101 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 13.9960P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
Extinction coefficient: 0.00037 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

I1—Nb3	2.8196 (12)	Nb1—Nb3	2.7801 (10)
I1—Nb1	2.8241 (9)	Nb2—S1	2.435 (2)
I1—Nb2	2.8382 (10)	Nb2—Nb3	2.7671 (10)
Nb1—S1	2.420 (2)	Nb3—S1	2.413 (2)
Nb1—Nb2	2.7759 (10)		
Nb3—I1—Nb1	59.02 (2)	Nb3—Nb2—Nb1	60.21 (2)
Nb3—I1—Nb2	58.56 (2)	Nb3—S1—Nb1	70.23 (5)
Nb1—I1—Nb2	58.71 (2)	Nb3—S1—Nb2	69.61 (5)
Nb2—Nb1—Nb3	59.74 (2)	Nb1—S1—Nb2	69.74 (6)

The crystal quality, initial cell parameters and symmetry information were determined from DeJong photographs taken at 298 K. This was useful because the crystals show a tendency towards twinning. The lattice metrics ($a/c = 2$ with $\cos\beta^* = 1/6$) provide a geometrical condition for partial merohedric twinning of index 3. This leads to coincidental reciprocal lattice points for $l = 3n$ (n = 0, 1, 2, ...). For the crystal structure analysis an untwinned specimen was selected. Intensity data were processed (Keller, 1981) and corrected for absorption (Sheldrick, 1994). The final refinement included anisotropic displacement parameters and an extinction parameter. The largest feature in a final difference electron-density map was 1.66 e Å^{-3} at a distance of 0.81 Å from I6.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4/*CAD*-6 (Keller, 1981). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SCHAKAL*92 (Keller, 1992).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1212). Services for accessing these data are described at the back of the journal.

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Fe_3W_3N: a Rietveld Refinement Using X-ray Powder Diffraction

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Abstract

A new ternary nitride, triiron tritungsten nitride, has been synthesized by the ammonolysis of a metal-organic precursor. The structure, found to be face-centered cubic ($Fd\bar{3}m$), was determined by powder X-ray diffraction and Rietveld refinement of the resulting diffraction pattern. The ideal structure of Fe_3W_3N is similar to the η-carbide structure exhibited by many ternary transition metal carbides.

Comment

A growing number of new ternary transition metal–transition metal nitride compounds have been synthesized over the past several years. Thus far, the crystal structures of these compounds fall predominantly into one of two categories: (*a*) layered hexagonal or rhombohedral structures such as $FeWN_2$ and $MnMoN_2$ (Bem, Lampe-Önnerud, Olsen & zur Loye, 1996), $CrWN_2$ (Weil & Kumta, 1997), $CoWN_2$ and $NiWN_2$ (Herle, Vasanthacharya, Hegde & Gopalakrishnan, 1995), and $MnWN_2$ (Bem, Houmes & zur Loye, 1993); and (*b*) cubic, η-carbide-like structures such as Fe_3Mo_3N and Co_3Mo_3N (Houmes, Bem & zur Loye, 1993). We have recently synthesized a new intermetallic tungsten nitride with the η-carbide structure, Fe_3W_3N, which has been characterized by X-ray diffraction and Rietveld analysis (Rietveld, 1969). The results of this analysis are reported in this paper.

