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Structure of Iron Diniobium Hexaoxide, FeNb₂O₆: An Example of Metal-Disordered Trirutile Structure

BY A. ARUGA, E. TOKIZAKI, I. NAKAI AND Y. SUGITANI

Department of Chemistry, The University of Tsukuba, Ibaraki 305, Japan

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Abstract. $M_r = 337.7$, tetragonal, $P\bar{4}2_1m$, $a = 4.7270(5)$, $c = 9.216(2)$ Å, $V = 205.93(5)$ Å³, $Z = 2$, $D_m = 5.39$, $D_x = 5.44$ Mg m⁻³, $\lambda(\text{Mo } K\alpha_1) = 0.70926$ Å, $\mu(\text{Mo } K\alpha_1) = 8.79$ mm⁻¹, $F(000) = 312$, room temperature. $R = 0.033$, $wR = 0.029$ for 476 reflections with $|F| > 3\sigma_F$. A superstructure of the rutile structure. The single crystal was synthesized by the floating-zone method. Metal sites are statistically occupied by disordered Fe and Nb atoms located in the octahedral interstices in the h.c.p. arrangement of the O atoms. The structure consists of chains of MO₆ octahedra, in which each octahedron shares a pair of opposite edges.

Introduction. FeNb₂O₆ is known to have two types of crystal structures. One is found in a structure of ferrocolumbite (Fe,Mn)(Nb,Ta)₂O₆ known as having the columbite (or niobite) structure with orthorhombic symmetry. The other is a high-temperature modification of ferrocolumbite, produced in a reducing atmosphere (Turnock, 1966). This compound was once reported as a mineral, mossite, but the mineral name is currently discredited (Dunn, Gaines & Kristiansen, 1979). The structure of this phase has been believed to belong to the trirutile (or tapiolite) structure with tetragonal symmetry. Distributions of the metal ions in both of the structures have been considered as 'ordered'. Recently,

however, rutile structures having a statistical cation distribution were reported for (Fe_{0.5}Ta_{0.5})O₂ and (Fe_{0.45}Nb_{0.53})O₂ (Langhof, Weitzel, Wölfel & Scharf, 1980). In this paper, the crystal structure of tetragonal FeNb₂O₆, which may correspond to so-called mossite, is reported. Also discussed is whether the Fe and Nb atoms in metal sites are disordered or ordered.

Experimental. Single crystals of FeNb₂O₆ were grown by the floating-zone technique. A stoichiometric powder mixture of Fe₂O₃ (99.9% pure) and Nb₂O₅ (99.99% pure) was sintered under an atmosphere of CO₂-H₂ [$\log(\text{CO}_2/\text{H}_2) = -1$] at 1123 K for 10 h. The FeNb₂O₆ obtained was then ground into a fine powder and pressed under a hydrostatic pressure of 400 kg cm⁻² to form a rod. A single crystal (90 × 6 mm \varnothing) of FeNb₂O₆ was grown from the rod by the floating-zone apparatus of an infrared-radiation convergence type in the atmosphere $\log(\text{CO}_2/\text{H}_2) = 2$, at a growth rate of 5 mm h⁻¹.

Electron microprobe analysis gave Fe, 15.75; Nb, 53.21; O, 27.42; total, 96.38 wt%. The corresponding chemical formula assumed as Fe + Nb = 3 is Fe_{0.99}Nb_{2.01}O_{6.02}, and was simplified to FeNb₂O₆.

Density measured by Berman balance. Crystal of ellipsoid shape (0.150 \varnothing × 0.175 mm) elongated parallel to the c axis. Rigaku AFC-5 automated four-circle

diffractometer equipped with Rotaflex RU-200 X-ray generator (operating conditions: 50 kV, 160 mA). Graphite-monochromated $Mo K\alpha$ radiation. Cell parameters obtained from 2θ values (44 – 56°) of 25 reflections. Data collection: 2θ – ω scan mode, scan speed 2° min^{-1} , maximum $\sin\theta/\lambda = 1.08 \text{ \AA}^{-1}$, with $0 \leq h \leq 11$, $0 \leq k \leq 7$ ($h \geq k$), $0 \leq l \leq 20$; three standard reflections (400, 330, and 006) every 50 observations (maximum fluctuation 1.0%), 710 unique reflections, 476 with $|F| > 3\sigma_F$, correction for Lorentz-polarization factors, and for absorption with *ACACA* (Wuensch & Prewitt, 1965): transmission factors 0.063–0.099 with 1200 sampling points. Linear absorption coefficients from *International Tables for X-ray Crystallography* (1974).

