(5)	−0.0112(77)	10(2)
O(3)	0.3532(5)	0.1577(4)	−0.0042(82)	6(1)
O(4)	0.1763(5)	0.2170(4)	−0.0085(82)	10(2)
O(5)	0.2512(5)	0.1108(4)	0.4872(62)	5(1)
O(6)[a]	0.0000(0)	0.0000(0)	0.5000(0)	9(2)
O(7)	0.0743(4)	0.4470(4)	0.0231(47)	5(2)
Ta(1)	0.0000(0)	0.0000(0)	0.0000(0)	4(1)
Ta(2)	0.2203(0)	0.1035(1)	−0.0076(9)	3(1)
Ta(3)	0.6760(1)	0.1187(0)	0.0005(9)	3(1)
V	0.0000(0)	0.5000(0)	0.2500(0)	4(2)
O(1)	0.4891(9)	0.2191(8)	0.4804(108)	5(3)
O(2)	0.9508(9)	0.1157(9)	−0.0158(145)	8(3)
O(3)	0.3553(10)	0.1573(9)	−0.0159(116)	10(3)
O(4)	0.1756(9)	0.2175(8)	−0.0061(148)	10(3)
O(5)	0.2523(9)	0.1132(8)	0.4701(78)	2(3)
O(6)	0.0000(0)	0.0000(0)	0.5000(0)	6(5)
O(7)	0.0751(9)	0.4445(8)	−0.0030(149)	9(3)

Note. $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j \times 10^3$.
[a] Population factor: 0.90(2).

Results and Discussion

Crystal growth. Crystals of VNb_9O_{25} were black needles which suggested some oxygen nonstoichiometry. The employed crucible looked strongly soaked with a dark-colored material, probably V_2O_5 with some oxygen deficiency, as it can appear at temperatures between 700 and 1200°C. By this reason a much smaller amount of V_2O_5 was employed for the Ta oxide. In this case the crucible appeared almost clean, contained a sintered material of dark-brown color which consisted of transparent light-brown prismatic crystals of VTa_9O_{25} mixed with a powder of high crystallinity. Examined by X-ray powder diffraction, the powder was identified as VTa_9O_{25}.

Crystal structure. Atomic position coordinates and temperature factors as well as main interatomic distances and angles are included in Tables II–IV. The coordination polyhedra for the metals are VO_4 tetrahedra and MO_6 octahedra. The crystal structure of VM_9O_{25} is built of ReO_3-like blocks, consisting of (3 × 3) MO_6 octahedra which are joined at one level to form infinite planar slabs, perpendicular to the c-direction, at $z = 0, \frac{1}{2}, \ldots$ and mutually displaced as it corresponds to the $I\bar{4}$ symmetry (Fig. 1). These slabs are further linked by sharing nonequatorial edges at the perimeters of the blocks, to give a 3D structure. This kind of union forms double chains in the c direction by an assembly of edge-sharing octahedra (Fig. 2), of the high-temperature Nb_2O_5 type (*7*). Also in the c-direction simple chains of vertex-sharing octahedra are situated in the center of each ReO_3 block (M(1)). There are thus two kinds of nonequivalent octahedra, one of them, $M(1)O_6$ octahedra, quite regular, and those of $M(2)$ and $M(3)$ more distorted due to the double-chain formation. In the resulting 3D framework of MO_6 octahedra, there exists a small number of tetrahedral holes where the V atoms are situated.

$M(1)$ has an isotropical thermal factor larger than the other two M atoms. Because some V could enter into that position, a refinement was performed to determine this possibility. As a result, the R-value in-

TABLE III

ANISOTROPIC THERMAL PARAMETERS FOR VM_9O_{25} (M = Nb AND Ta)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb(1)	89(6)	89(6)	473(17)	0	0	0
Nb(2)	46(4)	94(4)	65(5)	−7(3)	−29(12)	−31(13)
Nb(3)	93(4)	62(4)	70(4)	28(3)	4(14)	21(13)
V	94(11)	94(11)	109(21)	0	0	0
Ta(1)	46(9)	17(0)	67(9)	0	0	0
Ta(2)	21(3)	33(3)	28(5)	−5(2)	21(8)	−7(9)
Ta(3)	40(3)	21(3)	39(4)	8(2)	−6(11)	4(11)
V	11(35)	19(0)	86(40)	0	0	0

Note. Anisotropic thermal parameters are of the form $\exp -2\{\pi^2 \cdot \Sigma(u_{ij} \cdot a_i^* a_j^* \cdot h_i \cdot h_j)\} \cdot 10^4$.

