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Supporting information for article:

Investigation of thermal behavior of mixed-valent iron borates vonsenite and hulsite containing [O*M*4]$^{n+}$ and [O*M*5]$^{n+}$ oxocentred polyhedra by *in situ* high-temperature Mössbauer spectroscopy, X-ray diffraction and thermal analysis

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Table S1

Chemical composition (in wt. %) of vonsenite and hulsite

Vonsenite	Constituent	Mean	Range	Stand. Dev.	Probe Standard
	[FeO_{total}]	77.88	74.67-78.29	0.89	FeS_2
	MgO	1.87	1.53-2.36	0.44	MgO
	MnO	1.56	1.49-1.60	0.06	Mn
	Al_2O_3	0.38	0.19-0.29	0.10	Al_2O_3
	TiO_2	0.02	0.00-0.06	0.04	Ti
	SnO_2	2.85	2.12-3.74	0.82	Sn
	B_2O_3*	13.38			
	[FeO]**	52.71			
	[Fe_2O_3]**	27.99			
	Total	97.93	97.67-98.12	0.23	
Hulsite	Constituent	Mean	Range	Stand. Dev.	Probe Standard
	[FeO_{total}]	78.88	77.29-80.71	1.22	FeS_2
	MgO	1.83	1.65-2.08	0.15	MgO
	MnO	1.52	1.26-1.66	0.16	Mn
	Al_2O_3	0.21	0.00-0.36	0.13	Al_2O_3
	TiO_2	0.01	0.00-0.06	0.03	Ti
	SnO_2	2.31	0.46-3.89	1.24	Sn
	B_2O_3*	13.38			
	[FeO]**	50.24			
	[Fe_2O_3]**	29.51			
	Total	98.13	98.06-98.23	0.08	

*calculated from crystal structure **by Mössbauer spectroscopy

Table S2

Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for vonsenite

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}(Å^2)	Occupancy
			293 K		
Fe1	0	0	0	0.0086 (5)	0.76 (2)
Mg1'	0	0	0	0.0086 (5)	0.24 (2)
Fe2	0.5	0	0.5	0.0125 (5)	
Fe3	0.00114 (14)	0.27499 (10)	0	0.0093 (4)	0.77 (2)
Mg3'	0.00114 (14)	0.27499 (10)	0	0.0093 (4)	0.23 (2)
Fe4	0.74397 (12)	0.38759 (9)	0.5	0.0095 (4)	
O1	0.8450 (5)	0.0425 (4)	0.5	0.0095 (16)	
O2	0.3865 (5)	0.0780 (4)	0	0.0095 (16)	
O3	0.6233 (5)	0.1398 (4)	0.5	0.0080 (16)	
O4	0.1123 (5)	0.1409 (4)	0	0.0062 (15)	
O5	0.3438 (6)	0.2640 (4)	0.5	0.0095 (16)	
B1	0.2706 (9)	0.3625 (6)	0.5	0.006 (2)	
			400 K		
Fe1	0	0	0	0.0087 (5)	0.76
Mg1'	0	0	0	0.0087 (5)	0.24
Fe2	0.5	0	0.5	0.0125 (4)	
Fe3	0.00133 (11)	0.27511 (8)	0	0.0099 (3)	0.77
Mg3'	0.00133 (11)	0.27511 (8)	0	0.0099 (3)	0.23
Fe4	0.74361 (10)	0.38726 (7)	0.5	0.0095 (3)	
O1	0.8454 (4)	0.0431 (3)	0.5	0.0107 (13)	
O2	0.3871 (4)	0.0788 (3)	0	0.0100 (14)	
O3	0.6244 (4)	0.1399 (3)	0.5	0.0105 (14)	
O4	0.1119 (4)	0.1412 (3)	0	0.0081 (13)	
O5	0.3434 (5)	0.2638 (3)	0.5	0.0104 (14)	
B1	0.2705 (7)	0.3622 (5)	0.5	0.006 (2)	

