$Zr_{6.45}Nb_{4.55}P_4$, a New Mixed-Transition-Metal Phosphide Structure

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A new structure which is similar to that of many known binary early-transition-metal phosphides, sulfides, and selenides has been found in the ternary Zr–Nb–P system. The compound $Zr_{6.45}Nb_{4.55}P_4$ was synthesized using high-temperature techniques and characterized through X-ray single-crystal experiments. The space group is *Immm* with lattice parameters a = 15.917 (1) Å, b = 9.5684 (9) Å, and c = 3.5892 (3) Å. Bond order calculations revealed the approximate metal site occupancies and anomalous scattering allowed refinement of the metal site occupancies.

Introduction

A number of early-transition-metal-rich binary phosphides, sulfides, and selenides including Ti_2S,[2] Zr_2S,[3] Ti_2Se,[4] Zr_2Se,[5] $Nb_{21}S_8$,[6] $Nb_{14}S_5$,[7] Ti_8S_3,[8] Ta_2P,[9] Hf_2P,[10] Nb_8P_5,[11] Nb_7P_4,[12] Nb_5P_3,[13] Zr_2P,[14] and others have been found to form in structures which share the following characteristics: (1) a short axis, 3.3–3.6 Å (dependent upon the specific metal constituents) perpendicular to mirror planes which contain all atoms; (2) capped trigonal prismatic coordination of the nonmetals; (3) metal coordinations related to bcc. Two ternary Nb–Ta sulfides ($M_{11}S_4$ and $M_{12}S_4$) were recently[15,16] found to form in structures of this general type with occupancy of the metal atom positions by long-range averages of Nb and Ta. Since these two structures are unknown among the binaries, it was concluded[17] that long-range averages of transition metals can have a different structural chemistry than do the corresponding binaries. In an effort to further explore this concept, the ternary phosphide, $Zr_{6.45}Nb_{4.55}P_4$, reported here was synthesized, and its structure was determined by single-crystal X-ray diffraction.

Experimental Section

A sample of nominal composition $Zr_9Nb_4P_4$ was prepared from Zr and NbP (prereacted for 1 month while slowly increasing the temperature to 800 °C) and arc-melted (10 V, 75 A) for 45 s under an Ar atmosphere on a water-cooled copper hearth. The pellet was subsequently inverted and arc-melted twice more to promote homogenization. The elements were obtained from Alfa with the following specifications: Zr (−60 +20 mesh) 99.9% pure, Nb (−60 mesh) (0.1–1% Ta) 99.8% pure, and P (−100 mesh), red amorphous 99% pure.

Table I. Crystal Data for $Zr_{6.45}Nb_{4.55}P_4$

space group	*Immm* (No. 71)
a, Å	15.917(1)
b, Å	9.5684(9)
c, Å	3.5892(3)
V, Å^3	546.62(13)
Z	2
d_{calc}, g/cm^3	6.896
μ(Mo Kα), cm^{-1}	107.02
temp, °C	23
octants measured	hkl, $-hkl$
no. of reflns measured	1183
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	610, 536
no. parameters refined	31
abs correction	ψ scans
ratio of trans. factors, max/min	1.20
secondary ext coeff (10^{-7})	4.5(4)
R,[a] R_w,[b] GOF[c]	0.019, 0.027, 1.307
largest peak, e/Å^3	1.847
largest negative peak, e/Å^3	−1.586

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] GOF $= \Sigma((|F_o| - |F_c|)/\sigma_i)/(N_{obs} - N_{parameters})$.

Needlelike crystals grew from the surface of a partially melted sample of $Zr_9Nb_4P_4$ when it was inductively annealed at approximately 1700 °C for 3 h with a residual pressure of $<1 \times 10^{-7}$ Torr. A single crystal of dimensions 0.51 × 0.11 × 0.08 mm^3 was selected and aligned along the needle direction (short axis) on a Weissenberg camera. Rotation and zero- and first-layer Weissenberg photographs showed the lattice to be body-centered orthorhombic with cell dimensions of approximately a = 3.6 Å, b = 9.7 Å, and c = 16 Å. An intensity data set was collected on a Rigaku AFC6 rotating anode diffractometer with monochromated Mo Kα radiation using the ω–2θ scan technique out to 60° in 2θ. The observed intensities were corrected for Lorentz polarization and absorption effects and final least-squares lattice parameters were calculated from X-ray powder patterns of the bulk sample obtained with a vacuum Guinier camera FR552 (Enraf-Nonius, Delft, The Netherlands) using Cu Kα_1 radiation and a NBS silicon internal standard. The crystal data for this new structure was given in Table I.

