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Preparation of a New Tungsten(V) Phosphate and Its Polymorph

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Under reducing conditions, $WOPO_4$ crystallizes with a monoclinic cell of $a = 11.172(8)$, $b = 5.217(1)$, $c = 6.543(2)$ Å, and $\beta = 90.34(4)°$. It is the second member of the monophosphate tungsten bronzes, $(PO_2)_4(WO_3)_{2m}$. A tetragonal form of this compound was prepared at 900°C and 6 GPa using the monoclinic form as a starting material; lattice constants are $a = 6.250(1)$ and $c = 4.066(1)$ Å. The volume reduction on transformation is 16.7%. Both forms of $WOPO_4$ are paramagnetic in the temperature range 80 to 500 K, having effective magnetic moments of 1.6 μ_B for the monoclinic form and 1.5 μ_B for the tetragonal form. Electric resistivity of the monoclinic form measured on pressed pellet was 0.11 Ω m at room temperature with an activation energy of 8.6×10^{-2} eV, while that of the tetragonal form was $>3 \times 10^3$ Ω m.

Introduction

Two allotropic forms are known for $MOPO_4$ phosphates (M = Nb and Ta) (*1*, *2*). In $NbOPO_4$, the α form is a tetragonal phase stable at low temperature (*3*) and the β form is a monoclinic phase prepared at high temperature. The phase transformation from the monoclinic to tetragonal phase was observed under high pressure for $TaOPO_4$. In addition to this type of transformation, $VOPO_4$ and $VOSO_4$ show another series of polymorphs; the α form is tetragonal and the β form is orthorhombic (*4*, *5*). The tetragonal form of $VOPO_4$ was reported to have a structure similar to α-$NbOPO_4$, but differs in the disordered arrangement of oxygen atoms (*6*). The transformation in $NbOPO_4$ is accompanied by a large volume change (>10%) which is considerably greater than that observed for $VOPO_4$ and $VOSO_4$. The difference in the structures of the monoclinic and tetragonal forms is expected to be significant. The structure of the monoclinic form was proposed by Chahboun *et al.* (*7*) for β-$TaOPO_4$ from its powder data and high-resolution electron microscopic data and was confirmed by Leclaire *et al.* (*8*) using a single crystal of β-$NbOPO_4$. They described the structure as built up from MO_6 octahedral slabs linked with PO_4 tetrahedra and having pentagonal tunnels, indicating rather an

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open structure when compared with the α form.

$MoOPO_4$ has been observed only in the tetragonal $NbOPO_4$ form (*9*). Tungsten(V) phosphates analogous to any of the forms mentioned above have not been prepared previously. During the course of preparation of phosphates with transition metals in low valence states (*10–12*), we found that the monoclinic and tetragonal forms of $WOPO_4$ could be synthesized under reducing conditions. Here, we report the preparation of $WOPO_4$ and its allotropic change.

Experimental

Preparation was carried out in two steps: preparation of WOP_2O_7 and reaction of this compound with metallic tungsten. Powders of WO_3 (99.9%) and $(NH_4)_2HPO_4$ were used for synthesis of WOP_2O_7 as described elsewhere (*13*). The well-mixed WOP_2O_7 and metallic tungsten (99.99%) powders, in the molar ratio of 2 : 1, were sealed in an evacuated silica tube. The ampoule was heated in the temperature range 900 to 1200°C. The crystals were washed with acid solution and distilled water.

High-pressure synthesis was carried out using a cubic anvil-type apparatus. The starting material, a powder of the low-pressure form, was heated at 900°C and 6 GPa for 1 hr in a platinum container then quenched to room temperature. The color of the powder prepared was reddish black.

The lattice constants of products were determined by a least-squares refinement of powder X-ray diffraction data measured with Ni-filtered Cu*Kα* radiation using silicon as an internal standard. Since β of the low-pressure form is close to 90°, a pseudo-orthorhombic cell is obtained from powder diffraction data. The true monoclinic cell was deduced from single-crystal photographs and a least-squares refinement based on 24 reflections measured by a four circle diffractometer with Mo*Kα* monochromatized radiation. Tungsten was determined by inductive coupled plasma (ICP) emission spectroscopy, while phosphorus was determined by the gravimetric analysis for the monoclinic (low-pressure) form only.

Anal. Calcd. for $WOPO_4$: W, 62.36; P_2O_5, 24.07 wt%. Found: W, 62.4; P_2O_5, 24.2 wt%.

The electric resistivity was measured on compact bodies of both forms of $WOPO_4$ by the two-probe method from 77 to 420 K. The magnetic susceptibility was measured using a Faraday balance in the temperature range between 77 and 500 K at applied fields of 5.6, 7.8, and 10.3 KOe. The susceptibility of the phosphates showed a weak field dependence. The field-dependent part of the susceptibility was considered to be caused by a small amount of impurities. Gram susceptibility values χ_g and reciprocal values of the applied fields H showed a linear relation over a wide temperature range. The field-independent part of the susceptibility was obtained by extrapolation of the line to $H^{-1} \rightarrow 0$, as in other cases (*14, 15*).

