



High-pressure synthesis, crystal and electronic structures of a new scandium tungstate, $\text{Sc}_{0.67}\text{WO}_4$

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ABSTRACT

Negative thermal expansion (NTE) materials possess a low-density, open structure that can respond to high pressure conditions, leading to new compounds and/or different physical properties. Here we report that one such NTE material – white, insulating, orthorhombic $\text{Sc}_2\text{W}_3\text{O}_{12}$ – transforms into a black compound when treated at 4 GPa and 1400 °C. The high pressure phase, $\text{Sc}_{0.67}\text{WO}_4$, crystallizes in a defect-rich wolframite-type structure, a dense, monoclinic structure (space group $P2_1/c$) containing 1-D chains of edge-sharing WO_6 octahedra. The chemical bonding of $\text{Sc}_{0.67}\text{WO}_4$ vis-à-vis the ambient pressure $\text{Sc}_2\text{W}_3\text{O}_{12}$ phase can be understood on the basis of the Sc defect structure. Magnetic susceptibility, resistivity, thermoelectric power and IR spectroscopic measurements suggest that the $\text{Sc}_{0.67}\text{WO}_4$ sample is a paramagnet whose conductivity is that of a metal in the presence of weak localization and electron–electron interactions. Oxygen vacancies are suggested as a potential mechanism for generating the carriers in this defective wolframite material.

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1. Introduction

Negative thermal expansion (NTE) compounds are opportune candidates for seeking out new compounds at high pressure. This is due to the combination of their flexible, low-density framework structure, [1,2] and the presence of lattice modes that soften on compression [3–6]. The $\text{A}_2\text{M}_3\text{O}_{12}$ family of NTE materials [7,8] are one such group of oxides that have been studied extensively under high pressures and high temperatures [9–21]. Prototype material of the above family, orthorhombic $\text{Sc}_2\text{W}_3\text{O}_{12}$ – a white insulating powder – has been known to transform to a monoclinic structure on compression, [16,17,21] and to undergo pressure-induced amorphization under more extreme pressure conditions [9]. To date, no experimental data for simultaneous high-temperature (> 400 °C), [22,23] and high-pressure processing of $\text{Sc}_2\text{W}_3\text{O}_{12}$ have been published.

Here we report that orthorhombic $\text{Sc}_2\text{W}_3\text{O}_{12}$ transforms into a new metallic compound, $\text{Sc}_{0.67}\text{WO}_4$, when treated at 4 GPa and 1400 °C. $\text{Sc}_{0.67}\text{WO}_4$ crystallizes in a highly defective wolframite structure, a dense, monoclinic structure (space group $P2_1/c$) characterized by 1-D chains of edge-sharing WO_6 octahedra isostructural to that of multiferroic MnWO_4 [24–28]. To our

knowledge, this new scandium tungstate, $\text{Sc}_{0.67}\text{WO}_4$, is the first reported compound crystallizing in the wolframite-type structure with trivalent A-site cations. $\text{Sc}_{0.67}\text{WO}_4$ is an n-type conductor that shows Pauli-type magnetic susceptibility, a negative thermopower linear in T , and nearly linearly increasing electrical conductivity in the range 3–300 K with a finite $T \rightarrow 0$ intercept. These data indicate that $\text{Sc}_{0.67}\text{WO}_4$ is a poor metal with a finite density of states at E_f with conductivity akin to that of highly defective amorphous semiconductors. We suggest that a small concentration of O defects introduces carriers into an impurity state-derived band, and that the mobility of these carriers may be influenced by the highly defective structure of $\text{Sc}_{0.67}\text{WO}_4$. More generally, the present study confirms the expectation that NTE compounds can serve as precursors to high-pressure synthesis of new and interesting materials via modification of bonding and electronic structure under extreme conditions.

2. Experimental

2.1. Sample preparation

$\text{Sc}_2\text{W}_3\text{O}_{12}$ powder was prepared from Sc_2O_3 (99.9%, Strem Chemicals, Newburyport, MA) and WO_3 (99.9%, Aldrich, Milwaukee, WI). Stoichiometric amounts of the two oxides were thoroughly mixed and ground. The mixture was initially heated at 1000 °C for 5 h and, after regrinding, it was heated at 1200 °C for

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an additional 12 h in air. Powder XRD (PANalytical X'Pert Pro, Co $K\alpha$ radiation) showed this precursor to be single phase. Polycrystalline samples of $\text{Sc}_{0.67}\text{WO}_4$ were prepared from $\text{Sc}_2\text{W}_3\text{O}_{12}$ powder by high-pressure synthesis in a cubic multi-anvil press (Rockland Research Co, West Nyack, NY). The high-pressure apparatus is described elsewhere [29]. $\text{Sc}_2\text{W}_3\text{O}_{12}$ powder was loaded into a sealed Pt capsule and compressed to ~ 4 GPa. The Pt cells containing the samples were resistively heated to ~ 1400 °C, held for 1 h, then quenched to room temperature before releasing the pressure slowly. The sintered sample pellet was dense and black. The face of the pellet was polished to remove any potential contaminations. Two samples, S1 and S2, were prepared in this way. Sample mass in each case was ~ 0.1 g.