The space group *Immm* was selected for this crystal, and the structure was easily found using direct methods for the initial model and refined with anisotropic thermal parameters to the

(1) The Ames Laboratory is operated for the Department of Energy by Iowa State University under Contract W-7405-Eng-82. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences Division.

(2) Owens, J. P.; Conard, B. R.; Franzen, H. F. *Acta Crystallogr.* **1967**, *23*, 77.
(3) Conard, B. R.; Franzen, H. F. *High Temp. Sci.* **1971**, *3*, 49.
(4) Franzen, H. F.; Smeggil, J. G.; Conard, B. R. *Mater. Res. Bull.* **1967**, *2*, 1087.
(5) Franzen, H. F.; Norrby, L. J. *Acta Crystallogr.* **1968**, *B24*, 601.
(6) Franzen, H. F.; Beineke, T. A.; Conard, B. R. *Acta Crystallogr.* **1968**, *B24*, 412.
(7) Chen, H.-Y.; Tuenge, R. T.; Franzen, H. F. *Inorg. Chem.* **1973**, *12*, 552.
(8) Owens, J. P.; Conard, B. R.; Franzen, H. F. *Acta Crystallogr.* **1974**, *B30*, 427.
(9) Nylund, A. *Acta Chem. Scand.* **1966**, *20*, 2393.
(10) Lundström, T.; Ersson, N.-O. *Acta Chem. Scand.* **1968**, *22*, 1801.
(11) Anugul, S.; Pontchour, C.; Rundqvist, S. *Acta Chem. Scand.* **1963**, *27*, 26.
(12) Rundqvist, S. *Acta Chem. Scand.* **1966**, *20*, 2427.
(13) Hassler, E. *Acta Chem. Scand.* **1971**, *25*, 129.
(14) Ahlzén, P.-J.; Rundqvist, S. *Z. Kristallogr.* **1989**, *189*, 117.
(15) Yao, X.; Franzen, H. F. *J. Solid State. Chem.* **1990**, *86*, 88.
(16) Yao, X.; Franzen, H. F. *Z. Anorg. Allg. Chem.* **1991**, *598/599*, 353.
(17) Yao, X.; Marking, G.; Franzen, H. F. *Ber Bunsen-Ges. Phys. Chem.* **1992**, *96*, 1552.

0897-4756/93/2805-0678$04.00/0

Table II. Positional Parameters and Occupancies for $Zr_{6.45}Nb_{4.55}P_4$

atom	x	y	z	B_{equiv}	%Zr	%Nb
M1	0.29200(2)	0.16228(4)	0	0.49(1)		100
M2	0	0	0	0.48(3)	58(8)	42
M3	0.90161(4)	1/2	0	0.65(2)	94(6)	6
M4	0.34113(4)	1/2	0	0.49(2)	100	
M5	0	0.72960(6)	0	0.56(2)	100	
P	0.12147(7)	0.2053(1)	0	0.50(3)		

values $R = 0.025$, $R_w = 0.045$ using TEXSAN[18] software. Initially, M2 was refined as Nb and M1, M3, M4, and M5 were refined as Zr, and it was anticipated that Zr and Nb occupancies would be unresolvable from X-radiation since their electron densities are nearly the same. The refined thermal parameters were well-behaved and offered no information which appeared to be useful in determining the mixing of Zr and Nb on particular sites. To determine the correct placement of the two metals in the structure, a bond order calculation were performed. This calculation was consistent with M1 occupation by Nb (as discussed later). With the occupancies M2 = M3 = M4 = M5 = Zr and M1 = Nb, a dramatic improvement in the values to $R = 0.020$, $R_w = 0.028$ was found.