Since the Patterson maps show that the arrangement of the atoms is that of the trirutile structure, its true space group is considered to be $P4_21m$ and not $P4_22_1$. Fourier and ΔF syntheses with *GSFFR* (Ohmasa, 1972) using three atomic positions of the Fe, Nb, and O atoms, whose shifts from the model structure were estimated by modified *MULTAN80* (Fan, Yao, Main & Woolfson, 1983), revealed the remaining O and Fe atoms. The atomic parameters were refined on F by the full-matrix least-squares refinement program *RFINE-II* (Finger, 1969) using 476 unique reflections. Three models were examined to determine the distribution of the metal atoms: $R = 0.173$ for an 'ordered'-distribution-like trirutile structure which was believed to be correct structure of so-called 'mossite'; $R = 0.123$ for 'disordered'-distribution-like rutile type $NiNb_2O_6$ ($=Ni_{1/3}Nb_{2/3}O_2$) (Wichman & Müller-Buschbaum, 1983); $R = 0.107$ for a model in which the site occupancies of the metal sites were refined by the program. The third model gave the lowest value, and consequently it was chosen as the correct one for the present crystal. Refinements with anisotropic thermal parameters and secondary-extinction corrections ($g = 7.293 \times 10^{-2}$) gave $R = 0.033$, $wR = 0.029$ ($w = 1$), with shift/error for all the parameters less than 0.01. Scattering factors of neutral atoms from Cromer & Mann (1968), and anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The final atomic parameters are given in Table 1,* and interatomic distances and bond angles in Table 2 calculated with *UMBADTEA* (Finger, 1968). Fig. 1 shows the crystal structure drawn by *ORTEP* (Johnson, 1976), where broken lines signify the trirutile-type cell.

Metal ions occupy one-half of the octahedral interstices in the h.c.p. arrangement of the O atoms.

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42007 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Each O atom has three coplanar neighbours. The structure consists of chains of MO_6 octahedra ($M = Fe, Nb$), in which an octahedron shares a pair of opposite edges forming continuous chains parallel to the c axis. The MO_6 chains are linked by sharing vertices to form a three-dimensional structure.

Table 1. Atomic coordinates and thermal parameters (\AA^2) with e.s.d.'s in parentheses

$$B_{eq} = 4(2\beta_{11}a^2 + \beta_{33}c^2)/3.$$

	x	y	z	B_{eq}	$\Sigma \sigma_v$
$Fe_{0.43}Nb_{0.57}(1)$	0.0	0.5	0.2441 (1)	0.74	—
$Fe_{0.39}Nb_{0.61}(2)$	0.0	0.5	0.9196 (2)	1.15	—
$Fe_{0.18}Nb_{0.82}(3)$	0.0	0.5	0.5858 (2)	1.04	—
O(1)	0.2975 (7)	0.7975	0.9114 (13)	1.08	1.99
O(2)	0.3032 (12)	0.8032	0.2559 (8)	1.10	1.97
O(3)	0.2997 (7)	0.7997	0.5798 (9)	0.82	1.92

Table 2. Selected bond lengths (\AA) and bond angles ($^\circ$) with e.s.d.'s

$M(1)-O(1)$	$1.971(9) \times 2$	$O(1^{ii})-M(1)-O(1^{ii})$	$86.7(5)$
$M(1)-O(2)$	$2.030(6) \times 2$	$O(1^{ii})-M(1)-O(2)$	$92.2(2)$
$M(1)-O(3)$	$2.104(7) \times 2$	$O(1^{ii})-M(1)-O(3^{ii})$	$97.1(3)$
Mean	2.035	$O(1^{ii})-M(1)-O(3^{ii})$	$176.2(3)$
		$O(2)-M(1)-O(2)$	$173.9(4)$
$M(2)-O(1)$	$1.990(3) \times 2$	$O(2)-M(1)-O(3^{ii})$	$87.6(2)$
$M(2)-O(1)'$	$2.064(9) \times 2$	$O(3^{ii})-M(1)-O(3^{ii})$	$79.1(3)$
$M(2)-O(2)$	$2.085(7) \times 2$	$O(1)-M(2)-O(1^{ii})$	$91.6(3)$
Mean	2.046	$O(1)-M(2)-O(1')$	$175.7(7)$
		$O(1)-M(2)-O(2^{ii})$	$88.3(3)$
$M(3)-O(2)$	$1.964(7) \times 2$	$O(1^{ii})-M(2)-O(1^{ii})$	$82.0(5)$
$M(3)-O(3)$	$2.030(7) \times 2$	$O(1^{ii})-M(2)-O(2^{ii})$	$99.9(3)$
$M(3)-O(3)'$	$2.004(3) \times 2$	$O(1^{ii})-M(2)-O(2^{ii})$	$178.1(3)$
Mean	1.999	$O(2^{ii})-M(2)-O(2^{ii})$	$78.3(4)$
		$O(2^{ii})-M(3)-O(2^{ii})$	$84.1(4)$
$M(1)-M(2)$	$2.991(2)$	$O(2^{ii})-M(3)-O(3)$	$91.2(3)$
$M(1)-M(3)$	$3.149(2)$	$O(3)-M(3)-O(3)$	$176.8(5)$
$M(2)-M(3)$	$3.076(3)$	$O(3^{ii})-M(3)-O(2^{ii})$	$96.7(3)$
		$O(3^{ii})-M(3)-O(2^{ii})$	$179.2(3)$
		$O(3^{ii})-M(3)-O(3)$	$88.8(2)$
		$O(3^{ii})-M(3)-O(3^{ii})$	$82.5(4)$

Symmetry code: (i) $-x, -y, z$; (ii) $-y, x, -z$; (iii) $y, -x, -z$.

