HIGH-PRESSURE SYNTHESIS, CRYSTAL AND ELECTRONIC STRUCTURE OF THE NEW SCANDIUM TUNGSTATE $Sc_{0.67}WO_4$

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INTRODUCTION

Flexible framework solid materials such as negative thermal expansion (NTE) compounds possess a structure that predisposes them to intriguing high-pressure behavior.[1-4] The $A_2M_3O_{12}$ family of NTE materials is a class of oxides that can serve as precursors to high-pressure synthesis with modification of bonding and electronic structure.[5]

RESULTS

Prototype material of the above family, orthorhombic $Sc_2W_3O_{12}$, a white, insulating powder, transforms into a new phase, a black, metallic compound, when treated at 4 GPa and 1400 ^oC (Figure 1). The crystal structure of the recovered phase $Sc_{0.67}WO_4$ was determined from synchrotron x-ray powder diffraction data. It crystallizes in the wolframite structure, a dense, monoclinic structure (space group *P12/c1*) containing 1-D chains of edge-sharing WO_6 octahedra (Figure 2) similar to that of multiferroic $MnWO_4$.[6, 7] $Sc_{0.67}WO_4$ is a para-magnetic metal (Figure 3). The evolution of the electronic structure in correlation with atomic rearrangement over the transition to the new metallic phase is discussed on the basis on valence band calculations. The Sc electronic states are admixed with O 2p to form the valence band. At precisely the $Sc_{0.67}WO_4$ composition, the Fermi level will lie at the gap, with the valence band being largely weighted by W 5d levels. Metallicity may result from a small concentration of defects adding carriers to the conduction band.

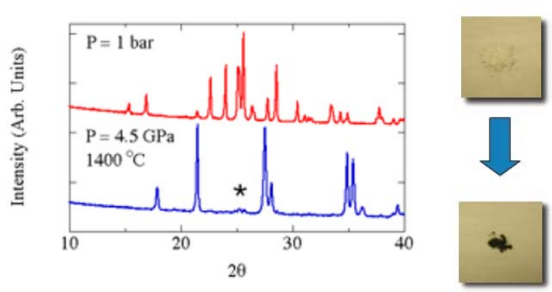

Figure 1: Comparison of the x-ray diffraction patterns and appearance of orthorhombic $Sc_2W_3O_{12}$ (red curve, white powder), and monoclinic $Sc_{0.67}WO_4$ (blue curve, black powder).

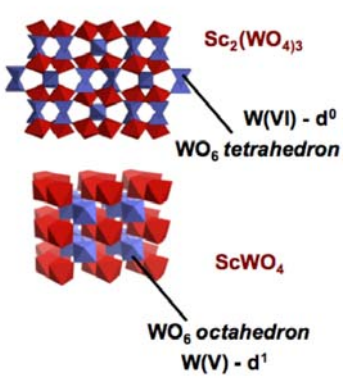

Figure 2: Crystal structure of orthorhombic $Sc_2W_3O_{12}$, and monoclinic $Sc_{0.67}WO_4$ visualized by polyhedra. Red octahedra: ScO_6.

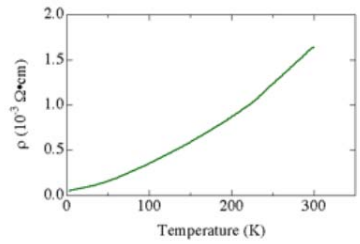

Figure 3: Electrical resistivity of $Sc_{0.67}WO_4$ showing metallic conductivity.

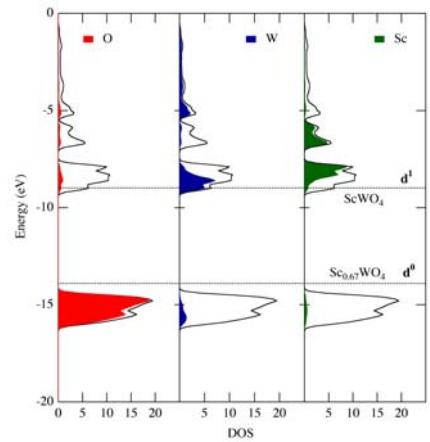

Figure 4: Tight-binding electronic structure of $Sc_{0.67+x}WO_4$ showing rigid-band Fermi levels for x=0 and x=0.33 with d^0 and d^1 electron counts on W, respectively.

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