Topochemical Synthesis of Anion-Intercalated Transition Metal Dichalcogenide Superconductor $S_{0.66}WS_2$

Ruijin Sun [a, #], Haodong Li, [a, #] Duo Zhang, [a] Zhaolong Liu, [b] Yuxin Ma, [a] Dezhong Meng, [a] Changchun Zhao [a*]

a. School of Science, China University of Geosciences, Beijing (CUGB), Beijing, 100083, China.

b. Institute of Physics, Chinese Academy of Science, Beijing, 100190, China.

E-Mail: srj@cugb.edu.cn

Experimental and Methods Section

Sample synthesis.

K_xWS_2 Crystal: W, S powder were ground with a reactive flux K_2S_2. The molar ration of K_2S_2:W:S was kept constant at about 0.5: 1: 1. After all the starting materials were thoroughly mixed, they were loaded into a Al_2O_3 crucible and then sealed in a quartz tube. The quartz tube was placed in a muffle furnace, the furnace was heated at a rate of 20 degree/min to 1223.15 K, then kept at 1223.15 K for 5 hours, and then cooled to 823.15 K at a rate of 3-10 K/hour Following natural cooling to room temperature, silver needle-like single crystal K_xWS_2 was obtained.

$S_{0.66}WS_2$ Crystal: K_xWS_2 crystals, 2 g thiourea and 0.3 g $LiOH{\bullet}H_2O$ were placed in a 25-mL Teflon-lined autoclave filled 60% of its capacity with deionized water. The autoclave was then tightly closed and heated at 140 °C for 7 days, the sliver $(S)_{0.66}WS_2$ crystals were filtered after washing with deionized water.

Characterization

Powder X-ray diffraction (PXRD) patterns were collected at room temperature on a Rigaku smart Lab X-ray diffractometer operated at 40 kV voltage and 40 mA current using Cu Ka radiation (λ=1.5406 Å). The 2θ range was 10–80°with a step size of 0.01. Indexing and Rietveld refinement were performed using the DICVOL91, Fullprof, and MDI Jade programs. Single crystal X-ray diffraction (SCXRD) patterns at 295 K were collected using a Bruker D8 VENTURE PHOTO II diffractometer with multilayer mirror monochromatized Mo Kα (λ = 0.71073 Å) radiation. Unit cell refinement and data merging were performed using the SAINT program, and an absorption correction was applied using Multi-Scans scanning. Structural solutions were obtained by intrinsic phasing methods using the program APEX3, and the final refinement was completed with the Jana 2020 suite of programs. The electron density maps of the two samples were firstly constructed by the charge flipping method implemented in the Jana2020 software. Scanning electron microscopy (SEM) images were taken on a Phenom pro XL microscope equipped with an electron microprobe analyzer for the semiquantitative elemental analysis in the energy-dispersive X-ray spectroscopy (EDS) mode.

The density functional theory (DFT) calculations

The density functional theory (DFT) calculations were performed within the Vienna ab initio simulation package[i]. We adopted the generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) for the exchange-correlation potentials[ii]. The projector augmented-wave (PAW) pseudopotentials were used with a plane wave energy of 500 eV; $3p^6 3d^4 4s^1$ for V, and $3s^2 3p^4$ for S electron configuration were treated as valence electrons. The van der Waals interaction was considered using DFT-D3 method of Grimme. The GGA+*U* method with Dudarev's approach was applied to V-*d* orbitals, where the effective *U* parameter U_{eff} = *U-J* was set as 1 eV. A Monkhorst-Pack Brillouin zone sampling grid with a resolution of $0.02\times2\pi$ $Å^{-1}$ was used. The self-consistent field procedure was considered convergent when the energy difference between two consecutive cycles was lower than 10^{-6} eV. The lattice constants and atomic coordinates were relaxed until all the forces on the ions were less than 0.01 eV/Å.

