

## Electronic Supplementary Information

### Formation energy, phase transition and negative thermal expansion of

### $\text{Fe}_{2-x}\text{Sc}_x\text{W}_3\text{O}_{12}$

Gaojie Zeng,<sup>†a</sup> Chunyan Wang,<sup>†abc</sup> Huanli Yuan,<sup>ac</sup> Xi Zhen,<sup>a</sup> Qilong Gao,<sup>a</sup> Juan Guo,<sup>a</sup> Mingju Chao,

<sup>a</sup> Xiansheng Liu<sup>\*b</sup> and Erjun Liang<sup>\*a</sup>

<sup>a</sup> School of Physics & Microelectronics, and Key Laboratory of Materials Physics of Ministry of Education of China, Zhengzhou University, Zhengzhou 450052, China

<sup>b</sup> Henan Key Laboratory of Photovoltaic Materials and School of Future Technology (Quantum Information), Henan University, Kaifeng 475004, China

<sup>c</sup> School of Physics and Telecommunication Engineering, Zhoukou Normal University, Zhoukou 466001, China

<sup>†</sup> Gaojie Zeng and Chunyan Wang contributed equally to this work.

\*Corresponding author. Tel.: +86 371 67767838; fax: +86 371 67766629.

E-mail: xsliu@henu.edu.cn,

ejiang@zzu.edu.cn.

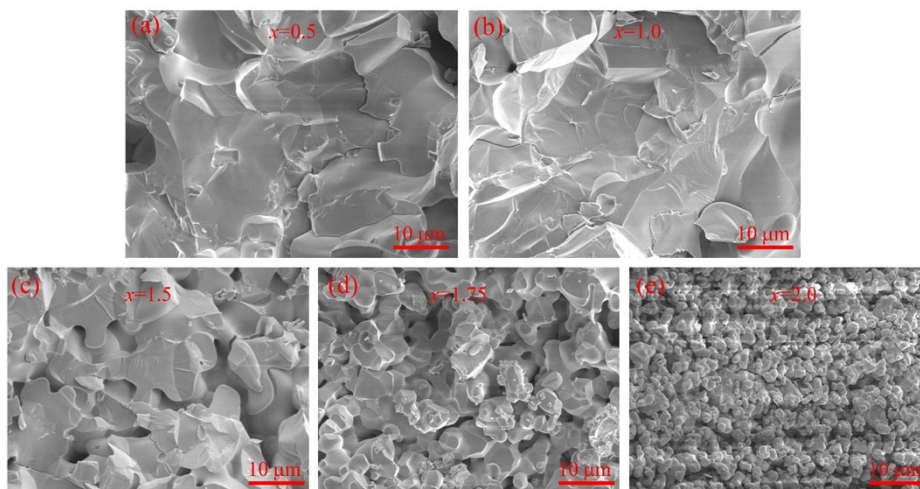


Fig. S1. SEM images (a-e) of  $\text{Fe}_{2-x}\text{Sc}_x\text{W}_3\text{O}_{12}$  ( $x = 0.5, 1.0, 1.5, 1.75, 2.0$ ).

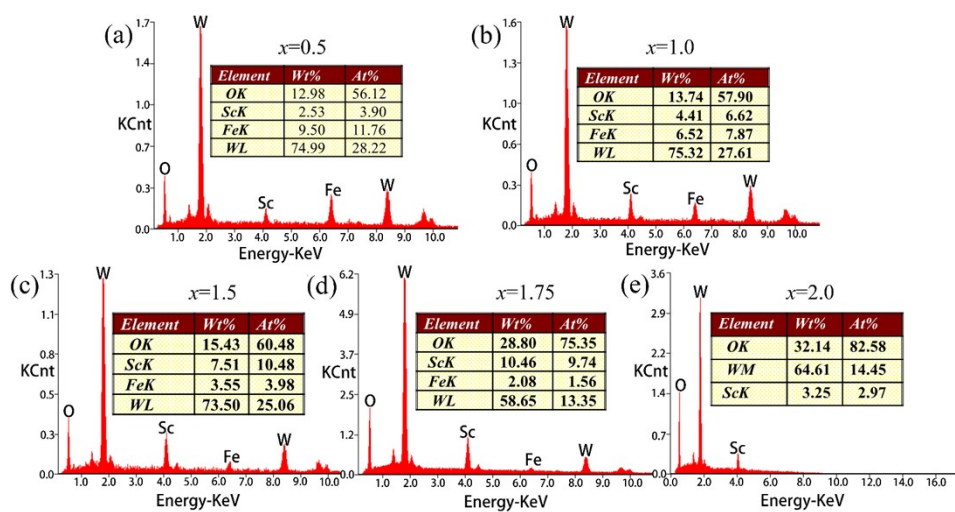


Fig. S2 EDS spectra (a-e) of  $\text{Fe}_{2-x}\text{Sc}_x\text{W}_3\text{O}_{12}$  ( $x = 0.5, 1.0, 1.5, 1.75, 2.0$ ).