2.2. Sample characterization

Synchrotron powder X-ray diffraction (SXRD) data were collected on sample S1 at a wavelength of 0.401555 Å at the 11-BM-B beamline of the Advanced Photon Source at Argonne National Laboratory. Structural determination was carried out by Rietveld refinement [30] using the software package GSAS+EXPGUI [31,32]. For the Rietveld analysis, atomic coordinates, independent isotropic temperature factors for each site, 16 terms determining a Shifted Chebyshev fit to the background, three Gaussian broadening terms, one Lorentzian term and nine microstrain broadening terms in the peak shape model were refined for the main phase. Structural parameters and agreement indices from all these refinements are available as Supplementary Material. Semiquantitative microprobe elemental analysis was performed on several $\text{Sc}_{0.67}\text{WO}_4$ crystals using a Hitachi S-2700 scanning electron microscope (SEM) equipped with a Noran energy-dispersive spectroscopy (EDS) detector. Magnetization and specific heat measurements were performed on a quantum design magnetic property measurement system (MPMS). Four-probe electrical transport data were measured on a home-built system. Thermoelectric power of the sample was measured under vacuum between 305 and 600 K in 5 K steps, on a Seebeck coefficient measurement system from MMR Technologies using 100 mW power. Thermogravimetric analysis (TGA) was carried out on a Mettler-Toledo TGA851 instrument in both nitrogen and oxygen atmospheres. For the determination of the band gap, a spectrum was recorded in the Mid-IR region (4000 – 400 cm^{-1}) at room temperature with a Nicolet 6700 FT-IR Spectrometer equipped with a diffuse reflectance collector from Spectra-Tech Inc. The optical band gap was determined using the Kubelka–Munk theory [33–35].

3. Results

A comparison of the powder X-ray diffraction patterns of the starting material orthorhombic $\text{Sc}_2\text{W}_3\text{O}_{12}$, and the end product (Sample S1) containing the new phase is shown in Fig. 1; data from S2 were similar. Indexing the strong lines led to a monoclinic cell, $a=4.80$ Å \times $b=5.76$ Å \times $c=4.99$ Å, $\beta=91.18^\circ$, in space group $P2_1/c$. As is typically the case in high-pressure synthesis, all samples were contaminated by impurity phases. The impurity phases present in Sample S1 include ~ 3.5 wt% residual starting orthorhombic $\text{Sc}_2\text{W}_3\text{O}_{12}$, ~ 9.5 wt% of an orthorhombic non-stoichiometric perovskite phase of unknown composition, and some other unidentified impurities, in minor amounts (see Fig. 1). A search of the ICDD-JCPDS database [36] revealed a good match of the lattice constants to the wolframite-type structure of MnWO_4 [24]. To refine the structure of the new phase, we collected SXRD data on the sample and analyzed these data with the Rietveld method, using the published crystal structure of MnWO_4 [24] as the starting model. The lattice parameters,

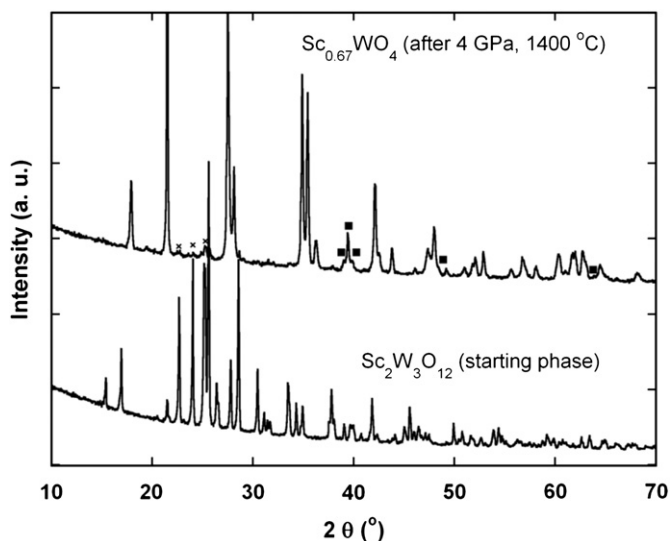


Fig. 1. Comparison of the X-ray diffraction patterns and appearance of orthorhombic $\text{Sc}_2\text{W}_3\text{O}_{12}$ (bottom pattern), and monoclinic $\text{Sc}_{0.67}\text{WO}_4$ (top). \times : residual orthorhombic $\text{Sc}_2\text{W}_3\text{O}_{12}$; \blacksquare : “ $\text{Sc}_{0.3}\text{W}_{0.85}\text{O}_3$ ” impurity. Data collected using Co $K\alpha$ radiation (0.78901 Å). Data are from sample S1.

compared to those of MnWO_4 , measured Sc/W fractional occupancies and the fractions of crystalline phases present obtained from the Rietveld fit to the SXRD data are tabulated in Table 1, and the fractional atomic coordinates are listed in Table 2. A representative Rietveld profile fit is shown in Fig. 2. Fractional coordinates, interatomic distances and bond angles are listed in the Supplementary Material.

$\text{Sc}_{0.67}\text{WO}_4$ crystallizes in the wolframite structure, a dense, monoclinic structure (space group $P2_1/c$) containing 1-D chains of edge-sharing WO_6 octahedra (Fig. 3). Neglecting the few weak unindexed lines, the sample contained 86.96(10) wt% $\text{Sc}_{0.67}\text{WO}_4$, 3.55(6) wt% $\text{Sc}_2\text{W}_3\text{O}_{12}$, and 9.49(6) wt% of a perovskite-type phase of unknown composition.