Results

The powder pattern for the low-pressure form of $WOPO_4$ was similar to those for the low-pressure form of $TaOPO_4$ and the high-temperature form of $NbOPO_4$, which are considered to be isostructural. Although the pattern (Table I) was indexed with a pseudo-orthorhombic cell of a = 11.19(1), b = 5.235(1), c = 6.566(1) Å, the true symmetry was found to be monoclinic with a = 11.172(8), b = 5.217(1), c = 6.543(2) Å, and β = 90.34(4)° from single-crystal data. The observed density for the low-pressure form of $WOPO_4$ was 5.1 g/cm^3 and coincides with the calculated value of 5.15 g/cm^3 using the monoclinic lattice constants given above and four formula units per cell.

A powder pattern for products prepared

TABLE I

X-RAY POWDER DATA FOR THE LOW-PRESSURE FORM OF $WOPO_4$

$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	*hkl*[a]	$100 \times I/I_0$
5.59	5.66	101	56
	5.60	200	
4.26	4.26	201	58
4.09	4.09	011	100
3.840	3.844	111	61
3.301	3.304	211	58
3.241	3.243	301	17
3.151	3.150	102	4
2.834	2.832	202	7
2.757	2.757	311	17
2.697	2.699	112	42
2.616	2.618	020	23
2.574	2.574	401	15
2.490	2.491	212	11
2.468	2.467	410	42
2.371	2.371	220	13
2.229	2.230	221	11
	2.230	312	
2.146	2.148	103	13
	2.143	320	
2.036	2.038	203	5
	2.037	321	
2.013	2.013	122	4
1.971	1.972	412	4
1.967	1.964	511	5
1.924	1.922	222	9
1.851	1.849	502	7
1.835	1.835	421	15
1.6864	1.6865	031	9
1.6606	1.6604	123	18
1.6147	1.6147	231	5
1.5513	1.5512	114	4
1.5266	1.5264	132	5

[a] Indexed with the pseudo-orthorhombic cell. See text.

under high pressure was found to resemble those for $MoOPO_4$, α-$VOPO_4$, the low-temperature form of $NbOPO_4$, and the high-pressure form of $TaOPO_4$. This pattern was indexed with a tetragonal cell of $a = 6.250(1)$ and $c = 4.066(1)$ Å, as shown in Table II. Observed and calculated densities are 6.1 and 6.16 g/cm^3, respectively. The transformation from the low-pressure form to the high pressure form is accompanied with a volume reduction of 16.7%, which is indicative of a drastic structural change.

The temperature dependence of the reciprocal susceptibility for the low- and high-pressure forms of $WOPO_4$ is shown in Fig. 1. Both forms showed paramagnetic behavior in the measured temperature range, although a downward deviation from the line obtained in the high-temperature region was observed at low temperatures for the monoclinic form. The effective magnetic moment and paramagnetic Curie temperature were calculated to be 1.6 μ_B and -269 K for the monoclinic form, and 1.5 μ_B and -19 K for the high-pressure form, respectively. Assuming all the tungsten are pentavalent ($6d^1$ configuration) as expected from the chemical formula, the effective magnetic moment is calculated to be 1.73 μ_B which coincides with the observed values fairly well.

Figure 2 shows temperature dependence

TABLE II

X-RAY POWDER DATA FOR THE HIGH-PRESSURE FORM OF $WOPO_4$

$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	*hkl*	$100 \times I/I_0$
4.42	4.42	110	43
3.408	3.408	101	100
3.124	3.125	200	58
2.991	2.992	111	19
2.303	2.303	211	29
2.210	2.210	220	14
2.033	2.033	002	1
1.977	1.976	310	21
1.933	1.933	102	4
1.853	1.854	301	23
1.848	1.847	112	14
1.7775	1.7774	311	6
1.7043	1.7042	202	8
1.6437	1.6442	212	8
1.5949	1.5946	321	17
1.5621	1.5624	400	8
1.4959	1.4961	222	3
1.4203	1.4203	411	2
1.4171	1.4172	312	1
1.3975	1.3975	420	1

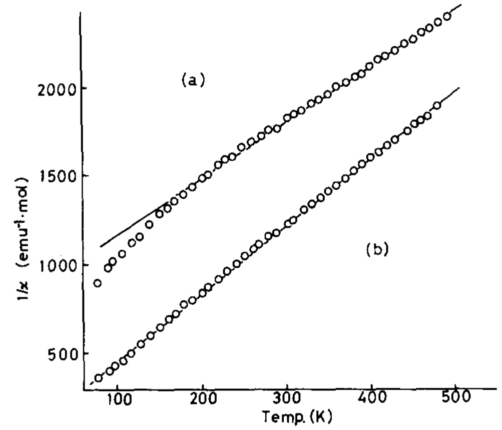

FIG. 1. Temperature dependence of the reciprocal susceptibility for $WOPO_4$: (a) low-pressure form, (b) high-pressure form.

of electric resistivity for the low-pressure form of $WOPO_4$. As seen in this figure, the low-pressure form is a semiconductor with the activation energy of 8.6×10^{-2} eV in high temperature region. Its conductivity at room temperature was $9.5\ \Omega^{-1}\ m^{-1}$. The resistivity at lower temperature deviated from linearity as observed in the higher temperature region. A similar behavior is noted for the temperature dependence of the magnetic susceptibility. The deviations from the linearities observed in the low-temperature region for the electric conductivity and magnetic susceptibility of the low-pressure monoclinic form might indicate a beginning of magnetic ordering. The resistivity of the high-pressure form at room temperature was $>1.2 \times 10^8\ \Omega$, so that measurement of its temperature dependence was not attempted.