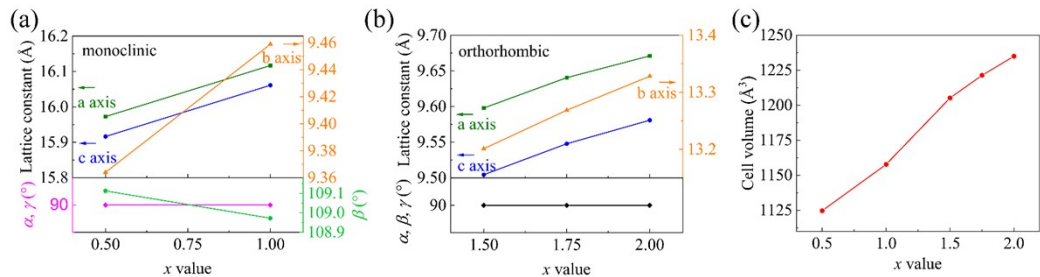


Fig. S3. Cell parameters with  $\text{Sc}^{3+}$  substituting ratio of  $\text{Fe}_{2-x}\text{Sc}_x\text{W}_3\text{O}_{12}$  at RT (detailed cell parameters are given in Table S1): (a) the monoclinic phase for  $x = 0.5, 1.0$ , (b) the orthorhombic phase for  $x = 1.5, 1.75, 2.0$  acquired by Rietveld refinement with FullProf software, (c) cell volume increasing with substituting ratio of  $\text{Sc}^{3+}$  (To facilitate comparison, the cell volumes of monoclinic phase of  $x=0.5, 1.0$  have been divided by 2 as calculated in Ref. <sup>30</sup>)

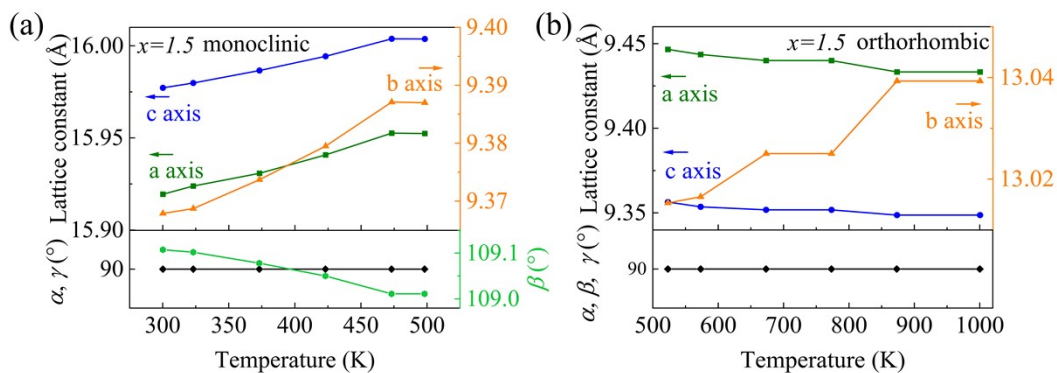


Fig. S4. (a) The monoclinic phase, and (b) the orthorhombic phase parameters change with temperature acquired by Rietveld refinement with FullProf software of  $\text{Fe}_{1.5}\text{Sc}_{0.5}\text{W}_3\text{O}_{12}$ .

## Computational methods

The first-principles calculations are performed based on density of functional theory (DFT) with in the VASP code. The projected augmented wave method is used to describe the valence and core electrons, and the generalized gradient approximation proposed by Perdew–Burke–Ernzerhof for the exchange correlation potential is adopted. The electron wave function is expanded with a cut-off energy of 520 eV, and  $\Gamma$ -centered  $2 \times 4 \times 2$  k-meshes are used to sample their reducible Brillouin zone (BZ). The total energy is calculated with high precision, converged to  $10^{-8}$  eV/atom, and the structural relaxation is stopped when the residual forces become less than  $10^{-4}$  eV/Å. These parameters ensure a good convergence. Derived structural details from the VASP DFT code are at 0 K.