The η-carbide structure has been previously described in detail by Westgren (1933) for the stoichiometry $T^{\rm I}{}_3T^{\rm II}{}_3$C (where $T^{\rm I}$ and $T^{\rm II}$ represent two different transition metals) and by Kislyakova (1943) for the stoichiometry $T^{\rm I}{}_2T^{\rm II}{}_4$C. These structures have been observed for carbides, such as Fe_3W_3C (Westgren & Phragmen, 1928) and Co_6Mo_6C (Fraker & Stadelmaier, 1969), and for nitrides and oxides, such as Fe_2Ta_4N and Ni_2Nb_4O (Holleck & Thummler, 1967). Both structural descriptions are derived from that for the Ti_2Ni intermetallic structure (Yurko, Barton & Parr, 1959) with the interstices at the 16*c* Wyckoff positions filled by C atoms. As shown in Fig. 1, separate clusters of $T^{\rm II}$ and $T^{\rm I}$ atoms in the Westgren $T^{\rm I}{}_3T^{\rm II}{}_3$C structure essentially define two interpenetrating diamond cubic lattices. The T^{II} atoms cluster in regular octahedra on the first diamond cubic lattice, while the T^{I} atoms can be found in groups of four as tetrahedra on a second diamond lattice which interpenetrates the first through a (1/2, 1/2, 1/2) unit-cell translation. Sixteen additional T^{I} atoms are tetrahedrally coordinated around the T^{I} tetrahedra and sixteen C atoms surround the T^{II} octahedra in tetrahedral coordination. The C atoms are located centrally between any two T^{II} octahedra, producing a sixfold trigonal antiprismatic, or a distorted octahedral, environment of T^{II} atoms around each C atom.

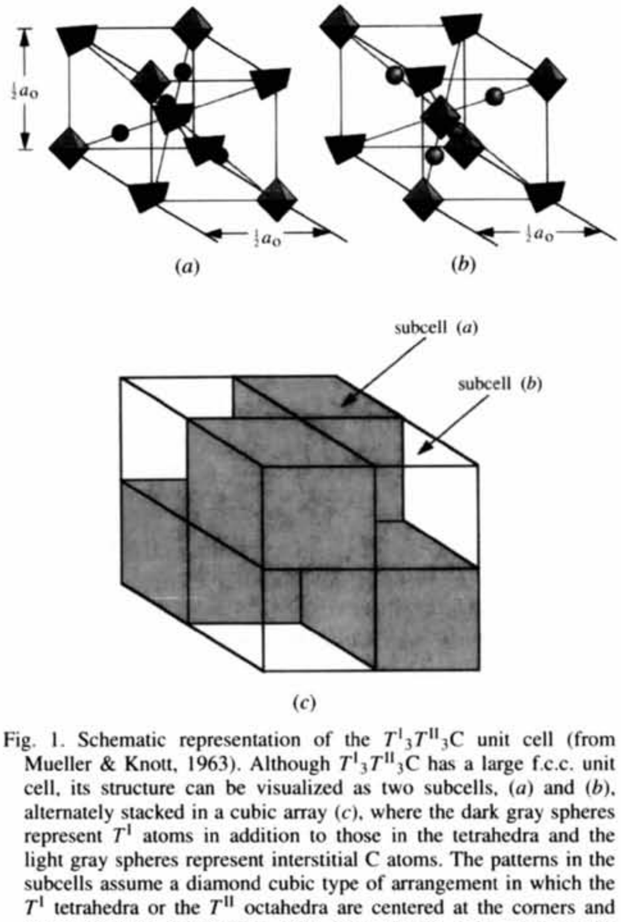

Fig. 1. Schematic representation of the $T^{I}{}_3T^{II}{}_3C$ unit cell (from Mueller & Knott, 1963). Although $T^{I}{}_3T^{II}{}_3C$ has a large f.c.c. unit cell, its structure can be visualized as two subcells, (*a*) and (*b*), alternately stacked in a cubic array (*c*), where the dark gray spheres represent T^{I} atoms in addition to those in the tetrahedra and the light gray spheres represent interstitial C atoms. The patterns in the subcells assume a diamond cubic type of arrangement in which the T^{I} tetrahedra or the T^{II} octahedra are centered at the corners and center of these small cubic cells. Note that in order to show the internal arrangement of the subcells, the tetrahedra and octahedra in this figure have been collapsed about their centers.