Table S3

Anisotropic atomic displacement parameters (Å^2) of vonsenite

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
			293 K			
Fe1	0.0085 (10)	0.0067 (10)	0.0105 (9)	−0.0021 (8)	0	0
Mg1'	0.0085 (10)	0.0067 (10)	0.0105 (9)	−0.0021 (8)	0	0
Fe2	0.0215 (10)	0.0059 (9)	0.0101 (8)	−0.0031 (7)	0	0
Fe3	0.0107 (7)	0.0065 (7)	0.0108 (7)	0.0015 (6)	0	0
Mg3'	0.0107 (7)	0.0065 (7)	0.0108 (7)	0.0015 (6)	0	0
Fe4	0.0112 (6)	0.0080 (6)	0.0095 (6)	0.0017 (5)	0	0
B1	0.005 (4)	0.010 (4)	0.002 (4)	−0.002 (4)	0	0
O1	0.012 (3)	0.005 (3)	0.012 (3)	−0.002 (2)	0	0
O2	0.006 (3)	0.009 (3)	0.014 (3)	0.000 (2)	0	0
O3	0.009 (3)	0.003 (3)	0.012 (3)	0.002 (2)	0	0
O4	0.003 (3)	0.008 (3)	0.007 (3)	0.003 (2)	0	0
O5	0.012 (3)	0.002 (3)	0.014 (3)	−0.002 (2)	0	0
			400 K			
Fe1	0.0087 (8)	0.0086 (8)	0.0088 (8)	−0.0017 (6)	0	0
Mg1'	0.0087 (8)	0.0086 (8)	0.0088 (8)	−0.0017 (6)	0	0
Fe2	0.0206 (8)	0.0099 (7)	0.0069 (7)	−0.0027 (6)	0	0
Fe3	0.0109 (6)	0.0089 (6)	0.0099 (6)	0.0016 (5)	0	0
Mg3'	0.0109 (6)	0.0089 (6)	0.0099 (6)	0.0016 (5)	0	0
Fe4	0.0107 (5)	0.0104 (5)	0.0074 (5)	0.0012 (4)	0	0
B1	0.005 (4)	0.012 (4)	0.001 (3)	−0.002 (3)	0	0
O1	0.011 (2)	0.009 (2)	0.012 (2)	−0.0022 (19)	0	0
O2	0.007 (2)	0.010 (2)	0.013 (2)	−0.0002 (19)	0	0
O3	0.010 (3)	0.009 (2)	0.012 (2)	0.0005 (18)	0	0
O4	0.005 (2)	0.011 (2)	0.008 (2)	0.0018 (18)	0	0
O5	0.014 (2)	0.007 (2)	0.011 (2)	−0.0014 (19)	0	0

Table S4

Selected bond lengths (Å) of vonsenite

Atom	Distance (Å)	Atom	Distance (Å)
293 K		400 K	
Fe1—O4	2.029 (5)	Fe1—O4	2.038 (4)
Fe1—O4	2.029 (5)	Fe1—O4	2.038 (4)
Fe1—O1	2.179 (4)	Fe1—O1	2.186 (3)
Fe1—O1	2.179 (4)	Fe1—O1	2.186 (3)
Fe1—O1	2.179 (4)	Fe1—O1	2.186 (3)
Fe1—O1	2.179 (4)	Fe1—O1	2.186 (3)
<Fe1—O>$_6$	2.13	<Fe1—O>$_6$	2.14
Fe2—O3	2.073 (5)	Fe2—O3	2.088 (4)
Fe2—O3	2.073 (5)	Fe2—O3	2.088 (4)
Fe2—O2	2.101 (4)	Fe2—O2	2.110 (3)
Fe2—O2	2.101 (4)	Fe2—O2	2.110 (3)
Fe2—O2	2.101 (4)	Fe2—O2	2.110 (3)
Fe2—O2	2.101 (4)	Fe2—O2	2.110 (3)
<Fe2—O>$_6$	2.09	<Fe2—O>$_6$	2.10
Fe3—O4	1.952 (6)	Fe3—O4	1.955 (4)
Fe3—O2	2.105 (6)	Fe3—O2	2.101 (4)
Fe3—O3	2.184 (4)	Fe3—O3	2.195 (3)
Fe3—O3	2.184 (4)	Fe3—O3	2.195 (3)
Fe3—O5	2.184 (5)	Fe3—O5	2.195 (4)
Fe3—O5	2.184 (5)	Fe3—O5	2.195 (4)
<Fe3—O>$_6$	2.13	<Fe3—O>$_6$	2.14
Fe4—O4	2.002 (4)	Fe4—O4	2.009 (3)
Fe4—O4	2.002 (4)	Fe4—O4	2.009 (3)
Fe4—O2	2.080 (4)	Fe4—O2	2.092 (3)
Fe4—O2	2.080 (4)	Fe4—O2	2.092 (3)
Fe4—O1	2.081 (6)	Fe4—O1	2.100 (4)
Fe4—O5	2.087 (6)	Fe4—O5	2.090 (5)
<Fe4—O>$_6$	2.06	<Fe4—O>$_6$	2.07
B1—O1	1.362 (10)	B1—O1	1.366 (8)
B1—O3	1.384 (10)	B1—O3	1.377 (8)
B1—O5	1.393 (10)	B1—O5	1.396 (8)
<B1—O>$_3$	1.38	<B1—O>$_3$	1.38