The temperature dependence of the field-cooled ($H=0.1$ kOe) DC susceptibility of our $\text{Sc}_{0.67}\text{WO}_4$ sample (S1) is consistent with temperature-independent Pauli paramagnetism superimposed with local moments at lower temperatures. Across the 2–300 K temperature range, the data shown in Fig. 4(a) obey a modified Curie–Weiss law of the form, $\chi = \chi_{\text{Pauli}} + \chi_{\text{core}} + \chi_{\text{vv}} + C/(T - \theta_{\text{W}})$, where χ_{Pauli} is a temperature independent Pauli paramagnetic (TIP) term, χ_{core} (-65×10^{-6} emu/mol) [37] is the diamagnetic core correction and χ_{vv} (35×10^{-6} emu/mol), estimated from data reported for WO_3 [38] is the temperature-independent Van Vleck contribution, and C and θ_{W} are the Curie constant and Weiss temperature, respectively. The fit yields $\theta_{\text{W}} = -0.33(1)$ K and an effective moment, $\mu_{\text{eff}} = 0.15$ μ_{B} /f.u. and $\chi_{\text{Pauli}} = 4.4 \times 10^{-4}$ emu/mol. We note that the core and Van Vleck corrections are $< 10\%$ of the total, implying that the residual TIP arises from carriers at E_{F} . The thermoelectric power of the sample above 300 K (Fig. 5(a)) is small and negative with a linear T -dependence, consistent with a metallic n-type density of states. Fig. 5(b) shows that the electrical conductivity, σ , increases linearly with T in the range 30–300 K. Attempts to fit the data to various activated models (e.g., simple exponential, variable-range hopping, adiabatic small polaron, etc.) were unsuccessful. The data reveal that the sample has a finite $T \rightarrow 0$ conductivity, albeit that of a poor metal. Below 30 K, the conductivity can be fit by introducing an additional $T^{1/2}$ term as discussed below. The band gap measured by FT-IR is ~ 0.15 eV, far smaller than that found in related wolframite tungstate compounds [39–41]. Thermogravimetric analysis revealed that the sample (S1) is stable up to 600 °C

Table 1

Lattice parameters, Sc/W fractional occupancies, and the amounts of crystalline phases present obtained from the Rietveld fits to synchrotron powder diffraction data from sample S1. Literature data for the model structure MnWO_4 are also included for comparison [4].

Measured formula	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (deg.)	<i>V</i> (Å ³)	Sc occup.	W occup.	Sc _{0.67} WO ₄ (wt%)	Sc ₂ W ₃ O ₁₂ (wt%)	Perovskite (wt%)
Sc _{0.67} WO ₄	4.80282(4)	5.75801(6)	4.98611(5)	91.177(1)	137.860(2)	0.669(4)	1.0	86.96(10)	3.55(6)	9.49(6)
MnWO ₄	4.830(1)	5.7603(9)	4.994(1)	91.14(2)	138.9207	Mn: 1.0	1.0	n/a	n/a	n/a

Table 2

Fractional atomic coordinates for Sc_{0.67}WO₄ obtained from the Rietveld refinement of synchrotron powder diffraction data of sample S1.

Name	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>U</i> _{iso} 100
Sc1	0.500000	0.676553	0.250000	0.114
W1	0.000000	0.177219	0.250000	0.935
O1	0.213337	0.095884	0.954937	0.689
O2	0.258938	0.365431	0.379564	1.760

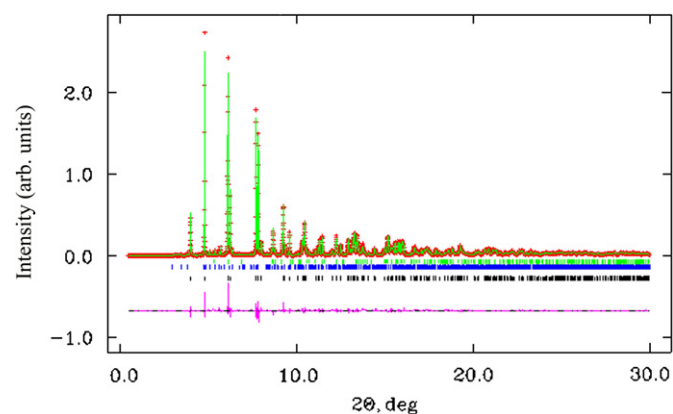


Fig. 2. Typical Rietveld fit of the Sc_{0.67}WO₄ and its impurities. Data collected on sample S1 at a wavelength of 0.401555 Å. Tickmarks for the phases present are shown: black—Sc_{0.67}WO₄; blue—Sc₂W₃O₁₂; green—perovskite. χ^2 : 5.951, wR_p : 0.1158, $R(F^2)$: 0.0503. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

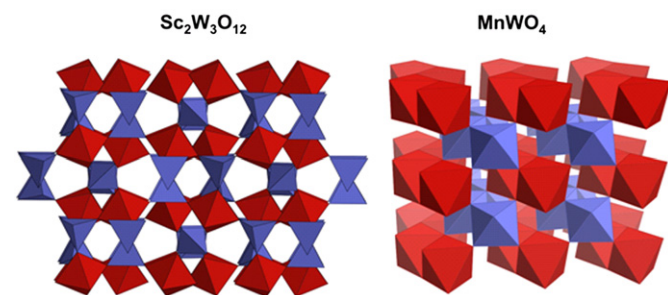


Fig. 3. Structure of orthorhombic Sc₂W₃O₁₂ and monoclinic MnWO₄ represented by polyhedra. Dark octahedra: ScO₆ (left) and MnO₆ (right); light polyhedra: WO₄ (left) and WO₆ (right).

when heated in an oxygen atmosphere; see mass loss data in the Supplementary Material.