Both Zr and Nb have absorption edges near the wavelength of Mo Kα radiation and anomalous scattering was important in this diffraction experiment. The atomic scattering factors drop off rapidly with $(\sin\theta)/\lambda$ but the anomalous scattering corrections remain approximately constant, with the result that the difference between Nb and Zr scattering becomes increasingly resolvable as 2θ increases.

The metal site occupancies were refined for all metal sites, indicating the M1 = Nb, M2 and M3 have mixed occupancy, and M4 = M5 = Zr, and the resulting decrease to the values $R = 0.019$, $R_w = 0.027$ was found to be significant to greater than 99.5% probability using the Hamilton R factor test. The atomic positions, metal occupancies, and equivalent B values are listed in Table II. The anisotropic thermal parameters are all positive definite and well behaved with ratios of the maximum-to-minimum mean-square amplitudes of thermal vibration <2.3 for the metals and <1.2 for the phosphorus. Comparison of the calculated to observed structure factors show a large difference for the 0,0,2 reflection ($F_c/F_o \approx 1.18$) and a lesser difference for the 0,0,4 reflection ($F_c/F_o \approx 1.06$). All other reflections have $F_c/F_o \approx 1$.

These two reflections were removed from the least-squares refinement in an attempt to improve the structural model which resulted in a decrease of R and R_w to 0.016 and 0.024 respectively. All refined occupancies, positional parameters, and B_{equiv} were invariant to within their esd's. The largest change for any one U_{ij} was less than 3%. The only refined parameter that showed a significant difference was the secondary extinction coefficient which decreased from $4.5(4) \times 10^{-7}$ to $2.5(4) \times 10^{-7}$.

The authors suggest that this indicates the presence of an anisotropic secondary extinction effect which is strongest along the direction of the short c axis and which cannot be modeled correctly with commercially available crystallographic software. The structural model shows negligible dependence upon the secondary extinction so that the results are presented here for a refinement based upon all the collected data.

Discussion

As mentioned in the Introduction, this new ternary phosphide structure has characteristics in common with many known structures of binary metal-rich sulfides, selenides, and phosphides. Examination of this new structure as depicted in Figure 1 reveals known coordinations[19] for all M and P sites. The metal positions, M1 to M5, are labeled according to the convention that the

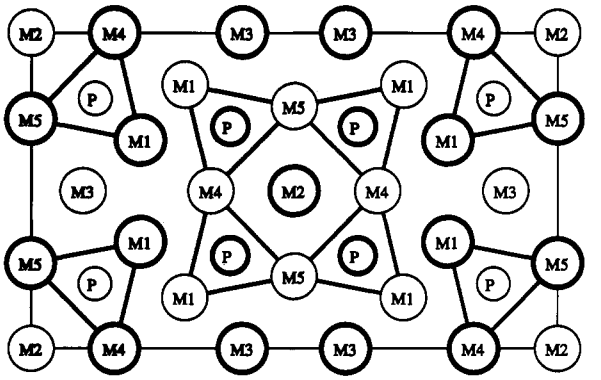

Figure 1. Projection down short c axis of unit cell for $Zr_{6.45}Nb_{4.55}P_4$ showing tricapped trigonal prismatic coordination of phosphorus. Bold circles represent atoms at $z = 1/2$, all other atoms are on the $z = 0$ plane.

amount of Nb on the site decreases (and the amount of Zr increases) as the numbering increases.

The phosphorus coordination is a slightly distorted vertical trigonal prism of metal atoms tricapped with metal atoms. M1, M2, and M3 coordinations can be derived from bcc. M1 centers a cubelike unit of metal atoms with one edge substituted by phosphorus and capped by 1 P and 3 M atoms horizontally and two more M1 atoms vertically, M2 centers a distorted cube of metal atoms capped with four P atoms in the horizontal a–b plane and with two M2 atoms vertically, and M3 centers another cubelike unit of all metal atoms capped by 2 P and 2 M atoms horizontally and two M3 atoms vertically.