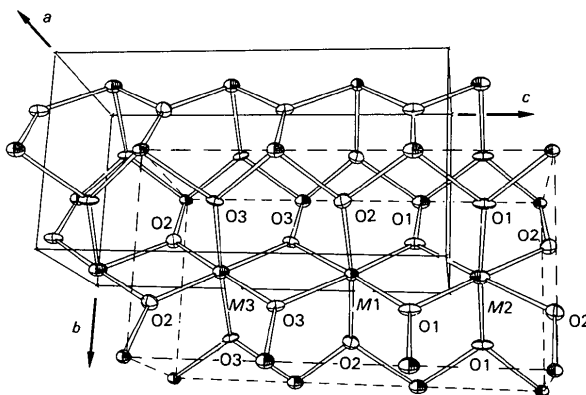


Fig. 1. An *ORTEP* (Johnson, 1976) drawing of $FeNb_2O_6$ down the a axis with 50% probability thermal ellipsoids.

The c axis of the present structure is three times longer than that of the simple tetragonal unit cell of rutile. The intensities of hkl reflections with $l = 3n$ are strong, while those with $h = 3n \pm 1$ are extremely weak indicating that the structure is a superstructure of the rutile structure. A superstructure having three unit cells of the rutile structure is referred to as the trirutile structure. The trirutile cell is indicated by the broken lines in Fig. 1. However, the normal trirutile structure requires an ordered arrangement of metal atoms. The scheme of cation distribution in the present structure is intermediate between disordered rutile-type and ordered trirutile-type. The occupancies of the Fe and Nb atoms in the $M(1)$ and $M(2)$ sites are nearly equal. The $M(3)$ site is mainly occupied by the Nb atom, while the Fe occupancies in the $M(1)$ and $M(2)$ sites are twice as large as that of the $M(3)$ site. This reflects on the metal-metal distances along the c axis (see Table 2): the $M(1)$ – $M(2)$ distance is shorter than $M(2)$ – $M(3)$ or $M(3)$ – $M(1)$. These observations indicate that a slight ordering of the metal atoms exists in the structure. In addition, the present crystal gave rather diffuse diffraction spots. Since the crystal was synthesized by the floating-zone method under conditions of high temperature >1823 K, rapid growth rate 5 mm h^{-1} , and rapid cooling, these synthetic conditions may disturb the ordering of the metal atoms. As a result, this substance has a structure intermediate between rutile and trirutile types.

Valence bond sums $\sum v$ were calculated using the parameters of Brown & Wu (1976) and are listed in Table 1. The valence sums for O(1), O(2), and O(3) are 1.99, 1.97, and 1.92, respectively, and are slightly smaller than 2.00 of the ideal valence for O^{2-} ions. The Mössbauer study showed a small existence of the

trivalent Fe atom in the present compound (Tokizaki & Sugitani, 1984). It is considered that vacancies occur in the cation site to balance the charge, though no estimation of vacancies was taken into account in the present study.

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Structure of a New Form of Rubidium Dihydrogenphosphate, RbH_2PO_4

BY M. T. AVERBUCH-POUCHOT AND A. DURIF

Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à l'USMG, 166X, 38042 Grenoble CEDEX, France

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Abstract. $M_r = 182.4$, monoclinic, $P2_1/a$, $a = 9.606$ (5), $b = 6.236$ (5), $c = 7.738$ (5) Å, $\beta = 109.07$ (5)°, $V = 438.1$ Å³, $Z = 4$, $D_x = 2.765$ Mg m⁻³, $\lambda(\text{Ag } K\alpha) = 0.5608$ Å, $\mu = 6.598$ mm⁻¹, $F(000) = 344$, $T = 293$ K, final $R = 0.032$ for 695 independent reflexions. This salt is closely related to

the monoclinic form of CsH_2PO_4 and its atomic arrangement may be considered as a superstructure of this salt, identical to the intermediate form of RbD_2PO_4 . The PO_4 tetrahedra are interconnected by H bridges [O...O distances 2.518 (11) and 2.518 (5) Å, and O–H...O angles 156 (10) and 171 (11)°].

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