4. Discussion

4.1. Structure

The monoclinic wolframite structure, and the related tetragonal scheelite structure are known for many metal (alkaline

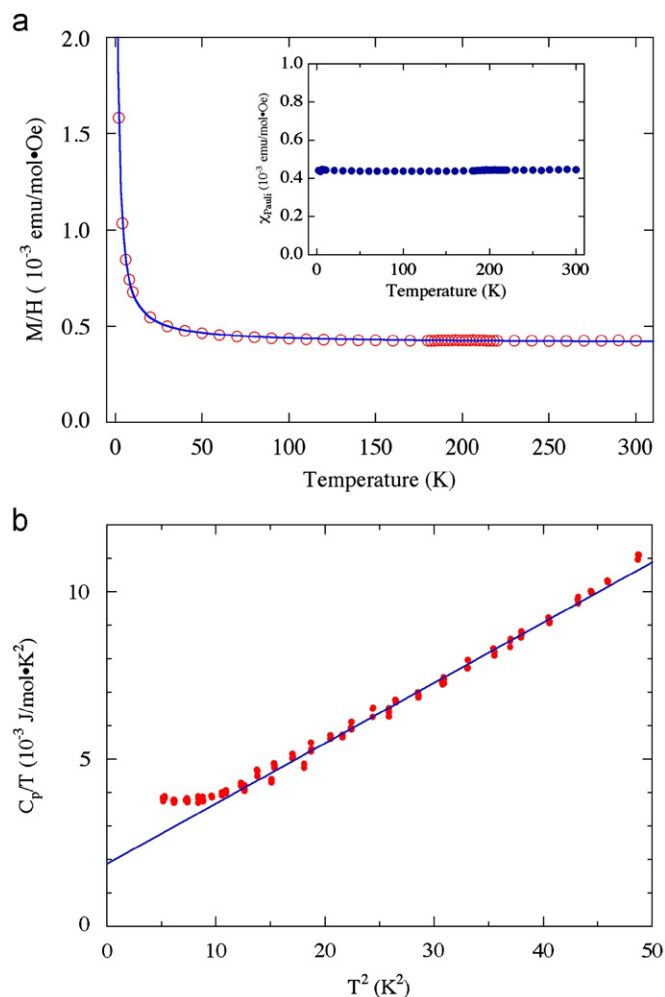


Fig. 4. (a) Temperature dependence of the magnetization of Sc_{0.67}WO₄ on cooling from 300 to 2 K. Applied field was 1 T. Inset: data with low-temperature Curie tail subtracted showing temperature-independent Pauli component. (b) Specific heat of Sc_{0.67}WO₄ (Sample S2) plotted as C_p/T vs. T^2 .

earth, transition and rare earth) tungstates and molybdates with the ABO₄ general formula, mainly for A=2+ cations [28]. Molybdates of trivalent metals Eu, Y, and Gd–Lu with a tetragonal scheelite-type structure were first reported by Banks et al., [42] and specifically a disordered scheelite-type Eu_{0.67}MoO₄ compound containing Eu(III) and Mo(VI) was made, [42] which appeared to be similar to a La₂(MoO₄)₃ phase previously suggested by Jeitschko [43]. However, no monoclinic ABO₄ phase with A being a 3+ cation and B being Mo or W has been reported to our knowledge.

Prompted by the black color of the sample, we considered the possibility of reduction of W from +6 (*d*⁰) to +5 (*d*¹) during the high pressure, high temperature reaction. Considering the wolframite structure, this leads to a hypothetical “ScWO₄” composition. Of relevance in this case is the report by Doumerc et al.