Table S5

Crystallographic data of hulsite by (Yamnova *et al.*, 1978) and this work

Mineral	Hulsite (Yamnova *et al.*, 1978)	Hulsite (this work, Rietveld refinement of cell parameters)
Formula	$(Fe^{2+},Mg,Fe^{3+},Sn)_3(BO_3)O_2$	
Crystal system, space group	Monoclinic, *P*2/*m*	
a, *b*, *c* (Å)	10.681 (5), 3.094 (2), 5.433 (3)	10.6786 (1), 3.0767 (1), 5.4641 (2)
β (°)	94.15 (4)	93.73 (2)
V (Å^3)	179.07	179.14 (2)
Z		2
R_p (%)	–	3.78
R_{wp} (%)	7.8	5.63
R_{exp} (%)	6.6	2.81
GOF	–	2.01

Table S6

Atomic positional and isotropic displacement parameters (Å^2) of hulsite (Yamnova *et al.*, 1978)

Atom	*x*	*y*	*z*	B_{iso}
Fe1	0	0	0	–0.75
Fe2	0	0.5	0.5	1.05
Fe3	0.5	0	0	0.17
Fe4	0.5	0	0.5	0.19
Fe5	0.2751 (4)	0.5	0.2190 (7)	0.83
O1	0.303 (1)	0	0.493 (3)	0.14
O2	0.470 (1)	0.5	0.240 (3)	0.20
O3	0.694 (1)	0	0.051 (3)	0.27
O4	0.890 (1)	0	0.308 (3)	0.17
O5	0.093 (1)	0.5	0.183 (3)	0.51
B1	0.760 (2)	0	0.288 (4)	0.37

Table S7

Selected bond lengths (Å) of hulsite (Yamnova *et al.*, 1978)

Atom	Distance (Å)
Fe1—O5 (×4)	2.05
Fe1—O1 (×2)	2.11
<Fe1—O>$_6$	2.07
Fe2—O4 (×4)	2.18
Fe2—O5 (×2)	2.03
<Fe2—O>$_6$	2.13
Fe3—O2 (×4)	2.08
Fe3—O3 (×2)	2.09
<Fe3—O>$_6$	2.08
Fe4—O2 (×4)	2.08
Fe4—O1 (×2)	2.09
<Fe4—O>$_6$	2.08
Fe5—O1 (×2)	2.18
Fe5—O2	2.10
Fe5—O3	2.19
Fe5—O5	1.96
<Fe5—O>$_6$	2.13
B1—O1	1.39
B1—O3	1.38
B1—O4	1.38
<B1—O>$_3$	1.38

Table S8

Equations of approximation of temperature dependencies of unit cell parameters of vonsenite and hulsite

Mineral	Equation $l(t) = l_0 + l_1t + l_2t^2$				
	$a(t)$ (Å)	$b(t)$ (Å)	$c(t)$ (Å)	$\beta(t)$ (°)	$V(t)$ (Å^3)
Vonsenite	9.3203(3) + 0.000103(5)×t – 0.00000005(2)×t^2	12.2911(4) + 0.000149(7)×t – 0.00000004(2)×t^2	3.0619(7) + 0.000021(1)×t + 0.000000041(4)×t^2		350.76(2) + 0.0106(3)×t + 0.000002(2)×t^2
Hulsite	10.6748(4) + 0.000131(6)×t + 0.00000009(2)×t^2	3.0763(1) + 0.000021(1)×t + 0.00000003(4)×t^2	5.4607(6) + 0.000089(9)×t – 0.00000017(3)×t^2	93.732(2) – 0.091(3)×t + 1.83(8)×t^2	178.94(2) + 0.0063(3)×t – 0.000003(1)×t^2

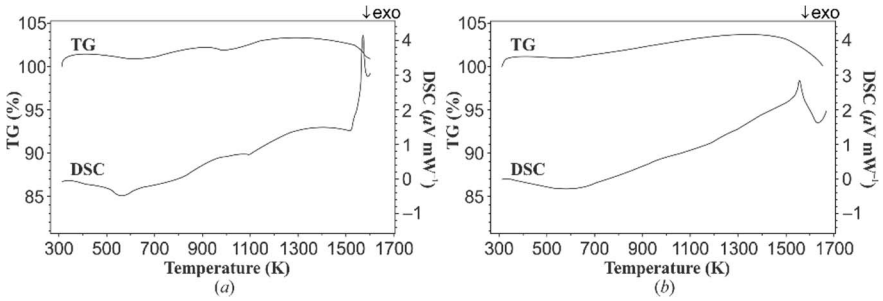

Figure S1 TG and DSC curves of (*a*) vonsenite and (*b*) hulsite.