Chemical analysis results (Galbraith Laboratories, Knoxville, Tennessee) for two samples of the nitride verify that the stoichiometry of the compound is Fe_3W_3N (Table 1). Expected impurities in this material (*i.e.* O, C, and Cl) are all relatively low in concentration (below 1200 p.p.m.). The systematic absences obtained by indexing and analysis of the powder diffraction pattern showed that this material has the space group $Fd\bar{3}m$, the same as Fe_3W_3C. Therefore, the atomic coordinates of Fe_3W_3C were used as the starting model for Rietveld refinement. The refined atomic parameters for Fe_3W_3N are given in Table 2. A comparison of the experimental X-ray diffraction profile with that obtained by refinement is shown in Fig. 2, along with the calculated residuals.

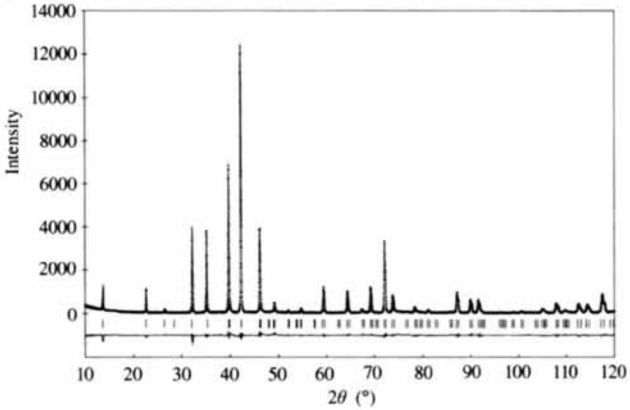

Fig. 2. The observed (crosses) and calculated (solid) X-ray diffraction profiles for Fe_3W_3N. Tick marks below the diffractogram represent the allowed Bragg reflections. The difference profile is located at the bottom of the figure.

An alternative to the Westgren method of visualizing the η-carbide structure is to focus on the interstitial sites of the structure, or the 16*c* and 16*d* Wyckoff positions. As shown in Fig. 1(*b*), each non-metallic atom, in this case N, is coordinated by six W atoms, forming a slightly distorted NW_6 octahedron. Neighboring NW_6 octahedra share common vertices, collectively forming a three-dimensional lattice of corner-sharing octahedra similar to that seen in the pyrochlore structure. The Fe2 atoms at the 16*d* Wyckoff positions are also located at interstitial sites, this time between neighboring Fe1 tetrahedral clusters. As seen in Fig. 1(*a*), each Fe1 tetrahedral cluster is coordinated by four Fe2 atoms, each atom centrally located above and capping one of the four faces of the tetrahedron. The new polyhedron that is generated from this cluster of eight atoms is a stella quadrangula (Nyman, Andersson, Hyde & O'Keeffe, 1978). The Fe_8 stellae quadrangulae also share corners, at the 16*d* Fe positions, on a structural lattice separate from that formed by the NW_6 octahedra. Because these two lattices interpenetrate, each occupying the interstices of the other, their unit-cell edges are identical in size. Selected bond distances and angles are given in Table 3. The bond distances are in good agreement with their respective counterparts reported for Fe_3W_3C (Pollock & Stadelmaier, 1970).

Experimental

The Fe_3W_3N powder was prepared by the ammonolysis of a chelated metal-organic precursor, using an approach similar to that previously described by Weil & Kumta (1996). Essentially, anhydrous ferric chloride and tungsten hexachloride were dissolved in equivalent molar amounts in anhydrous acetonitrile. The two metal species were then simultaneously complexed with triethylamine, forming a viscous polymeric liquid which was separated from the acetonitrile phase and dried under vacuum to yield a solid precursor. This precursor was heated ($3\,K\,min^{-1}$) in ammonia to 1223 K for 4 h and furnace cooled, by turning the furnace off at the soak temperature, to form the single-phase ternary nitride. In preparation for the diffraction study, the nitride product was slurried in acetone and ground with an agate mortar and pestle. Two small samples of the product were sent to Galbraith Laboratories for chemical analysis, where a wet chemical technique to determine the concentration of the metal species, combustion analyses to evaluate the nitrogen, carbon, and oxygen contents, and ion chromatography to determine the chlorine level were employed.

