

supplementary information

## Hydrate formation and its effects on the thermal expansion properties of $\text{HfMgW}_3\text{O}_{12}$

Gaojie Zeng,<sup>a</sup> Huanli Yuan,<sup>a</sup> Juan Guo,<sup>a</sup> Qiang Sun,<sup>a</sup> Qilong Gao,<sup>a</sup> Mingju Chao,<sup>a</sup> Xiao Ren<sup>\*a</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  
E-mail: ejliang@zzu.edu.cn; rxphy@zzu.edu.cn

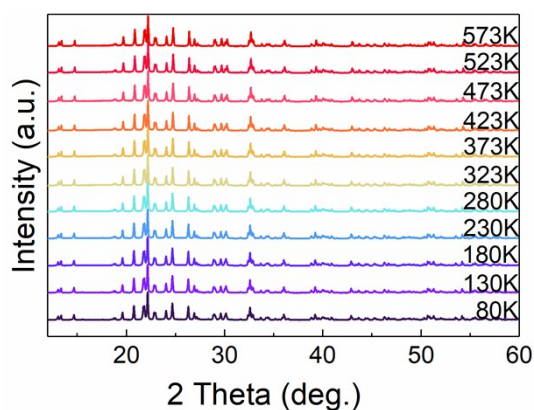


Fig. S1 Temperature dependent XRD patterns of dehydrated  $\text{HfMgW}_3\text{O}_{12}$ .