Both M4 and M5 center pentagonal prisms of metal atoms with two nonadjacent edges substituted by phosphorus. The pentagonal prism centered by M4 is capped by 4 M atoms horizontally and two M4 atoms vertically while the pentagonal prism centered by M5 is capped by 5 M atoms in the horizontal plane and two M5 atoms vertically. The M3–M4 distance is too large to consider M3 as capping the M4 centered pentagonal prism. Additionally, two of the bcc-like units centered by M1 share a face, as do two of the bcc-like units centered by M3, and significant lengthening of the M–M distances perpendicular to the short axis along these shared faces is observed.

One can also describe this structure through packing of one type of large cluster unit composed of 25 metal and 4 phosphorus atoms. This cluster has a bcc metal fragment centered by M2 and capped by four P which center four tricapped vertical trigonal prisms, each of which share one face with the central bcc fragment. By itself, this cluster has nearly tetragonal symmetry. Directly along the b axial direction four M3 capping atoms of the trigonal prisms in one cluster are shared capping atoms of the adjacent clusters. Along the body diagonals, the cluster units are condensed so that four M1 capping atoms of trigonal prisms in one cluster are part of the trigonal prisms in the next cluster and vice versa. All clusters are directly stacked one upon another along the short axial c direction. The condensation of this cluster can further be viewed as cluster slabs in the bc plane stacked in a staggered shear structure along the a direction.

Bond-order calculations, making use of the Pauling bond order equation,[20] $D(n) = D(1) - 0.6 \log n$, were carried out

(18) TEXSAN: Single Crystal Structure Analysis Software, Version 5.0, Molecular Structure Corporation, The Woodlands, TX, 1989.
(19) Franzen, H. F. *Prog. Solid State. Chem.* **1978**, *12*, 1
(20) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1948.

Table III. Total Bond Orders Calculated for Different $M_{11}P_4$ Models

atom	A	B	C	D
M1	8.69(4.0)	4.82(5.0)	4.79(5.0)	6.39(4.41)
M2	5.49(4.0)	5.49(4.0)	4.56(4.42)	4.10(4.41)
M3	5.85(4.0)	4.63(4.0)	4.50(4.06)	4.19(4.41)
M4	5.13(4.0)	4.50(4.0)	4.34(4.0)	3.88(4.41)
M5	4.73(4.0)	4.61(4.0)	4.45(4.0)	3.61(4.41)

Models (Expected Valence)

A: M1 = M2 = M3 = M4 = M5 = Zr
B: M1 = Nb M2 = M3 = M4 = M5 = Zr
C: refined occupancies for $Zr_{6.45}Nb_{4.55}P_4$
M1 = Nb M2 = (42% Nb/58% Zr) M3 = (6% Nb/94% Zr)
M4 = M5 = Zr
D: stoichiometric random occupancies
M1 = M2 = M3 = M4 = M5 = (41% Nb/59% Zr)

on the refined atomic positions of this structure and helped to determine the metal site occupancies reported here. Initially, all metal sites were assigned the metallic radius of Zr. The total bond order for the M1 site was drastically larger than for any other metal site, and this was taken to be an indication that M1 = Nb since Nb has an additional d electron relative to Zr and is therefore expected to participate in more bonding interactions than Zr. Nb is also smaller than Zr so that calculating the total bond order for a Nb site while using the metallic radius for Zr will yield an artificially large result. When it became apparent that anomalous scattering allowed differentiation between Zr and Nb, all metal site occupancies were refined with the constraint that greater than 100% or less than 0% occupancies were not allowed.

The results from bond-order calculations for different metal site occupancy models are listed in Table III. The following assumptions were made: (1) the total bond order should scale like the expected valence of a particular site, (2) the expected valence of Zr is four and that of Nb is five, (3) the expected valence of a mixed metal site will be linearly dependent upon the fractional occupancy, and (4) the radius for a particular site will be linearly dependent upon the fractional occupancy of that site relative to the metallic radii,[20] r_{Zr} = 1.454 Å and r_{Nb} = 1.342 Å. It is clear that the refined model gives the best agreement between observed and calculated values.