Crystal data

Fe_3W_3N
$M_r = 733.11$
Cubic
$Fd\bar{3}m$ (origin at $\bar{4}3m$)
$a = 11.1104\,(2)$ Å
$V = 1371.48\,(6)$ Å^3
$Z = 16$
$D_x = 14.201$ Mg m^{-3}
$D_m = 14.033$ Mg m^{-3}
D_m measured by helium pycnometry

Cu $K\alpha_1$, $K\alpha_2$ radiation
$\lambda = 1.540562, 1.544390$ Å
Cell parameters from 48 reflections
$\theta = 10–120°$
$\mu = 281.15$ mm^{-1}
$T = 293$ K
Powder
Black

Data collection

Rigaku θ–θ diffractometer equipped with a Cu tube source, a diffracted-beam equatorially mounted (0002)-oriented graphite monochromator and an NaI scintillation detector
Specimen mounting: 25 × 25 × 1 mm deep brass sample holder

Specimen mounted in reflection mode
$2\theta_{min} = 10.00$, $2\theta_{max} = 120.00°$
Increment in $2\theta = 0.02°$
5500 measured data points

Refinement

$R_p = 0.072$
$R_{wp} = 0.102$
$R_{exp} = 0.073$
$S = 1.3907$
48 reflections
23 parameters

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.770$ e Å^{-3}
$\Delta\rho_{min} = -1.008$ e Å^{-3}
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Chemical analysis results*

	Sample 1	Sample 2	Theoretical value
Fe (at.%)	42.21	42.86	42.86
W (at.%)	43.56	43.02	42.86
N (at.%)	14.11	13.99	14.28
C (p.p.m.)	1117	1095	
O (p.p.m.)	323	547	
Cl (p.p.m.)	124	110	

Table 2. *Fractional atomic coordinates and isotropic displacement parameters (Å^2)*

	Wyckoff position	x	y	z	B_{iso}
W	48*f*	0.1966 (9)	0	0	0.51 (2)
Fe1	32*e*	0.4185 (5)	0.4185 (5)	0.4185 (5)	1.58 (6)
Fe2	16*d*	5/8	5/8	5/8	0.06 (2)
N	16*c*	1/8	1/8	1/8	0.01 (9)

Table 3. *Selected geometric parameters (Å, °)*

Fe1—Fe1	2.559 (7)	×3	Fe2—W	2.789 (7)	×6
Fe1—W	2.777 (4)	×3	N—Fe2	3.928 (2)	×12
Fe1—W	2.666 (7)	×3	N—N	3.928 (2)	×12
Fe1—N	3.332 (5)	×3	N—W	2.119 (5)	×6
Fe2—Fe2	3.928 (1)	×12	W—W	2.901 (2)	×4
Fe2—Fe1	2.393 (7)	×6	W—W	3.090 (5)	×4
W—N—W	86.3 (4)		W—Fe1—W	70.8 (3)	
W—N—W	93.6 (6)		W—Fe1—W	61.8 (2)	
W—N—W	180		Fe2—Fe1—Fe2	69.6 (7)	
N—W—N	135.7 (9)		Fe1—Fe2—Fe1	64.5 (5)	
W—Fe2—W	62.6 (7)		Fe1—Fe1—Fe1	60	

Data collection and reduction were performed using *KaleidaGraph* software (Abelbeck Software, 1994). Cell refinement, structure solution, and structure refinement were conducted using *RIETAN*-94 (Izumi, 1993; Kim & Izumi, 1994). The profile shape was represented by a modified pseudo-Voigt function (Thompson, Cox & Hastings, 1987; Young, 1993), with profile asymmetry introduced by employing a multi-term Simpson's rule integration (Howard, 1982). In addition to profile, lattice, and structure parameters, the zero-point shift, nine background parameters, and the scale factor were refined without correction for preferred orientation. Atomic displacements were assumed to be isotropic. Graphics and geometric calculations: *CaRIne* software (Boudias & Monceau, 1989).