Discussion

The unit cell volumes of the tungsten phosphates are listed in Table III along with other isostructural phosphates. The ionic radius of W^{5+} is not given by Shannon and Prewitt (*16*), because only a limited number of compounds containing the ion, especially in the case of oxides, have been found so far. Assuming the ionic radius of W^{5+} is between those of W^{4+} and W^{6+}, the volumes of the tungsten phosphates are reasonable as compared with the other phosphates. In both forms, the tungsten isotypes have the smallest unit cell volumes.

TABLE III

UNIT CELL VOLUME OF MOPO$_4$ PHOSPHATES IN Å^3

	Monoclinic form ($Z = 4$)	Tetragonal form ($Z = 2$)	Ionic radius[a] (Å)	Ref.
$NbOPO_4$	394.1	167.0	0.64	(*1*)
$TaOPO_4$	392.3	165.2	0.64	(*1, 2*)
$MoOPO_4$		163.8	0.63	(*8*)
$VOPO_4$		160.4	0.54	(*6*)
$WOPO_4$	381.4	158.8	0.58–0.65 (IV) (VI)	This work

[a] Ionic radii are taken from Ref. (*16*).

Weissenberg photographs of a single crystal of the low-pressure form of $WOPO_4$ did not show a superstructure as was observed for β-$TaOPO_4$ and β-$NbOPO_4$ (*7, 8*), moreover the monoclinic cell similar to that reported by Levin and Roth (*1*), and by Stranford and Condrate (*17*) is observed. We conclude that the structure of the low-pressure form of $WOPO_4$ differs slightly

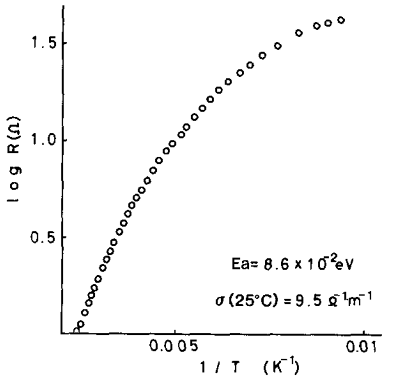

FIG. 2. Variation of electric resistance with temperature for the low-pressure monoclinic form of $WOPO_4$.

from that of β-$TaOPO_4$ and β-$NbOPO_4$. Structural analyses of both forms of $WOPO_4$ are in progress.

Both forms of $WOPO_4$ are different not only in the structure but also in the electric and magnetic properties. The monoclinic form shows better conductivity and stronger magnetic interaction than the tetragonal form. The paramagnetic Curie temperature of −19 K for the tetragonal form is very similar to that of −21 K for isostructural $MoOPO_4$ (*12*). In the structure of the tetragonal form of $MOPO_4$ linear chains of corner sharing MO_6 octahedra exist which are linked to one another through PO_4 tetrahedra. Since short M–O and long M–O distances are alternated along the chain (*2, 3, 9*), the magnetic interaction is expected to be rather weak in this structural type.

The best known examples of the formal valence of W^{5+} in oxide systems are the so-called tungsten bronzes with the perovskite structure. The itinerant electron contributes to the stabilization of this structural type (*18*). In $AlWO_4$, W–W bonding by d^1 electrons is considered to stabilize a rutile related structure (*19*). As seen from the electric and magnetic properties of both forms of the tungsten phosphates, these stabilizing factors are clearly not applicable here.

Raveau and his co-workers (*20–24*) have prepared and characterized phosphates containing mixed-valence tungsten. They are composed of ReO_3-type slabs connected through PO_4 tetrahedra or P_2O_7 groups. Among them the monophosphate tungsten bronzes having a general formula of $(PO_2)_4(WO_3)_{2m}$ (m = 4–16) (*20–23*) are correlated to the monoclinic form of $WOPO_4$ in their compositions and structures. $WOPO_4$ can be described as the second member of this series (m = 2) and contains only W^{5+}, while tungsten is in a mixed-valence state for all other compositions.

Two modifications of $WOPO_4$ were prepared here: a low-pressure form from a starting composition richer in phosphorus oxide than the stoichiometry in the sealed silica tube and a high-pressure form from the low-pressure form. They are unusual oxides containing only tungsten with a formal valence of W^{5+} despite the lack of stabilizing factors mentioned above.

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