Figure Section

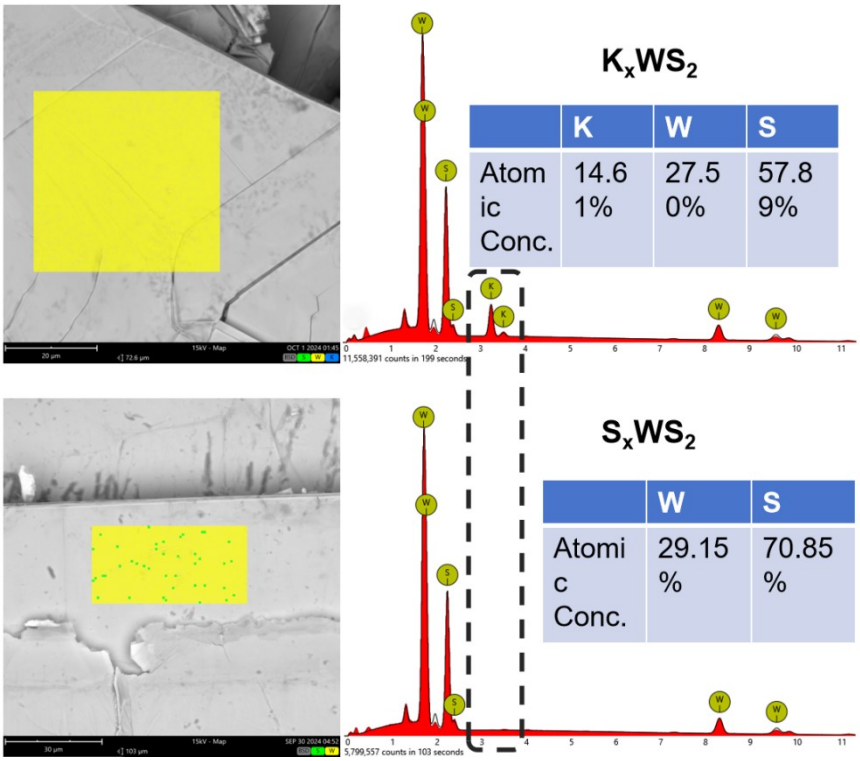


Fig. S1 EDS mapping for $K_{0.7}WS_2$ (upper) and $S_{0.66}WS_2$ (lower).

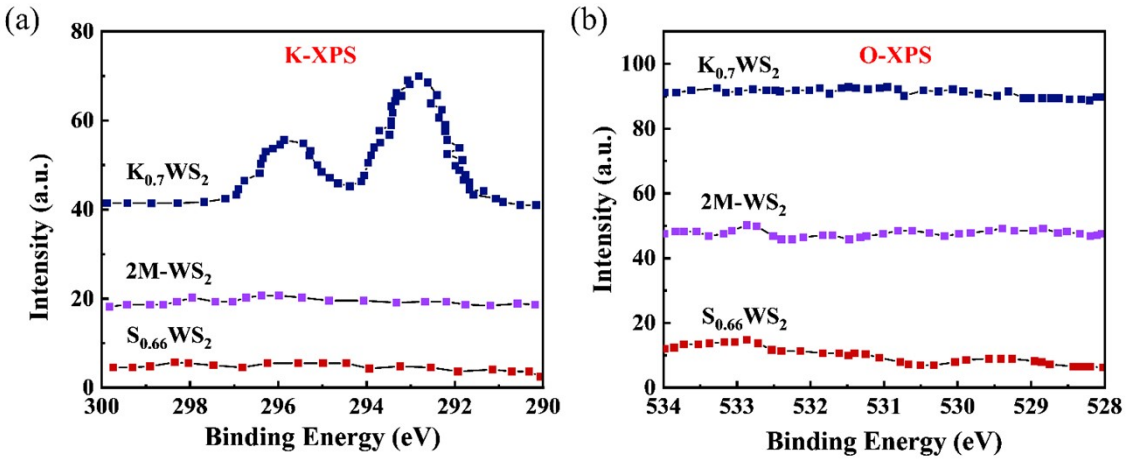


Fig. S2 XPS spectra for K and O in $K_{0.7}WS_2$, 2M-WS_2, and $S_{0.66}WS_2$.

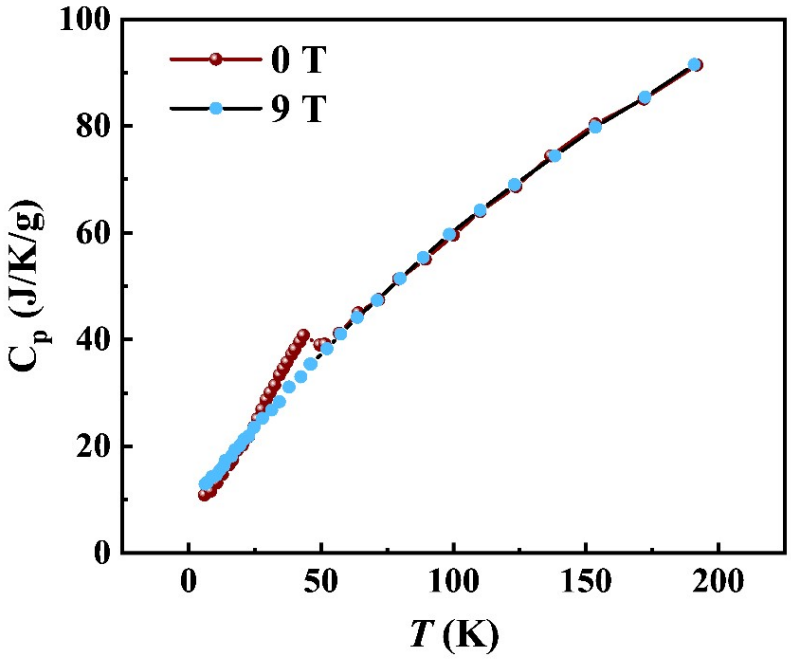


Fig. S3 The special heat measurement for $S_{0.66}WS_2$.