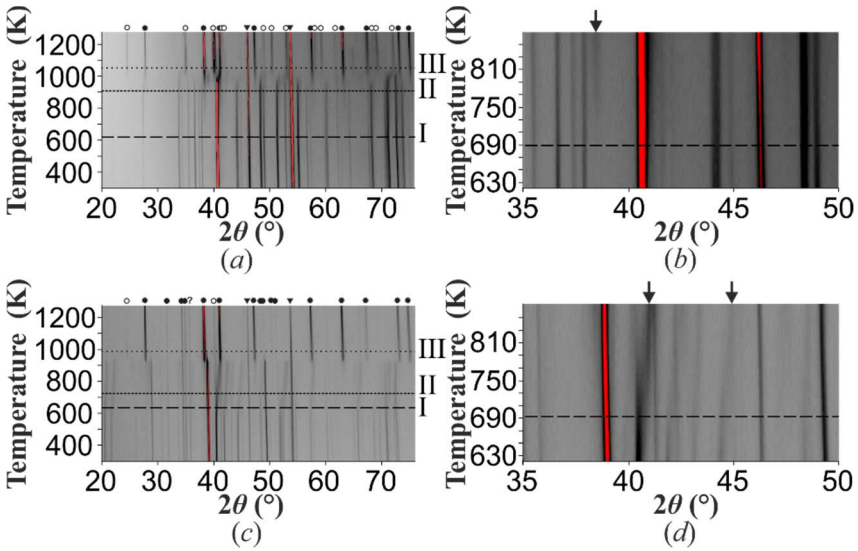

Figure S2 2D-images of the (*a, b*) vonsenite and (*c, d*) hulsite X-ray diffraction patterns (platinum peaks are marked by triangles, diopside – black circles, Fe_2O_3 – asterisks and arrows, warwickite – white circles, steps of the decomposition are shown by dashed horizontal lines and numbered).

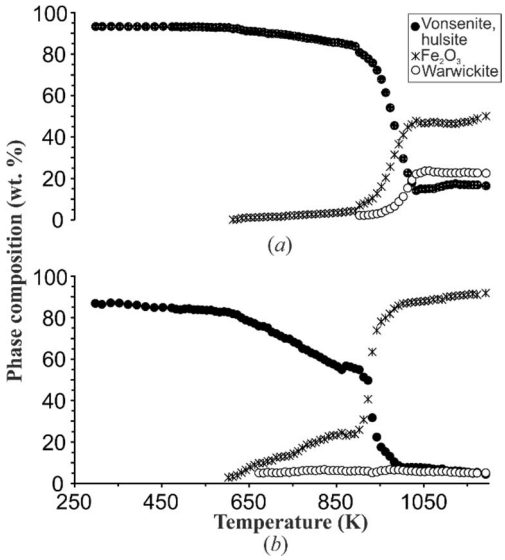

Figure S3 Change of quantitative phase compositions (in wt%) of (*a*) vonsenite and (*b*) hulsite with an increase in temperature (Pt and diopside peaks are not shown).

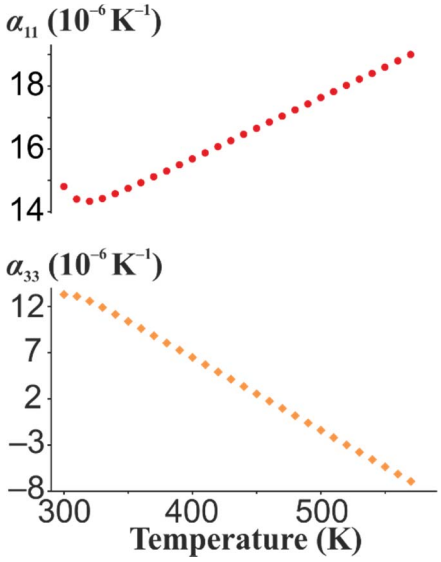

Figure S4 Temperature dependencies of the α_{11} and α_{33} eigenvalues of thermal expansion tensor of hulsite in the temperature range 300–600 K.