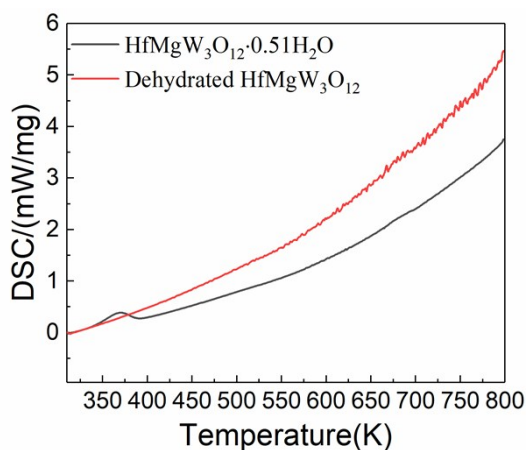
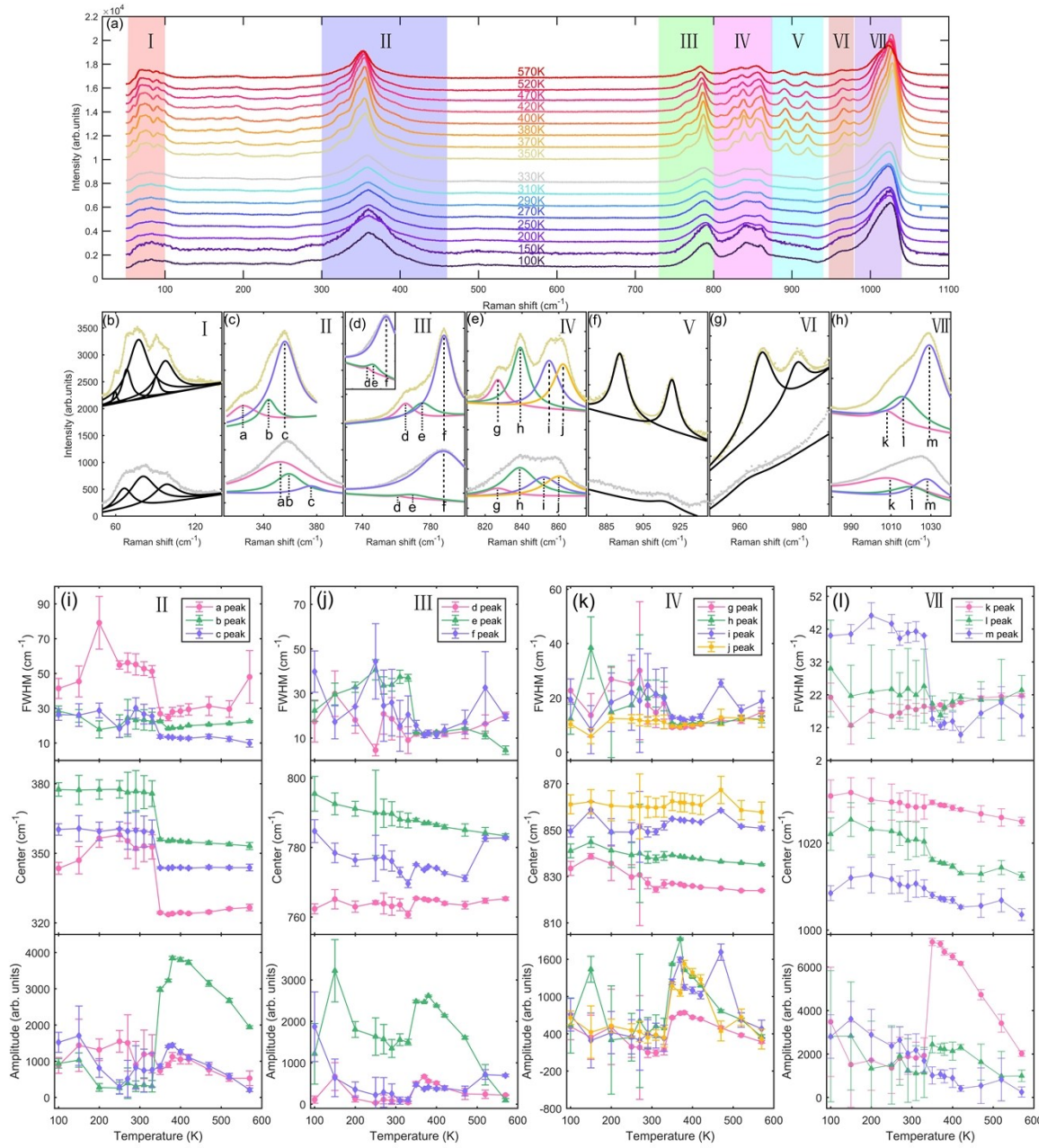
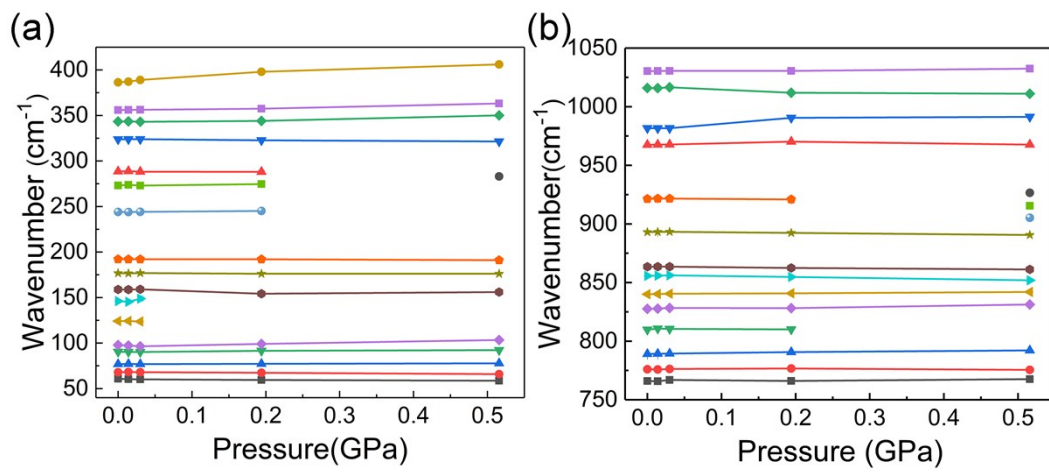


Fig. S2 DSC plots of  $\text{HfMgW}_3\text{O}_{12}\cdot 0.51\text{H}_2\text{O}$  and dehydrated  $\text{HfMgW}_3\text{O}_{12}$ .



**Fig. S3** Analysis of the temperature dependent Raman spectra of  $\text{HfMgW}_3\text{O}_{12}$ : (a) Raman spectra at different temperatures; (b), (c), (d), (e), (f), (g), (h) deconvolutions of the Raman modes at 330 K and 350 K in different regions by Lorentzian fitting; (h), (i), (j), (k) Full width at half maximum (FWHM, First row), peak positions (2<sup>nd</sup> row) and amplitude (3<sup>rd</sup> row) varying with temperature in regions of II, III, IV, VII, respectively .