Calculated interatomic distances for this structure are presented in Table IV. The shortest M–M distances fall in the order M1–M1 < M1–M3 < M2–M4 and the shortest M–P distances are M1–P < M5–P ~ M4–P ~ M2–P < M3–P. These are consistent with the assignments M1 = Nb and the other metal sites are mostly Zr given the metallic radii for Nb and Zr listed above.

X-ray powder patterns of the annealed bulk $Zr_9Nb_4P_4$ sample show that only two phases are present, the new $Zr_{6.45}Nb_{4.55}P_4$ compound and Zr metal. This phase information along with the substantial loss of sample, presumed to be mostly P, upon arc-melting makes the refined stoichiometry reasonable. A new sample of composition $Zr_{6.5}Nb_{4.5}P_{4.5}$ was arc-melted and annealed. Excess phosphorus was included in this sample to compensate for the presumed loss of P upon arc-melting. Guinier film techniques showed that the $(Zr,Nb)_{11}P_4$ phase reported here was the major phase.

Table IV. Interatomic Distances <4.0 Å for $Zr_{6.45}Nb_{4.55}P_4$

M1–P	2.5928(8)	×2	M4–P	2.7267(8)	×4
P	2.745(1)	×1	M4–M2	3.1008(5)	×2
M1–M1	2.7975(6)	×2	M4–M1	3.1814(5)	×4
M1–M3	2.9455(5)	×2	M4–M1	3.3247(5)	×2
M1–M1	3.1055(8)	×1	M4–M4	3.5892(3)	×2
M1–M4	3.1814(5)	×2	M4–M5	3.6178(6)	×2
M1–M4	3.3247(5)	×1	M4–M3	3.8637(9)	×1
M1–M5	3.3729(4)	×1	M5–P	2.7104(8)	×4
M1–M1	3.5892(3)	×2	M5–M2	3.1487(5)	×2
M2–P	2.756(1)	×4	M5–M3	3.2403(5)	×4
M2–M4	3.1008(5)	×4	M5–M1	3.3729(4)	×2
M2–M5	3.1487(5)	×4	M5–M5	3.5892(3)	×2
M2–M2	3.5892(3)	×2	M5–M4	3.6178(6)	×2
M3–P	2.843(1)	×2	P–M1	2.5928(8)	×2
M3–M1	2.9455(5)	×4	P–M5	2.7104(8)	×2
M3–M3	3.132(1)	×1	P–M4	2.7267(8)	×2
M3–M5	3.2403(5)	×4	P–M1	2.745(1)	×1
M3–M3	3.5892(3)	×2	P–M2	2.756(1)	×1
M3–M4	3.8637(9)	×1	P–M3	2.843(1)	×1
			P–P	3.5892(3)	×2
			P–P	3.867(2)	×1
			P–P	3.929(2)	×1

Guinier X-ray powder pattern phase analysis was carried out on annealed samples of $M_{11}P_4$ with metal stoichiometries ranging from 58% Zr to 69% Zr. A phase width for this new structure is suggested by the fact that in all cases, this is the major phase and the unit cell volume calculated from least squares lattice parameters increases from 538.92(1) Å^3 for the 58% Zr sample to 548.59(3) Å^3 for the 69% Zr sample. The refined stoichiometry $Zr_{6.45}Nb_{4.55}P_4$ appears to be on the Nb rich side of the phase width as there is a substantial amount of the M_2P phase[21] present in the 58% Zr sample. Furthermore, this amount decreases as the Zr percentage is increased. EDAX measurements were attempted, but the results were inconclusive because of the variability in the Zr/Nb ratio and the heterogeneity of the samples.

An unidentified minor phase was also present in several of the powder patterns and it seems possible that by varying the metal to metal and metal to phosphorus ratios in the Zr–Nb–P system one might find new structures. It also seems probable that other new ternary transition metal-rich phosphides remain to be synthesized in a variety of systems.

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Supplementary Material Available: Listing of and anisotropic thermal parameters (1 page); listing of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

(21) Marking, G. A.; Franzen, H. F., unpublished research.