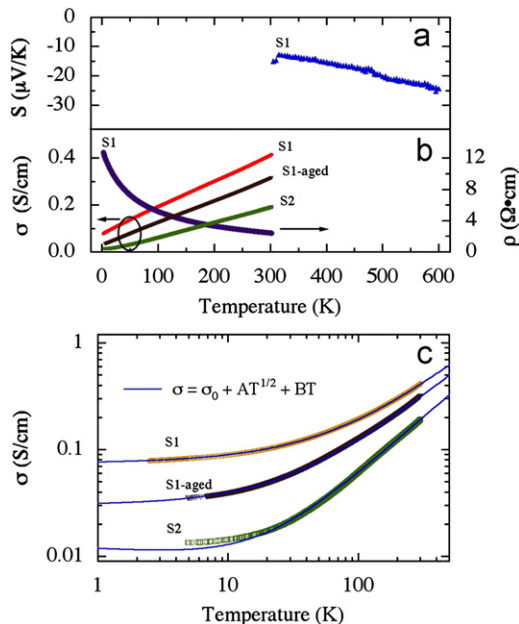


Fig. 5. (a) Temperature dependence of the thermoelectric power of $\text{Sc}_{0.67}\text{WO}_4$ (Sample S1) and the temperature dependence of electrical resistivity of $\text{Sc}_{0.67}\text{WO}_4$. (b) Temperature dependence of electrical conductivity and resistivity of $\text{Sc}_{0.67}\text{WO}_4$. (c) Temperature dependence of electrical conductivity of $\text{Sc}_{0.67}\text{WO}_4$ samples with fits to models of disordered metal. S1: sample 1 as-made; S1-aged: sample 1 after aging; S2: sample 2. Values of fitting coefficients: S1 (initial measurement): $\sigma_0=0.074 \text{ S cm}^{-1}$, $A=1.7 \times 10^{-3} \text{ S cm}^{-1} \text{ K}^{-1/2}$; $B=1.0 \times 10^{-3} \text{ S cm}^{-1} \text{ K}^{-1}$; S1-aged: $\sigma_0=0.029 \text{ S cm}^{-1}$, $A=3.4 \times 10^{-4} \text{ S cm}^{-1} \text{ K}^{-1/2}$; $B=9.2 \times 10^{-4} \text{ S cm}^{-1} \text{ K}^{-1}$; S2: $\sigma_0=0.014 \text{ S cm}^{-1}$, $A=-2.6 \times 10^{-4} \text{ S cm}^{-1} \text{ K}^{-1/2}$; $B=7.4 \times 10^{-4} \text{ S cm}^{-1} \text{ K}^{-1}$. See text for details.

on the synthesis and structure of AlWO_4 , [44] a high-pressure phase crystallizing in a monoclinic $C2/m$ structure, and containing W(V) stabilized by W–W pairs. However, “ ScWO_4 ” would be Sc-rich relative to the starting material $\text{Sc}_2\text{W}_3\text{O}_{12}$ and no Sc-rich phases were identified in the laboratory powder X-ray diffraction pattern. Prompted by EDS analysis, which gave an average Sc:W elemental ratio of 2:3, similar to that of the starting material, we collected SXRD data on the sample (S1) and carried out Rietveld analysis using the MnWO_4 structure as a starting model (see Table 1 and Fig. 2). Significantly, refinement of the site occupancies unambiguously demonstrates that the Sc site is only 2/3 occupied, giving an $\text{Sc}_{0.67}\text{WO}_4$ composition, that of the nominal starting composition and consistent with the EDS analysis. (Note: This agreement suggests that the rest of the impurities, the perovskite-type phase plus any amorphous phase, if present, also have an average Sc:W ratio of 2:3.) No evidence (super-cell reflections) indicating any small multiples of the original unit cell was found in the SXRD pattern; detailed electron diffraction experiments would be desirable to corroborate this conclusion.

The structure of $\text{Sc}_{0.67}\text{WO}_4$ consists of edge-sharing WO_6 and ScO_6 octahedra. The increase in the coordination of tungsten is consistent with what is generally seen on transformations into higher-density high-pressure phases. As expected, $\text{Sc}_{0.67}\text{WO}_4$ (volume/formula unit: $68.930(1) \text{ \AA}^3$) is much denser than the starting phase $\text{Sc}_2\text{W}_3\text{O}_{12}$ ($V/f.u.=308.49/3=102.83 \text{ \AA}^3/W$). This corresponds to a $\sim 33\%$ reduction in volume. The local structure of edge-sharing WO_6 and ScO_6 octahedra with W–O and Sc–O interatomic distances and bond angles are shown in Fig. 6. The WO_6 octahedra are highly distorted with O–W–O angles ranging from $72.73(14)$ to $163.78(14)^\circ$ (cf. orthorhombic $\text{Sc}_2\text{W}_3\text{O}_{12}$: $106.5(8)$ – $118.1(9)^\circ$ [45]). The smaller O–Sc–O angles range from $73.48(19)$ to $97.77(14)^\circ$ (cf. orthorhombic

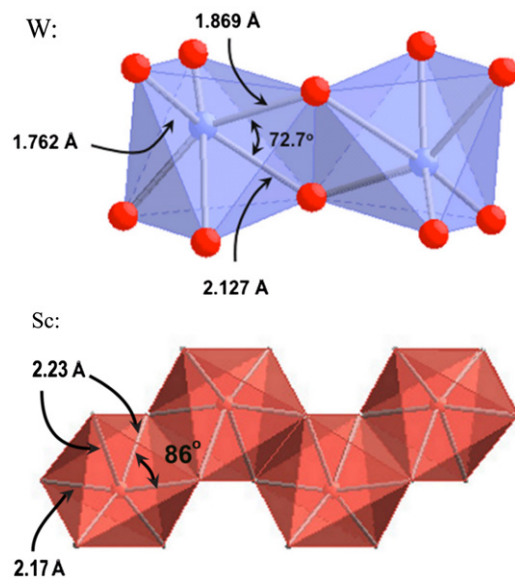


Fig. 6. Bonding environments of W and Sc determined from refinement of synchrotron X-ray powder diffraction data. Top: WO_6 octahedra; bottom: ScO_6 octahedra.