TABLE IV

MAIN INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN VM_9O_{25}

	M = Nb	M = Ta	
M(1)–O(2)	1.981 (7)	1.971(14)	(×4)
M(1)–O(6)	1.9086(4)	1.910(1)	(×2)
M(2)–O(1)	2.099 (7)	2.031(13)	(×1)
M(2)–O(2)	1.834 (7)	1.848(14)	(×1)
M(2)–O(3)	2.263 (7)	2.277(15)	(×1)
M(2)–O(4)	1.877 (7)	1.918(13)	(×1)
M(2)–O(5)	1.938 (23)	1.900(29)	(×1)
M(2)–O(5′)	2.016 (23)	2.063(29)	(×1)
M(3)–O(1)	1.783 (7)	1.820(14)	(×1)
M(3)–O(3)	1.995 (29)	2.032(43)	(×1)
M(3)–O(3′)	1.965 (29)	1.918(43)	(×1)
M(3)–O(4)	1.928 (7)	1.892(13)	(×1)
M(3)–O(5)	2.287 (7)	2.250(14)	(×1)
M(3)–O(7)	2.034 (7)	2.007(13)	(×1)
V –O(7)	1.673 (11)	1.753(33)	(×4)
O(6)–M(1)–O(6′)	180.0(1)	180.0(1)	(×1)
O(6)–M(1)–O(2)	91.2(9)	92. (2)	(×4)
O(6)–M(1)–O(2′)	88.8(9)	88. (2)	(×4)
O(2)–M(1)–O(2′)	177. (1)	176. (2)	(×2)
O(2)–M(1)–O(2)	90.0(3)	90.1(6)	(×4)
O(3)–M(2)–O(4)	89.5(3)	89.6(5)	(×1)
O(3)–M(2)–O(5)	75.1(8)	75. (1)	(×1)
O(3)–M(2)–O(5)	75.3(8)	74. (1)	(×1)
O(3)–M(2)–O(2)	172.8(4)	174.0(8)	(×1)
O(3)–M(2)–O(1)	83.6(3)	83.9(5)	(×1)
O(4)–M(2)–O(5)	93.6(9)	91. (2)	(×1)
O(4)–M(2)–O(5′)	92.1(9)	91. (2)	(×1)
O(4)–M(2)–O(2)	97.5(3)	96.0(6)	(×1)
O(4)–M(2)–O(1)	173.0(4)	173. (1)	(×1)
O(5)–M(2)–O(5′)	149.8(4)	149.3(6)	(×1)
O(5)–M(2)–O(2)	103. (1)	103. (2)	(×1)
O(5)–M(2)–O(1)	86.0(9)	84. (1)	(×1)
O(5)–M(2)–O(2′)	106. (1)	107. (2)	(×1)
O(5)–M(2)–O(1)	84.9(9)	90. (1)	(×1)
O(2)–M(2)–O(1)	89.4(3)	90.3(6)	(×1)
O(1)–M(3)–O(3)	106. (1)	102. (1)	(×1)
O(1)–M(3)–O(5)	176.7(3)	173. (1)	(×1)
O(1)–M(3)–O(3′)	104. (1)	107. (1)	(×1)
O(1)–M(3)–O(4)	95.6(3)	96.3(6)	(×1)
O(1)–M(3)–O(7)	93.0(3)	91.9(6)	(×1)
O(3)–M(3)–O(5)	73.5(7)	73.0(9)	(×1)
O(3)–M(3)–O(3′)	149.1(4)	150.5(7)	(×1)
O(3)–M(3)–O(4)	89.7(9)	91. (2)	(×1)
O(3)–M(3)–O(7)	89.5(5)	86. (2)	(×1)
O(3)–M(3)–O(4′)	91.6(9)	93. (2)	(×1)
O(3)–M(3)–O(7′)	84.6(5)	86. (2)	(×1)
O(4)–M(3)–O(7)	171.2(3)	171.7(6)	(×1)
O(5)–M(3)–O(3)	75.7(7)	77.9(9)	(×1)
O(5)–M(3)–O(4)	87.7(7)	87.8(5)	(×1)
O(5)–M(3)–O(7)	83.7(2)	83.9(5)	(×1)
O(7)–V –O(7)	117.6(7)	113. (2)	(×2)
O(7)–V –O(7′)	105.6(5)	108. (1)	(×4)

creased and the thermal factors did not improve. Hence, the possibility was rejected. The anisotropic refinement showed a high anisotropy of M(1) in the z-direction as indicated by the U_{33} values of Table III. This is explained because $M(1)O_6$ is the unique octahedron which shares vertexes in the z-direction forming pseudo-monodimensional chains. The high temperature factor of the O(6) atom in the Nb compound, approximately three times the average thermal parameter of the remaining oxygens, as well as the black color of the crystals, were signs that some reduction could have occurred during growing and the unique O(6) atom may have been affected. In order to elucidate this point, the indicated average thermal parameter was fixed for O(6), and the population factor was refined. After several cycles this factor fell to 0.90(2) and remained unchanged. The refined temperature factor obtained for O(6) with this population factor was similar to those of the other oxygen atoms. As for VTa_9O_{25} transparent crystals, the isotropic thermal factor for O(6) was similar to those of the remaining oxygens. In conclusion, single crystals of the Nb compound grown using a very large excess of V_2O_5 are oxygen deficient, as suggested by their aspect.

