



# 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  $\text{WO}_6$  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  $\text{WO}_6$  octahedra isostructural to that of multiferroic  $\text{MnWO}_4$  [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  $\text{Sc}_2\text{O}_3$  (99.9%, Strem Chemicals, Newburyport, MA) and  $\text{WO}_3$  (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  $\sim 4$  GPa. The Pt cells containing the samples were resistively heated to  $\sim 1400$  °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  $\sim 0.1$  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 ( $4000$ – $400$   $\text{cm}^{-1}$ ) 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  $\sim 3.5$  wt% residual starting orthorhombic  $\text{Sc}_2\text{W}_3\text{O}_{12}$ ,  $\sim 9.5$  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  $\text{MnWO}_4$  [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  $\text{MnWO}_4$  [24] as the starting model. The lattice parameters,

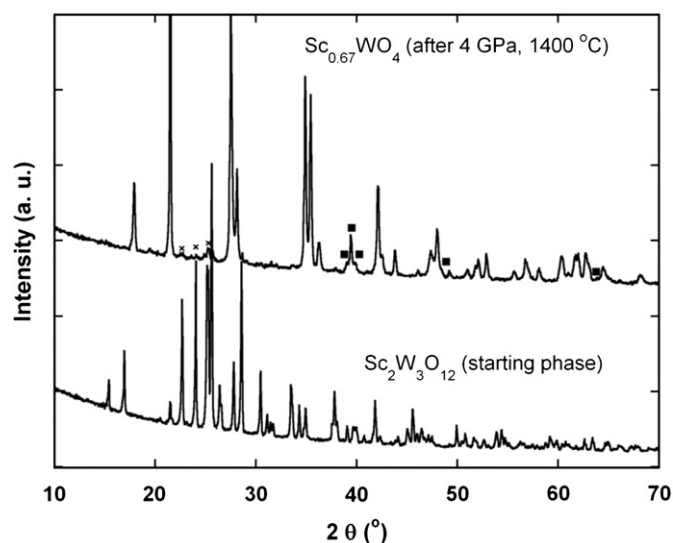


Fig. 1. Comparison of the X-ray diffraction patterns and appearance of orthorhombic  $\text{Sc}_2\text{W}_3\text{O}_{12}$  (bottom pattern), and monoclinic  $\text{Sc}_{0.67}\text{WO}_4$  (top).  $\times$ : residual orthorhombic  $\text{Sc}_2\text{W}_3\text{O}_{12}$ ;  $\blacksquare$ : “ $\text{Sc}_{0.3}\text{W}_{0.85}\text{O}_3$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

compared to those of  $\text{MnWO}_4$ , 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  $\text{WO}_6$  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  $\chi_{\text{Pauli}}$  is a temperature independent Pauli paramagnetic (TIP) term,  $\chi_{\text{core}}$  ( $-65 \times 10^{-6}$  emu/mol) [37] is the diamagnetic core correction and  $\chi_{\text{Vv}}$  ( $35 \times 10^{-6}$  emu/mol), estimated from data reported for  $\text{WO}_3$  [38] is the temperature-independent Van Vleck contribution, and  $C$  and  $\theta_{\text{W}}$  are the Curie constant and Weiss temperature, respectively. The fit yields  $\theta_{\text{W}} = -0.33(1)$  K and an effective moment,  $\mu_{\text{eff}} = 0.15$   $\mu_{\text{B}}$ /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  $E_{\text{F}}$ . 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,  $\sigma$ , 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  $\sim 0.15$  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

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