$\text{Sc}_2\text{W}_3\text{O}_{12}$: $84.0(5)$ – $95.8(6)^\circ$). The larger angles are on average more than 10 degrees smaller than those of the corresponding $\text{Sc}_2\text{W}_3\text{O}_{12}$ angles, suggesting that the ScO_6 octahedra are somewhat distorted. Comparison of the interatomic distances and angles with those of orthorhombic $\text{Sc}_2\text{W}_3\text{O}_{12}$ [8] shows that both the mean Sc–O and the W–O bond distances increase (from $2.096(12)$ to $2.193(7) \text{ \AA}$, and from $1.756(16)$ to $1.920(6) \text{ \AA}$, respectively), consistent with the change in the W coordination number from tetrahedral (WO_4) in $\text{Sc}_2\text{W}_3\text{O}_{12}$ to octahedral (WO_6) in $\text{Sc}_{0.67}\text{WO}_4$, and a slight distortion of the ScO_6 octahedra. The average W–O distance is similar to that found in MnWO_4 : 1.937 \AA [24]. Bond valence sum (BVS) calculations (soft valence [46]) result in BVS of 6.21 for W, and 2.36 for Sc. For comparison, the BVS of W in orthorhombic $\text{Sc}_2\text{W}_3\text{O}_{12}$ is 5.82, in MnWO_4 it is 5.94, while for Sc it is 2.88 in $\text{Sc}_2\text{W}_3\text{O}_{12}$. The deviation from the expected BVS in $\text{Sc}_{0.67}\text{WO}_4$ may be understood to result from the Sc vacancy structure. WO_6 octahedra proximate to Sc vacancies are expected to attract the now underbonded terminal O toward the W center, leading to an average d_{W-O} shorter than a hypothetical defect-free structure. Likewise the average d_{Sc-O} will be longer than expected for such a hypothetical structure. These defect-driven bonding effects lead to the calculated overbonded or underbonded BVS calculated for W and Sc, respectively.

Cation vacancies have been observed before in ABO_4 scheelites. For instance, Eu_xMoO_4 and Eu_xWO_4 ($0.67 \leq x \leq 1$) were shown to be mixed-valence phases containing both Eu(II) and Eu(III) ions, [42,47] with Eu being mostly Eu(II) in the vicinity of $x=1$ in Eu_xMoO_4 [48]. Based on density measurements, Banks et al. suggested that the scheelite Eu_xMoO_4 solid solution series is characterized by Eu lattice vacancies [42]. Their IR spectroscopic and lattice parameter measurements indicated that the vacancies are compensated by the presence of Eu^{3+} , and at $x=0.67$, $\text{Eu}^{\text{II}}\text{Mo}^{\text{VI}}\text{O}_4$ changes to $\text{Eu}_{0.67}^{\text{III}}\text{Mo}^{\text{VI}}\text{O}_4$. The oxidation state of Mo in Eu_xMoO_4 was confirmed to be +6 [49]. Our successful preparation of $\text{Sc}_{0.67}\text{WO}_4$ demonstrates that such A-site defects are also possible in the wolframite structure type.

Sleight has proposed a structure-sorting map for scheelites and wolframites based on unit cell volume of the ABO_4 phase and the cell edge of the corresponding AO rocksalt, [28] $\text{Sc}_{0.67}\text{WO}_4$ falls in expected range for wolframite type and indeed agrees well with the trends found in Fig. 1 of Ref. [28]. However, to our knowledge,

$\text{Sc}_{0.67}\text{WO}_4$ is the first wolframite-type with a trivalent A cation. Its formation at high pressure is consistent with the general picture that the wolframites are higher density phases (with close-packed oxygens) often obtained by a reversible transformation from the scheelite structure on compression [28]. It should be noted that in his early paper, Sleight reported that he prepared a black EuMoO_4 phase, and speculated on the presence of Eu^{3+} or Mo^{5+} in the material [28]. Later, the $\text{Eu}_{0.67}\text{MoO}_4$ scheelite phase was reported by Banks et al., and the presence of Eu^{3+} and Mo^{6+} cations was established by IR spectroscopy and measurement of lattice parameters, as mentioned above [42]. The divalent scheelite EuWO_4 , and mixed-valent scheelite phases with Eu_xWO_4 ($0.8 \leq x < 1.0$) composition were prepared and their magnetic properties studied by Greedan et al. [47].

4.2. Electrical and magnetic properties

There have been several studies on the electronic structure of ABO_4 scheelites (CaMoO_4 , CaWO_4 , CdMoO_4 , PbMoO_4 , PbWO_4 , [39–41,50] and BaWO_4 [41]) and wolframites (CdWO_4 [39] and ZnWO_4 [41]). The latter wolframites are wide-gap n-type semiconductors. [39,41,51] Their band gaps fall into the 2.4–6 eV range; e.g. 2.43 eV for CdMoO_4 , [39] and 5.97 eV for CaWO_4 [41]. Their valence and conduction bands are mainly composed of O 2p and W 5d states, respectively. There is some electronic contribution from Cd and Zn, mainly to the valence band, negligible to the conduction band [39,41]. In CdWO_4 , W has a distorted octahedral coordination causing the lower part of the conduction band to be threefold degenerate [39]. Conductivity studies on related systems such as AlWO_4 , [44] FeMoO_4 , [52,53] CoMoO_4 , [54] NiMoO_4 , [55] and La-doped PbWO_4 [56] revealed activated behavior, polaron hopping, and oxide-ion conduction mechanisms with activation energies in the 0.2–2 eV range [57]. With its (poor) metallic conductivity and no evidence for activated behavior (*vide infra*), $\text{Sc}_{0.67}\text{WO}_4$ is clearly distinct from these related scheelites and wolframites.