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Cerous Silver Nitrate, Ag$_6$Ce(NO$_3$)$_9$

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Abstract

The title compound was synthesized from a nitric acid solution of silver and cerium(III) nitrates at 333 K. The structure is built from irregular icosahedral $[Ce(NO_3)_6]^{3-}$ anions and Ag^+ cations. The O atoms around one of the two independent Ag atoms form a distorted bicapped trigonal prism, while a non-definite polyhedron is observed around the other. Two types of nitrate groups ensure the continuity and give a three-dimensional aspect to the crystal structure.

Comment

The present structure investigation was performed as part of a detailed study of the thermal behaviour of precursors of cerium oxide which have a high surface area, based on Ce$^{\text{III}}$ and Ce$^{\text{IV}}$ nitrates. Among these compounds, the cerium(III) precursors $M^{\text{I}}_2\text{Ce}^{\text{III}}(\text{NO}_3)_5.4\text{H}_2\text{O}$ with M = Rb (Audebrand, Auffrédic, Louër, Guillou & Louër, 1996) and NH$_4$ (Audebrand, Auffrédic & Louër, 1997*a*) have been thoroughly analysed. The family has been extended recently to include a mixed Ce$^{\text{III}}$ and Ag precursor, $Ag_2Ce(H_2O)(NO_3)_5$ (Audebrand, Auffrédic & Louër, 1997*b*). In the course of this study, a new phase was observed and identified from its powder diffraction pattern. In order to determine its chemical formula, single crystals were prepared successfully from a nitric acid solution of silver and cerium(III). Although the crystals were very unstable under ambient conditions, the structure determination could be performed. The solution reported here demonstrates that this new compound is the hexasilver cerium(III) nitrate $Ag_6Ce(NO_3)_9$, which is not isostructural with the chemically related ammonium neodymium phase (Manek & Meyer, 1993).

The structure of the title compound (Fig. 1) consists of independent $[Ce(NO_3)_6]^{3-}$ anions in the form of irregular icosahedra, in which Ce atoms are linked to six nitrate groups, as reported previously for the oxonium cerium(III) nitrate hydrate (Fig. 3 in Guillou, Auffrédic, Louër & Louër, 1993). The mean Ce—O distance (2.628 Å) is in agreement with the value (2.649 Å) calculated by the bond-valence method (Brown, 1981, 1996) for Ce$^{\text{III}}$ bonded to 12 O atoms. The $[Ce(NO_3)_6]^{3-}$ anions, centred at the origin of the cell in the 6(*b*) position of the $R\bar{3}c$ space group, fall into lines along the *c* axis with a periodicity of half the axis,

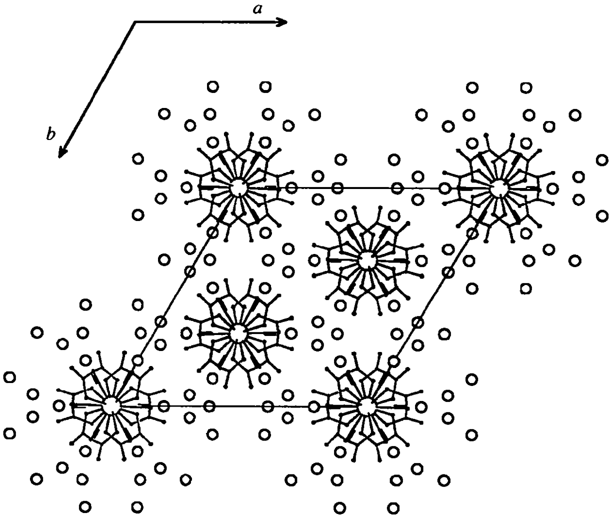

Fig. 1. Projection of the structure of $Ag_6Ce(NO_3)_9$ along the *c* axis. Large and medium circles represent Ce and Ag atoms, respectively. For clarity, nitrate groups around Ag atoms are omitted.

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