**Fig. S4**  $\text{HfMgW}_3\text{O}_{12}$  (a) low wavenumber and (b) high wave number mode frequencies of the various Raman modes at different pressure

**Table S1** Atomic positions and occupations in HfMgW<sub>3</sub>O<sub>12</sub>

Atom	x	y	z	B	occ.
Hf1	0.03224(2)	0.49820(4)	0.61646(3)	0.336(1)	1
Mg1	0.46656(20)	0.49823(32)	0.37885(16)	0.284(31)	1
W1	0.74791(3)	0.27705(1)	0.49040(3)	0.295(2)	1
W2	0.12328(2)	0.65300(2)	0.35448(2)	0.227(2)	1
W3	0.61103(2)	0.36350(2)	0.14293(0)	0.303(1)	1
O1	0.08839(38)	0.83577(42)	0.34841(34)	0.962(71)	1
O2	0.87121(43)	0.38910(43)	0.54846(26)	1.041(76)	1
O3	0.01896(42)	0.57784(44)	0.25879(33)	1.318(81)	1
O4	0.32587(39)	0.31998(46)	0.40408(33)	1.203(80)	1
O5	0.07719(40)	0.58259(42)	0.47292(33)	1.114(59)	1
O6	0.30617(39)	0.62166(42)	0.33342(34)	1.549(85)	1
O7	0.50443(41)	0.43465(43)	0.23497(30)	1.235(83)	1
O8	0.57029(39)	0.44213(42)	0.03010(30)	0.942(79)	1
O9	0.15359(39)	0.33888(45)	0.58141(33)	0.926(74)	1
O10	0.63594(41)	0.37356(41)	0.41935(26)	1.445(82)	1
O11	0.21422(37)	0.59986(37)	0.66605(30)	0.367(68)	1
O12	-0.09311(40)	0.68092(38)	0.63469(35)	1.216(75)	1

**Table S2** Bond Lengths of HfMgW<sub>3</sub>O<sub>12</sub>

Bond length type	Bond Length
Hf1-O2	2.067(4) Å
Hf1-O3	2.075(4) Å
Hf1-O5	2.105(4) Å
Hf1-O9	1.967(5) Å
Hf1-O11	2.102(4) Å
Hf1-O12	2.128(4) Å
Mg1-O1	2.005(5) Å
Mg1-O4	2.193(6) Å
Mg1-O6	2.027(5) Å
Mg1-O8	2.108(5) Å
Mg1-O10	2.081(5) Å
W1-O2	1.768(4) Å
W1-O4	1.647(5) Å
W1-O9	1.866(5) Å
W1-O10	1.698(4) Å
W2-O1	1.773(4) Å
W2-O3	1.765(4) Å
W2-O5	1.759(4) Å
W2-O6	1.803(4) Å
W3-O7	1.728(4) Å
W3-O8	1.714(4) Å
W3-O11	1.741(4) Å
W3-O12	1.748(4) Å

**Table S3** Bond angles of HfMgW<sub>3</sub>O<sub>12</sub>

Bond Angle type	Bond Angle
Hf1-O2-W1	172.7(3) deg
Hf1-O3-W2	157.8(3) deg
Hf1-O9-W1	153.4(3) deg
Hf1-O5-W2	177.3(3) deg
Hf1-O11-W3	147.0(3) deg
Mg1-O1-W2	150.9(3) deg
Mg1-O4-W1	144.9(3) deg
Mg1-O6-W2	142.2(3) deg
Mg1-O7-W3	152.0(3) deg
Mg1-O8-W3	168.9(3) deg
Mg1-O10-W1	160.9(3) deg

**Table S4** Mode frequencies and Grüneisen parameters in the Orthorhombic and monoclinic structure of  $\text{HfMgW}_3\text{O}_{12}$