The crystal structure of VM_9O_{25} (M = Nb, Ta) has resulted from the PNb_9O_{25} type. The two possible space groups, $I\bar{4}$ and $I4/m$, proposed for this compound showed a small difference in R-factors, 9.2 and 9.3%, respectively (*1*). For VM_9O_{25} (M = Nb, Ta) the $I\bar{4}$ space group has been chosen by various reasons: it allows a population factor of the unity for the vanadium site, whereas in $I4/m$ this factor is 0.5 because of the symmetry plane; it also allows a mixed refinement with all the thermal parameters positive, whereas those for Nb in $I4/m$ become negative; and it leads to a lower R-factor, 4.4% instead of 4.9% for $I4/m$.

The "$GeO_2 \cdot 9Nb_2O_5$" phase has also been refined (*7*) in the PNb_9O_{25} structure

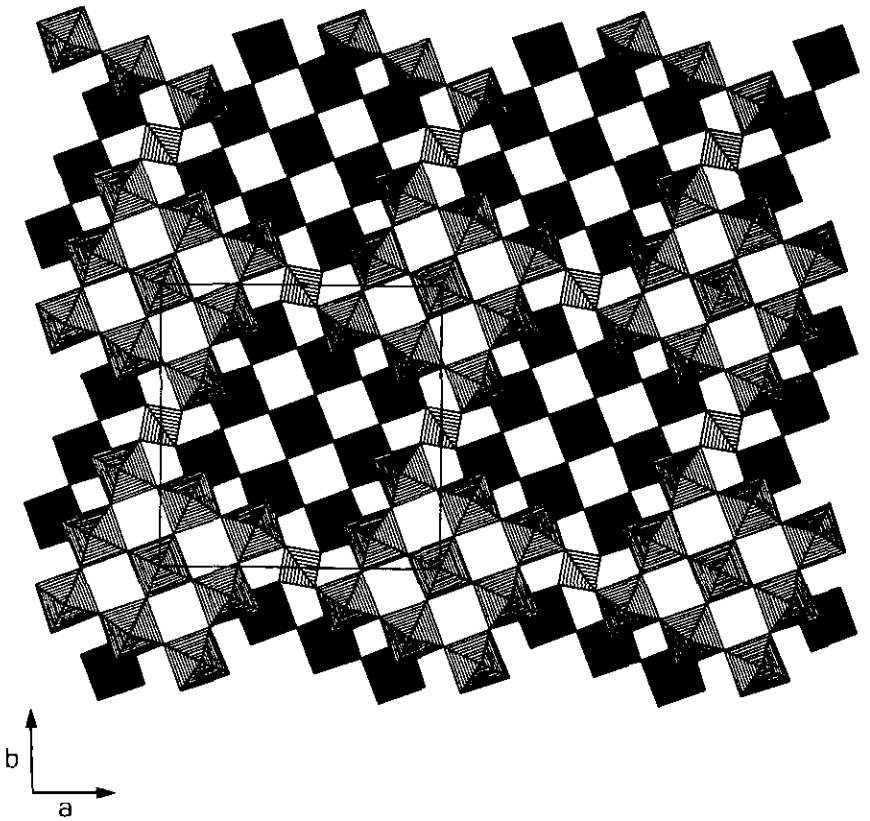

FIG. 1. STRUPLO (6) view along c of the VM_9O_{25} (M = Nb, Ta) structure showing the alternation of the slabs.

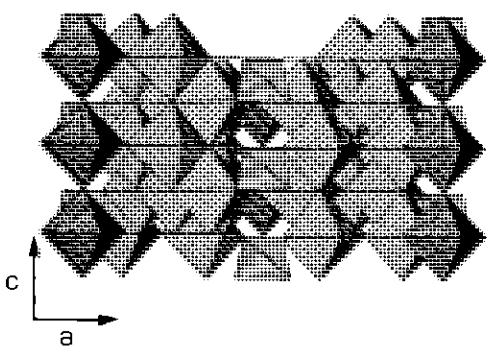

FIG. 2. STRUPLO (6) view of VM_9O_{25} (M = Nb, Ta) along the b direction showing the chains of vertex-sharing octahedra (dark octahedra) and the assembly of edge-sharing octahedra, both parallel to the c axis.

type, obtaining a composition range which implies an anion sublattice without defects, interstitial Nb atoms, and some mixing of Ge and Nb atoms at the 4(d) sites. This is not the case for VM_9O_{25} (M = Nb, Ta), which, like PNb_9O_{25}, has resulted to contain 10 unmixed (1 + 9) metallic atoms per formula VM_9O_{25}.

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