## Details of calculations and parameters

The formation energy of impurities ( $E_{\text{formation}}$ ) is a physical quantity used to judge the difficulty of incorporating different ions into the lattice and characterize the influence of doping on the stability of the system structure. The thermodynamic stability can be expressed by the formation energy ( $E_{\text{form}}$ ) both in monoclinic phase (1) and orthorhombic phase (2) as follows: <sup>37,38</sup>

$$E_{\text{form}} = E_{\text{tot}}(\text{subst}) - E_{\text{tot}}(\text{Fe}_2\text{W}_3\text{O}_{12}) - n\mu_{\text{Sc}} + n\mu_{\text{Fe}} \quad (1)$$

$$E_{\text{form}} = E_{\text{tot}}(\text{subst}) - E_{\text{tot}}(\text{Sc}_2\text{W}_3\text{O}_{12}) - n\mu_{\text{Fe}} + n\mu_{\text{Sc}} \quad (2)$$

where  $E_{\text{tot}}(\text{subst})$  is total energy of doped sample,  $E_{\text{tot}}(\text{Fe}_2\text{W}_3\text{O}_{12})$  and  $E_{\text{tot}}(\text{Sc}_2\text{W}_3\text{O}_{12})$  is the energy of pristine  $\text{Fe}_2\text{W}_3\text{O}_{12}$  and  $\text{Sc}_2\text{W}_3\text{O}_{12}$ ,  $n$  is the number of the Sc atom substituted by Fe atom in primitive cell and  $\mu_{\text{Sc}}$ ,  $\mu_{\text{Fe}}$  is the chemical potential of Sc and Fe, which is determined by the most stable (ground state) metal phase of Sc and Fe, respectively. With increasing the substitution of  $\text{Sc}^{3+}$ , the formation energy is lowered (Figure 1d), which means the material to be more stable.

The formation energy was calculated based on formula (1) and (2) as below:

The DFT calculation process for monoclinic phase:

$$x = 0.5$$

$$\begin{aligned} E_f &= E_{\text{total}}(\text{Fe}_{12}\text{Sc}_4\text{W}_{24}\text{O}_{96}) - E_{\text{total}}(\text{Fe}_{16}\text{W}_{24}\text{O}_{96}) - 4\mu_{\text{Sc}} + 4\mu_{\text{Fe}} \\ &= -1184.0198 - (-1157.1516) - 4(-1.8516866) + 4(-3.034032) \\ &= -31.5974 \text{ eV} \end{aligned}$$

$$x = 1.0$$

$$\begin{aligned} E_f &= E_{\text{total}}(\text{Fe}_8\text{Sc}_8\text{W}_{24}\text{O}_{96}) - E_{\text{total}}(\text{Fe}_{16}\text{W}_{24}\text{O}_{96}) - 8\mu_{\text{Sc}} + 8\mu_{\text{Fe}} \\ &= -1203.0771 - (-1157.1516) - 8(-1.8517) + 8(-3.034) \\ &= -55.3839 \text{ eV} \end{aligned}$$

The DFT calculation process for orthorhombic phase:

$$x = 1.5$$

$$E_f = E_{\text{total}}(\text{Sc}_6\text{Fe}_2\text{W}_{12}\text{O}_{48}) - E_{\text{total}}(\text{Sc}_8\text{W}_{12}\text{O}_{48}) - 2\mu_{\text{Fe}} + 2\mu_{\text{Sc}}$$

$$\begin{aligned}
&= -609.4511 - (-620.397) - 2(-3.0340323) + 2(-1.8516866) \\
&= 13.31205 \text{ eV}
\end{aligned}$$

$$x = 1.75$$

$$\begin{aligned}
E_f &= E_{total}(Sc_7Fe_1W_{12}O_{48}) - E_{total}(Sc_8W_{12}O_{48}) - \mu_{Fe} + \mu_{Sc} \\
&= -614.868 - (-620.397) - (-3.034) + (-1.8517) \\
&= 6.7173 \text{ eV}
\end{aligned}$$

Table S1 Cell parameters at RT of  $\text{Fe}_{2-x}\text{Sc}_x\text{W}_3\text{O}_{12}$  ( $x = 0.5, 1.0, 1.5, 1.75, 2.0$ ) acquired by Rietveld refinement with FullProf software.