We note here that as the physical property characterization was carried out on mixed-phase samples, the below interpretation of the magnetic and electrical data is based on the assumption that the relative contributions from the impurity phases are not significant. The validity of this assumption will also be discussed below. Consideration of the magnetic susceptibility, thermoelectric power and electrical conductivity indicate that $\text{Sc}_{0.67}\text{WO}_4$ is an n-type disordered metal. The modified Curie–Weiss fit to $\chi(T)$ reveals a TIP superimposed on a low-temperature Curie tail. Under the assumption that the local moments arise from localized $S=1/2$ sites, the extracted $p_{\text{eff}}=0.15 \mu_B/\text{f.u.}$ puts these magnetic impurities at a concentration of ~ 0.8 mole percent. This is too large to come from impurities originating in starting materials or introduced during sample manipulation, and so we attribute this Curie behavior to a small fraction of localized W^{5+} ($S=1/2$) sites in Sc–W–O sample. The origin of these local moments may be extrinsic (i.e. residing in impurity phases) or intrinsic to the $\text{Sc}_{0.67}\text{WO}_4$; our present data do not allow us to distinguish between these possibilities. Alternative explanations such as carrier ‘freeze out’ into localized states postulated recently in $\text{Na}_{0.3}\text{RhO}_2 \cdot 0.6\text{H}_2\text{O}$ are unlikely, [58] as the energy gap would have to be of order 2 K or less given the conductivity data of Fig. 5(b). The observed Pauli susceptibility reflects a finite density of states at the Fermi level, E_f . Using the free electron metal relationship $\chi_{\text{Pauli}} = \mu_B^2 N(E_f)$, we estimate $N(E_f) \sim 8 \times 10^{24}/\text{eV mol}$. An independent measure of $N(E_f)$ can be obtained from the specific heat (Fig. 4(b)), which at low temperatures is given by $C_p = \gamma T + \beta T^3$. The coefficient of the linear term, γ , is the electronic contribution, which in the free

electron model is proportional to $N(E_f)$, i.e., $N(E_f) = 3\gamma/\pi^2 k_B^2$. Analysis of the data measured on S2 [59] shown in Fig. 4(b) yields $N(E_f) \sim 5 \times 10^{23}/\text{eV mol}$. The discrepancy between the magnetic and thermodynamic measurements of $N(E_f)$ can be attributed to sample variation (S1 vs. S2), sample aging, and/or imprecise correction of the measured magnetic susceptibility data; the first two possibilities are perhaps more likely considering sample variation of conductivity data shown in Fig. 5. Nonetheless, these measurements independently argue for a substantial, finite density of states at E_f in the $\text{Sc}_{0.67}\text{WO}_4$ sample.

The finite density of states at E_f is corroborated by the thermoelectric data of Fig. 5(a), which in the range 300–600 K follow the T -linear behavior expected for a metal. An unusual feature of $\text{Sc}_{0.67}\text{WO}_4$ is the electrical conductivity (Fig. 5(b)), which is approximately proportional to T over two decades with a finite $T=0$ intercept of $\sim 0.08 \text{ S/cm}$, again arguing that $\text{Sc}_{0.67}\text{WO}_4$ is a (poor) metal [60]. Notably, there is no evidence for the activated behavior expected for semiconductors, polaronic metals, etc. Fig. 5(c) replots the conductivity data on logarithmic axes, revealing a low-temperature deviation from linearity. With the caveat that quantitative descriptions of conductivity in polycrystalline samples are inevitably subject to errors introduced by grain connectivity issues, the data can be well fit to a form appropriate for disordered metals, $\sigma = \sigma_0 + AT^{1/2} + BT$, [61] where the T and $T^{1/2}$ terms are characteristic of weak localization with a dominant dephasing by electron–electron scattering and Coulomb interaction terms, respectively. While this expression is strictly applicable to low-temperature conductivity, Helgren et al. [62] have successfully analyzed the conductivity of rare-earth and Y-doped Si up to 300 K using this expression. If such a model correctly describes the electrical conductivity in $\text{Sc}_{0.67}\text{WO}_4$, the disorder expressed by the Sc non-stoichiometry through its impact on the local structure of the WO_6 octahedra may be a relevant contributor to the localization mechanism.