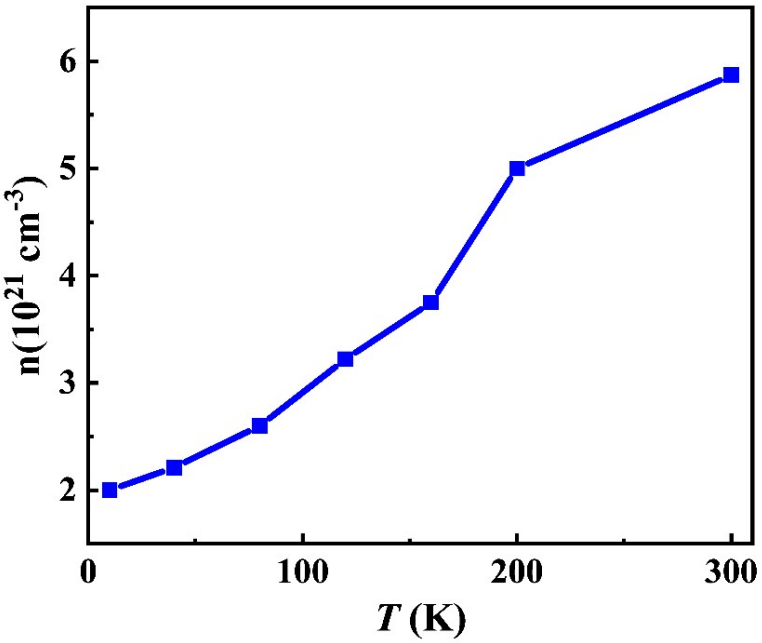
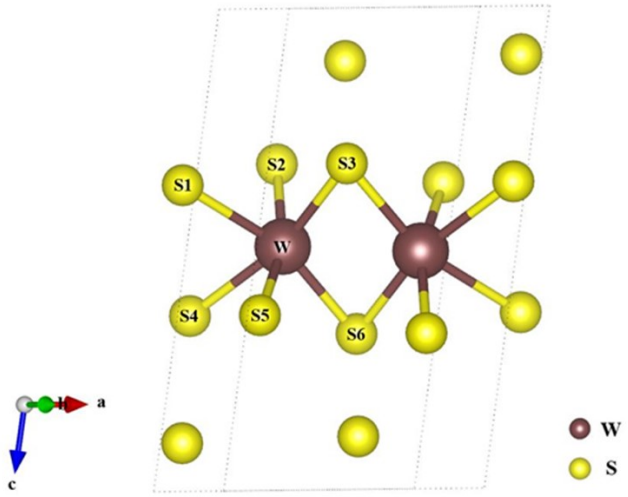


Fig. S4 The carrier concentration of $S_{0.66}WS_2$ at different temperatures calculated by Hall resistivity.



$S_{0.66(2)}WS_2$ (Å)					
W-S1	2.488(16)	W-S2	2.38(3)	W-S3	2.38(3)
W-S4	2.464(13)	W-S5	2.464(13)	W-S6	2.35(3)

$S_{0.66(2)}WS_2$ (deg.)					
S1-W-S2	84.4(6)	S1-W-S3	84.4(6)	S1-W-S4	79.7(5)
S1-W-S5	79.7(5)	S1-W-S6	162.0(8)	S2-W-S3	85.6(10)
S2-W-S4	93.9(6)	S2-W-S5	164.1(6)	S2-W-S6	108.5(7)
S3-W-S4	164.1(6)	S3-W-S5	93.9(6)	S3-W-S6	108.5(7)
S4-W-S5	82.2(6)	S4-W-S6	86.8(6)	S5-W-S6	86.8(6)

Fig. S5 Band length and angles for $S_{0.66(2)}WS_2$

Table Section

Table S1. Crystallographic data of $S_{0.66}WS_2$.

Formula	**S0.667 W1 S2**
Formula Weight	**174.8(2)**
Space group	***P 21/m***
a, c(Å)	**5.679(4), 3.240(2), 9.624(8)**
Z	**2**
Crystal size(μm^3)	**87 * 64 * 23**
Temperature(K)	**298**
Radiation(Å)	**Mo-Kα λ = 0.71073**
R_1, wR_2, S	**0.0544, 0.1189, 1.272**

Atomic positions and equivalent displacement parameters

Atom	Muti.	x	y	z	Occ.	U_{iso}
S1	2	0.370(3)	0.750000	0.323(3)	1	0.015(5)
S2	2	0.885(3)	0.250000	0.3641(15)	1	0.019(3)
W1	2	0.6991(4)	0.750000	0.5062(3)	1	0.040(13)
S3	2	0.444(9)	0.250000	0.110(4)	0.33(2)	0.038(15)
S4	2	0.983(10)	0.750000	0.1002(19)	0.33(1)	0.0184(5)

Table S2. Molar ratio for W, S via ICP-AES method.

Element	S	W
Molar ration	2.67	0.97

[i]. Kresse, G., Furthmuller, J., Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6** (1), 15-50 (1996).
[ii]. Perdew, JP., Burke, K., Ernzerhof, M., Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865-3868 (1996).