		$\text{Fe}_{1.5}\text{Sc}_{0.5}\text{W}_3\text{O}_{12}$	$\text{Fe}_{1.0}\text{Sc}_{1.0}\text{W}_3\text{O}_{12}$	
Monoclinic $P2_1/c$	$a$ (Å)	15.9726	16.1169	
	$b$ (Å)	9.3645	9.4591	
	$c$ (Å)	15.9163	16.0613	
	$\alpha$ (°)	90	90	
	$\beta$ (°)	109.1129	108.9722	
	$\gamma$ (°)	90	90	
	$V$ (Å <sup>3</sup> )	2249.426	2315.578	
		$\text{Fe}_{0.5}\text{Sc}_{1.5}\text{W}_3\text{O}_{12}$	$\text{Fe}_{0.25}\text{Sc}_{1.75}\text{W}_3\text{O}_{12}$	$\text{Sc}_2\text{W}_3\text{O}_{12}$
Orthorhombic $Pnca$	$a$ (Å)	9.5979	9.6405	9.6711
	$b$ (Å)	13.2011	13.2686	13.3282
	$c$ (Å)	9.5044	9.5478	9.5808
	$\alpha$ (°)	90	90	90
	$\beta$ (°)	90	90	90
	$\gamma$ (°)	90	90	90
	$V$ (Å <sup>3</sup> )	1205.197	1221.337	1234.937

Table S2. Structural parameters of  $\text{Sc}_2\text{W}_3\text{O}_{12}$  after refinement of XRD data at RT.

Atom	occ.	$x$	$y$	$z$	$B$
Sc1	1	0.4676	0.3810	0.2480	0.622
W1	0.5	1/4	0	0.4729	0.641
W2	1	0.1168	0.3557	0.3944	0.624
O1	1	0.0974	0.1397	0.0763	1.232
O2	1	0.1392	0.0705	0.3664	1.931
O3	1	0.0154	0.2598	0.3188	0.897
O4	1	0.3314	0.4072	0.0774	1.233
O5	1	0.0711	0.4722	0.3256	0.490
O6	1	0.2947	0.3288	0.3586	1.831

Table S3. Structural parameters of  $\text{Fe}_{0.25}\text{Sc}_{1.75}\text{W}_3\text{O}_{12}$  after refinement of XRD data at RT.

Atom	Occ.	$x$	$y$	$z$	$B$
Sc1	0.875	0.4678	0.3795	0.2498	0.001
Fe1	0.125	0.4678	0.3795	0.2498	0.001
W1	0.5	1/4	0	0.4730	0.516
W2	1	0.11678	0.3561	0.3956	0.348
O1	1	0.09261	0.1405	0.0881	1.069
O2	1	0.13184	0.0617	0.3631	3.014
O3	1	-0.01086	0.2669	0.3101	5.246
O4	1	0.34159	0.3986	0.0832	3.376
O5	1	0.05485	0.4759	0.3157	3.703
O6	1	0.30055	0.33181	0.3597	0.713

Table S4. Structural parameters of  $\text{Fe}_{0.5}\text{Sc}_{1.5}\text{W}_3\text{O}_{12}$  after refinement of XRD data at RT.

Atom	Occ.	$x$	$y$	$z$	$B$
Sc1	0.75	0.4672	0.3803	0.2494	0.104
Fe1	0.25	0.4672	0.3803	0.2494	0.104
W1	0.5	1/4	0	0.4735	0.515
W2	1	0.1175	0.3559	0.3955	0.429
O1	1	0.0884	0.1336	0.0871	1.286
O2	1	0.1272	0.0628	0.3728	2.922
O3	1	-0.0025	0.2692	0.3077	3.709
O4	1	0.3389	0.4001	0.0933	3.527
O5	1	0.0559	0.4727	0.3163	5.047
O6	1	0.2995	0.3346	0.3577	1.066

Table S5. Structural parameters of  $\text{Fe}_{1.0}\text{Sc}_{1.0}\text{W}_3\text{O}_{12}$  after refinement of XRD data at RT.