Also shown in Fig. 5(c) are data from S2 as well as data collected on S1 following several months of storage in a nitrogen-purged storage cabinet. The absolute conductivity of the first sample has changed substantially during the storage period, but the data are still well described by the same functional form as the initial data. We do not know why the conductivity of this sample has changed; possibly some reaction with the atmosphere has changed the carrier concentration and/or mobility. Alternatively an order–disorder process among defects in the structure may have occurred. Data from the second sample are clearly linear at $T > 30 \text{ K}$, but the low T agreement is not as satisfactory. Additionally, the coefficient of $T^{1/2}$ is positive in the case of the first sample and negative for the second. These sample-related inconsistencies make it impossible for us to claim definitively that the disordered model is appropriate to $\text{Sc}_{0.67}\text{WO}_4$. It is also conceivable that the configuration of the O vacancies (clustering, long-range order, etc.) changes over time, resulting in the aging effect observed in the electrical conductivity. Better samples and systematic studies will be necessary to answer this question. Regardless of the exact description of the conductivity mechanism, however, our sample is metallic with a finite density of states at E_f ; its conductivity is influenced by very strong disorder, and is perhaps not too different from heavily doped amorphous systems. In an extensive literature search, we have found no other reports of metallic conductivity in doped scheelites or wolframites. No similar electric or magnetic behavior was reported for starting phase orthorhombic $\text{Sc}_2\text{W}_3\text{O}_{12}$ (one of our impurity phases), either. A tungsten oxide (WO_3) based phase could be a possible impurity in a non-stoichiometric or doped form, as e.g. $\text{Er}_{0.05}\text{Ta}_{0.15}\text{W}_{0.85}\text{O}_3$ [63] has a structure similar to the orthorhombic perovskite phase, our unidentified impurity phase. This phase may be a Sc-containing tungsten oxide phase with a possible

reduced tungsten content. Neither can we rule out the possibility that such reduced tungsten affected the observed physical properties, nor can we determine its correct amount and oxidation state in an unknown (and potentially new) phase. WO_3 is known as a semiconductor with a band gap of 2.6–2.7 eV, [64–66] much greater than the ~ 0.15 eV measured for our sample. Metallic character was reported for tungsten intermediary oxides based on thermoelectric power measurements [67]. Our results are inconsistent with the T -dependent resistivity seen in these oxides. A marked decrease of the band gap at crystallite borders with a significant density of states lying 1.5 eV below the band midgap, and at the Fermi level was reported in WO_3 films, and was attributed to σ and π bonding states of $W5d$ electrons from W – W ion pairs at boundary planes between crystallites [65]. We note that while a similar behavior may be characteristic of both $\text{Sc}_{0.67}\text{WO}_4$, and a possible WO_3 -based impurity phase, we do not believe that, if this behavior would be exclusively attributed to the impurity phase present in < 10 wt%, it would dominate the observed electrical and magnetic behavior of our samples.

How are the carriers generated in this nominally d^0 compound? One potential mechanism for generating n -type carriers is through the introduction of oxygen vacancies, i.e., $\text{Sc}_{0.67}\text{WO}_{4-\delta}$. Many examples of such a mechanism are found in oxides: O vacancies are known to introduce carriers in WO_{3-x} , although the conduction mechanism in this compound is polaronic; [68] conductance through oxygen vacancy donor states is known to occur in the n -type semiconductor bismuth iron molybdate, $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$; [69–71] oxygen vacancies lead to metals in reduced bulk TiO_2 Magneli phases, [72] and in thin films of TiO_{2-x} [73]. Notably, in all of the above examples, electron-lattice contributions are important to the conductivity; the same does not appear to be the true in $\text{Sc}_{0.67}\text{WO}_4$.

If we attribute the $\sim 0.8\%$ W^{5+} concentration determined from magnetic susceptibility wholly to O defects in $\text{Sc}_{0.67}\text{WO}_4$ and assume each vacancy donates two free carriers to the band structure, this equates to an upper bound of 0.004 O vacancies per formula unit and a carrier concentration estimate of $n \sim 6 \times 10^{19} \text{ cm}^{-3}$. These vacancies can in principle form extended impurity states below and potentially merging with the conduction band. The measured IR feature at ~ 150 meV could reflect the residual presence of such impurity states. An alternative mechanism such as that proposed in $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$; [69–71] in which conduction occurs in the impurity band at low temperature and in the conduction band at high temperature seems unlikely given the lack of any energy scale other than temperature in the conductivity data.

Due to the potentially small concentration of vacancies, measurement of δ in the proposed $\text{Sc}_{0.67}\text{WO}_{4-\delta}$ composition by TGA was not considered reliable (see Supplementary Material). Further detailed studies on well-characterized single crystals will be required to establish whether or not this oxygen defect model is appropriate to describe the chemical as well as physical properties of $\text{Sc}_{0.67}\text{WO}_4$. Further studies on pure samples will also make interpretation of the magnetic and electronic data less doubtful.

5. Conclusion

We have prepared the new compound, $\text{Sc}_{0.67}\text{WO}_4$, from the NTE precursor material $\text{Sc}_2\text{W}_3\text{O}_{12}$ under high pressure, high temperature conditions. To our knowledge, $\text{Sc}_{0.67}\text{WO}_4$ is the first wolframite with a trivalent A-site cation. The bonding in $\text{Sc}_{0.67}\text{WO}_4$ can be understood by considering the defective Sc sublattice, while the magnetic and electrical properties are speculated to originate from a small concentration of oxygen

vacancies, leading to W^{5+} sites and band-like electron carriers that are strongly influenced by disorder. Albeit the magnetic and electrical properties of $\text{Sc}_{0.67}\text{WO}_4$ are rather conventional, this new phase, both structurally and electronically, stands as a unique example among the wolframite class of oxides. More generally, the findings here encourage us that NTE materials can serve as precursors to other interesting new high-pressure phases with modification of bonding and electronic structure.

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Appendix A. Supplementary Material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2010.04.039.

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