Orthorhombic Phase			Monoclinic phase			Assignment	
Mode frequency / $\text{cm}^{-1}$	$d\omega_i/dP / (\text{cm}^{-1}/\text{GPa})$	$\gamma_i$	Mode frequency / $\text{cm}^{-1}$	$d\omega_i/dP / (\text{cm}^{-1}/\text{GPa})$	$\gamma_i$		
61	-18.86	-17.65	59	1.77	1.63	Translational and librational motions of $\text{WO}_4$ tetrahedra	
68	4.55	3.80	67	-2.15	-1.72		
77	-1.03	-0.76	77	3.69	2.59		
90	-6.91	-4.35	91	2.42	1.44		
98	-45.05	-26.15	99	3.83	2.08		
124	-10.08	-4.61					
146	-21.97	-8.55					
159	3.57	1.28					
177	-0.63	-0.20					
192	-5.46	-1.62					
241	-45.40	-10.71				Bending vibrations of $\text{WO}_4$ tetrahedra	
273	0.95	0.20					
289	-10.02	-1.97					
324	2.85	0.50	318	6.54	1.11		
343	-9.54	-1.58	344	8.55	1.34		
356	10.80	1.72	355	16.40	2.50		
386	86.69	12.75	396	11.98	1.64		
766	30.28	2.25	771	-4.69	-0.33		Asymmetric stretching of $\text{WO}_4$ tetrahedra
776	8.71	0.64	777	-3.78	-0.26		
789	12.50	0.90	790	4.96	0.34		
810	20.31	1.42					
828	21.88	1.50	832	-2.21	-0.14		
840	13.52	0.91	840	2.97	0.19		
856	12.32	0.82	857	-9.11	-0.57		
863	5.58	0.37	861	1.21	0.08		
893	7.58	0.48	893	-3.12	-0.19		
921	7.16	0.44					
			906	-3.89	-0.23	Symmetric stretching of $\text{WO}_4$ tetrahedra	
			916	-2.24	-0.13		
			925	2.78	0.16		
968	6.35	0.37	970	-3.28	-0.18		
982	-1.81	-0.10	996	-4.46	-0.24		
1016	21.33	1.19	1010	3.62	0.19		
1030	7.03	0.39	1031	5.28	0.28		

We use Compressibility  $0.0176 \text{ GPa}^{-1}$  for Orthorhombic Phase and  $0.0185 \text{ GPa}^{-1}$  in the table.

**Table S5** The zone center frequencies for both  $\text{HfMgW}_3\text{O}_{12}$  and  $\text{H}_2\text{O}@ \text{HfMgW}_3\text{O}_{12}$

HfMgW <sub>3</sub> O <sub>12</sub> (cm <sup>-1</sup> )	1water+HfMgW <sub>3</sub> O <sub>12</sub> (cm <sup>-1</sup> )
27.3	29
30	34.7
32	36.4
34.2	36.9
36.1	40
43	44.3
43.4	47.4
44.2	50.9
46.3	53
52.9	56.7
55.2	58.5
56.6	60.9
59.9	62
62.1	63.3
66.9	67.1
68.1	69
68.9	70.4
69.6	71.5
70.1	72
71.3	74.3
74.2	75
74.4	77.4
75.1	79.4
78	82
80.5	83.8
82	84.3
82.3	86.5
84.9	87.9
88.2	88.6
88.9	89.4
90.6	92.1
90.6	92.3
91.3	95.3
92.4	96.4
92.6	97.4
94.3	99.8
98.3	100.8
99	104.7
108.8	109.1
110.2	113.6
116.4	116.2
116.5	118.8
121.7	123.8



121.9	125.9
127.8	128.1
129	128.9
130.1	129.6
131.7	133.1
133.9	135.3
134.3	137.5
136	138.3
142.1	141.2
144.5	142.6
146.2	148.7
150.6	150.4
151.1	151.7
153.4	153.9
153.7	155.5
157.4	158.5
157.6	158.8
163	161.2
166.5	164.5
166.8	167
170	170.3
171	171.6
171.5	176.5
178.3	177
179	179
180.3	183.4
184.7	187.3
187	188.8
189.4	191.3
190.9	192.5
191.2	194.7
195.1	197.1
204	203.1
205.5	207.1
214.1	210.6
218.5	213.6
218.6	215.5
222.3	219.9
236.2	222.8
237.8	234.2
240.9	238.2
244.7	240.3
246.1	243.1
248.7	244