Atom	Occ.	$x$	$y$	$z$	$B$
Fe0	1	0.0757	0.0160	0.1812	0.242
Sc1	1	0.5551	0.4524	0.1776	0.258
Fe2	1	0.1909	0.4671	0.0685	1.220
Sc3	1	0.6823	0.0006	0.0546	2.827
W5	1	0.0185	0.7527	0.0070	0.576
W6	1	0.1174	0.3845	0.2604	0.369
W7	1	0.2843	0.1212	0.1361	0.198
W8	1	0.4891	0.2511	0.4798	0.210
W9	1	0.6299	0.1300	0.2762	0.742
W10	1	0.7525	0.3927	0.1157	1.378
O11	1	0.0010	0.1373	0.0895	0.500
O12	1	0.0128	0.4604	0.2644	0.500
O13	1	0.0563	0.8536	0.1045	0.500
O14	1	0.0861	0.6099	0.0065	0.500
O15	1	0.0939	0.1889	0.4994	0.500
O16	1	0.1087	0.1938	0.2655	0.500
O17	1	0.1374	0.4432	0.1701	0.500
O18	1	0.1884	0.0661	0.1503	0.500
O19	1	0.1993	0.4378	0.3647	0.500
O20	1	0.2272	0.0194	0.4593	0.500
O21	1	0.2675	0.6171	0.1250	0.500
O22	1	0.2743	0.3171	0.1181	0.500
O23	1	0.3074	0.0403	0.0496	0.500
O24	1	0.3772	0.1027	0.2401	0.500
O25	1	0.3790	0.3423	0.4241	0.500
O26	1	0.4753	0.3088	0.0876	0.500
O27	1	0.4999	0.1128	0.4182	0.500
O28	1	0.5544	0.0026	0.2800	0.500
O29	1	0.5674	0.1182	0.0030	0.500
O30	1	0.5949	0.3063	0.2669	0.500
O31	1	0.6443	0.4253	0.1218	0.500
O32	1	0.6715	0.0925	0.1833	0.500
O33	1	0.7464	0.2146	0.0621	0.500
O34	1	0.8324	0.3935	0.2160	0.500



Table S6. Structural parameters of  $\text{Fe}_{1.5}\text{Sc}_{0.5}\text{W}_3\text{O}_{12}$  after refinement of XRD data at RT.

Atom	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Fe0	1	0.0759	0.0191	0.1781	0.228
Fe1	1	0.1809	0.4790	0.0744	1.220
Fe2	1	0.5508	0.4708	0.1834	0.258
Sc3	1	0.6893	0.0301	0.0607	2.827
W5	1	0.0152	0.7551	0.0026	0.349
W6	1	0.1157	0.3862	0.2618	0.601
W7	1	0.2840	0.1270	0.1355	0.198
W8	1	0.4848	0.2503	0.4837	0.210
W9	1	0.6340	0.1292	0.2728	0.742
W10	1	0.7536	0.3955	0.1106	1.378
O11	1	0.0010	0.1373	0.0889	1.098
O12	1	0.0128	0.4604	0.2680	1.098
O13	1	0.0563	0.8536	0.1035	1.098
O14	1	0.0861	0.6099	0.0000	1.098
O15	1	0.0939	0.1889	0.4990	1.098
O16	1	0.1087	0.1938	0.2650	1.098
O17	1	0.1374	0.4432	0.1650	1.098
O18	1	0.1884	0.0661	0.1520	1.098
O19	1	0.1993	0.4378	0.3660	1.098
O20	1	0.2272	0.0194	0.4610	1.098
O21	1	0.2675	0.6171	0.1250	1.098
O22	1	0.2743	0.3171	0.1181	1.098
O23	1	0.3074	0.0403	0.0496	1.098
O24	1	0.3772	0.1027	0.2401	1.098
O25	1	0.3790	0.3423	0.4241	1.098
O26	1	0.4753	0.3088	0.0876	1.098
O27	1	0.4999	0.1128	0.4182	1.098
O28	1	0.5544	0.0026	0.2800	1.098
O29	1	0.5674	0.1182	0.0030	1.098
O30	1	0.5949	0.3063	0.2669	1.098
O31	1	0.6443	0.4253	0.1218	1.098
O32	1	0.6715	0.0925	0.1833	1.098
O33	1	0.7464	0.2146	0.0621	1.098
O34	1	0.8324	0.3935	0.2160	1.098

Table S7. The lowest energy after optimizing structures by DFT calculation for  $\text{Fe}_{2-x}\text{Sc}_x\text{W}_3\text{O}_{12}$  both in monoclinic phase ( $x=0.0, 0.5, 1.0$ ) and orthorhombic phase ( $x=1.5, 1.75, 2.0$ ).