249.6	247.4
250.1	248.5
250.7	249.1
251.7	251.3
252	252.5
254.7	253.5
255.7	254.2
257	256.3
260.9	258.7
261.2	258.9
262.5	261.3
263	261.5
267.8	263.7
270.4	266.2
271.1	267.2
271.2	269.7
271.6	270.8
279.1	272.6
280.9	276.2
282.8	278.3
284.3	279
284.4	282.6
285.7	283.8
285.7	284.5
286.8	285.9
288.3	289
291.5	290.7
294.3	292.7
297.1	294
297.4	295.1
297.8	296
298.1	299.3
299.2	301
304.7	301.5
306.3	302.8
307.2	305.3
309.2	309.9
315.6	311.7
320.8	313.4
321.9	320.4
324.9	324.1
326.5	325.9
327.5	327.4
329.1	328.7

333.3	332.6
334.5	335.2
339.5	337.1
343.1	340.7
343.5	341.7
344.2	345.1
347.1	346.4
348.7	347.1
349.3	349.4
350.8	350
354.3	356.1
356.3	357.5
356.5	359.7
368.2	362.4
369	365.5
369.1	367.5
370.3	370.5
378.2	371.5
379.4	374.6
385.4	377.2
385.6	378.6
387.5	385.5
662.9	388.8
664.3	390.9
667	401.5
667.9	445.3
669.5	618.6
672.4	636.8
692.7	662.8
692.9	666
694.6	668.4
740	669.8
746.5	675
750.9	693.2
752.8	693.6
757.8	697.2
766.3	724.1
768.2	739.7
775.2	745.6
780.7	750.9
780.9	752.4
785.8	756.5
821.4	761
822.1	767

829.8	777.1
849.9	779.5
850.2	784.2
851.4	788.6
853.8	815.7
864.6	816.4
866.4	823.5
897.3	843.9
899.3	845.7
905.3	848.2
906.7	850.5
912.3	855.4
919.5	865.4
921.6	888.5
923.3	895.5
925.5	896.5
927.2	901.6
928.6	907.9
930.3	909.1
932.5	916.4
933.8	917.7
934.9	920.5
939.1	921.5
941.2	924.2
941.6	926.5
943.7	930.5
	930.8
	932.2
	935.4
	939.1
	943.4
	944.3
	1649.1
	3429
	3536.3

---

## Details of calculations and parameters

In order to gain detailed insights into the interaction of the H<sub>2</sub>O molecule with HfMgW<sub>3</sub>O<sub>12</sub> and understand the absorption behavior of hydrated structure formation, we have performed first-principles calculations. The first-principles calculations are performed based on the density functional theory(DFT) with a generalized gradient approximation(GGA) in the form of PBE (Perdew-Burke-Ernzerhof) <sup>1</sup>implemented in the VASP<sup>2-4</sup> (Vienna *ab-initio* Simulation Package) code, including van der Waals interaction corrections in the form of DFT-D2 method of Grimme<sup>5</sup>. Valence electrons are treated explicitly and their interactions with ionic cores are described by PAW<sup>6-7</sup>(Projector Augmented Wave) pseudopotentials. The wave functions are expanded in a plane wave basis set with an energy cutoff of 500 eV. A *k*-point sampling of 3×3×2 Monkhorst-Pack grids<sup>8</sup> in the first Brillouin zone of the unitcell and a Gaussian smearing with a width of  $\sigma= 0.02$  eV is used in the calculations. The H<sub>2</sub>O@HfMgW<sub>3</sub>O<sub>12</sub> system is modeled by having one H<sub>2</sub>O molecule in a HfMgW<sub>3</sub>O<sub>12</sub> unit cell. All atoms in the unit cell are allowed to relax until the forces on each atom are smaller than 0.01 eV/Å and the energy difference is smaller than 10<sup>-8</sup> eV/atom.

## Notes and references

- 1 J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865-3868
- 2 G. Kresse,; J. Furthmüller, *Comput. Mater. Sci.* 1996, **6**, 15-50
- 3 G. Kresse,; J. Hafner, *Phys. Rev. B* 1993, **47**, 558-561
- 4 G.Kresse, J. Furthmüller, *Phys. Rev. B* 1996, **54**, 11169-11186
- 5 S. Grimme, *J. Comput. Chem.* 2006, **27**, 1787-1799
- 6 P. E.Blöchl, *Phys. Rev. B* 1994, **50**, 17953-17979
- 7 G. Kresse, D. Joubert, *Phys. Rev. B* 1999, **59**, 1758-1775
- 8 H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* 1976, **13**, 5188-5192