Molecular formula	Unit cell formula	Total energy in a unit cell
<i>Mono</i> : $\text{Fe}_2\text{W}_3\text{O}_{12}$ ( $x=0.0$ )	$\text{Fe}_{16}\text{W}_{24}\text{O}_{96}$	-1157.1516 eV
<i>Mono</i> : $\text{Fe}_{1.5}\text{Sc}_{0.5}\text{W}_3\text{O}_{12}$ ( $x=0.5$ )	$\text{Fe}_{12}\text{Sc}_4\text{W}_{24}\text{O}_{96}$	-1184.0198 eV
<i>Mono</i> : $\text{Fe}_{1.0}\text{Sc}_{1.0}\text{W}_3\text{O}_{12}$ ( $x=1.0$ )	$\text{Fe}_8\text{Sc}_8\text{W}_{24}\text{O}_{96}$	-1203.0771 eV
<i>Orth</i> : $\text{Fe}_{0.5}\text{Sc}_{1.5}\text{W}_3\text{O}_{12}$ ( $x=1.5$ )	$\text{Sc}_6\text{Fe}_2\text{W}_{12}\text{O}_{48}$	-609.4511 eV
<i>Orth</i> : $\text{Fe}_{0.25}\text{Sc}_{1.75}\text{W}_3\text{O}_{12}$ ( $x=1.75$ )	$\text{Sc}_7\text{Fe}_1\text{W}_{12}\text{O}_{48}$	-614.8677 eV
<i>Orth</i> : $\text{Sc}_2\text{W}_3\text{O}_{12}$ ( $x=2.0$ )	$\text{Sc}_8\text{W}_{12}\text{O}_{48}$	-620.397 eV

The potential energy of Fe and Sc:  $\mu_{\text{Fe}} = -3.0340$  eV  $\mu_{\text{Sc}} = -1.8516$  eV

Table S8. List of electronegativity of elements used in this work.

Element	Allred-Rochow <sup>39, 40</sup>
Sc	1.2
Al	1.47
Fe	1.64
In	1.49
Ga	1.82
Hf	1.23
Mg	1.23
W	1.4

Table S9. Averaged effective electronegativities ( $\chi_{eff}$ ) of tungstate  $A_2W_3O_{12}$ -based compounds are calculated using the Allred-Rochow's scale and the corresponding phase transition temperatures acquired from references.

Tungstate $A_2W_3O_{12}$ -based compounds	$\chi_{eff}$	Phase transition temperature (K)	References
$In_2W_3O_{12}$	-0.101	521.15	
$In_{1.9}Sc_{0.1}W_3O_{12}$	-0.104	497.15	
$In_{1.7}Sc_{0.3}W_3O_{12}$	-0.108	487.32	Ref. <sup>43</sup>
$In_{1.5}Sc_{0.5}W_3O_{12}$	-0.113	420.15	
$InScW_3O_{12}$	-0.125	320.15	
$Al_2W_3O_{12}$	-0.105	251.25	
$Al_{1.9}Sc_{0.1}W_3O_{12}$	-0.107	237.95	
$Al_{1.8}Sc_{0.2}W_3O_{12}$	-0.109	212.75	Ref. <sup>44</sup>
$Al_{1.7}Sc_{0.3}W_3O_{12}$	-0.111	175.05	
$Al_{1.8}(ZrMg)_{0.1}W_3O_{12}$	-0.109	230	
$Al_2W_3O_{12}$	-0.105	252.15	
$Al_{1.9}Ga_{0.1}W_3O_{12}$	-0.102	294.15	
$Al_{1.8}Ga_{0.2}W_3O_{12}$	-0.099	333.15	Ref. <sup>44</sup>
$Al_{1.7}Ga_{0.3}W_3O_{12}$	-0.096	364.15	
$Al_{1.6}Ga_{0.4}W_3O_{12}$	-0.093	381.15	
$Fe_2W_3O_{12}$	-0.076	687	
$Fe_{1.5}Sc_{0.5}W_3O_{12}$	-0.095	490	Ref. <sup>34</sup>
$Fe_{1.0}Sc_{1.0}W_3O_{12}$	-0.113	320	this work
$Fe_{0.5}Sc_{1.5}W_3O_{12}$	-0.131	210	
$Fe_{1.0}(HfMg)_{0.5}W_3O_{12}$	-0.110	400	
$Fe_{1.4}(HfMg)_{0.3}W_3O_{12}$	-0.097	498	Ref. <sup>42</sup>