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Supporting information for article:

Low-temperature investigation of natural iron-rich oxoborates vonsenite and hulsite: thermal deformations of crystal structure, strong negative thermal expansion and cascades of magnetic transitions

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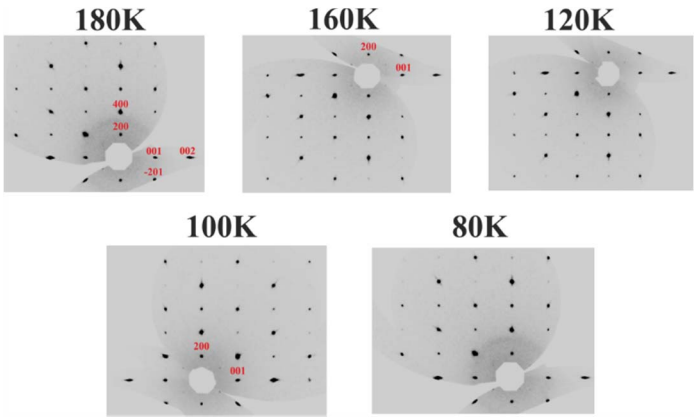

Figure S1 Reciprocal space for vonsenite at 80, 100, 120, 160 and 180 K.

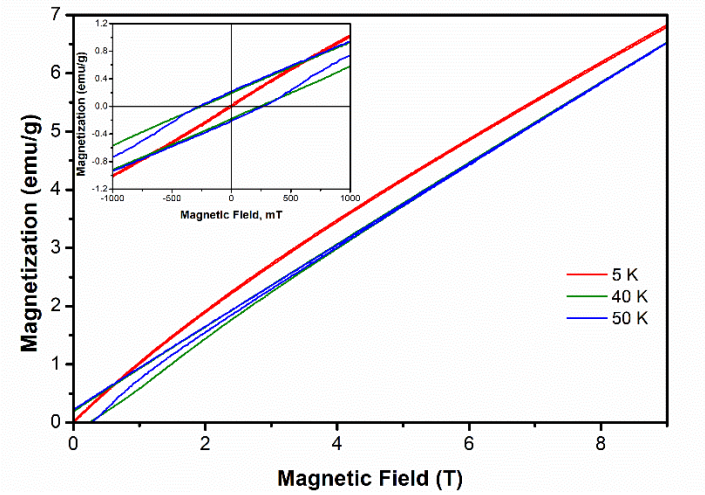

Figure S2 Field dependence of magnetization of hulsite recorded at 5, 40, and 50 K. Inset is the data in the region of low magnetic field.

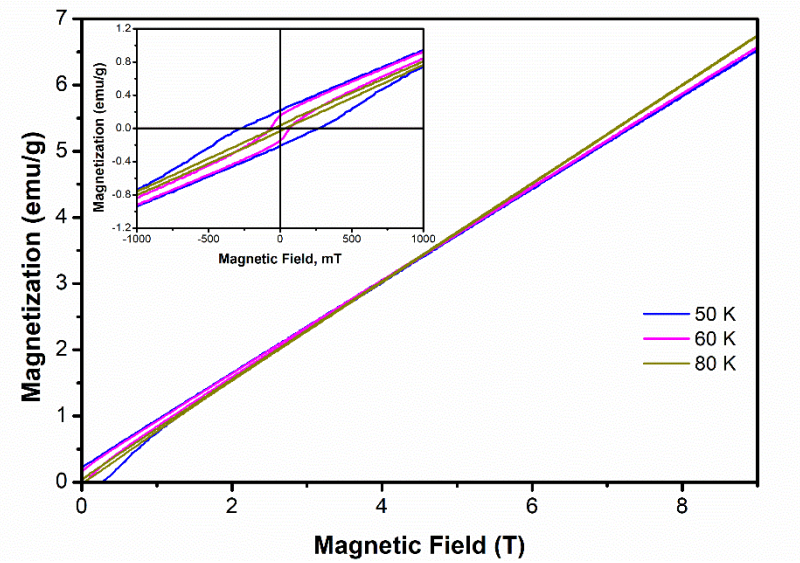

Figure S3 Field dependence of magnetization of hulsite recorded at 50, 60, and 80 K. Inset is the data in the region of low magnetic field.

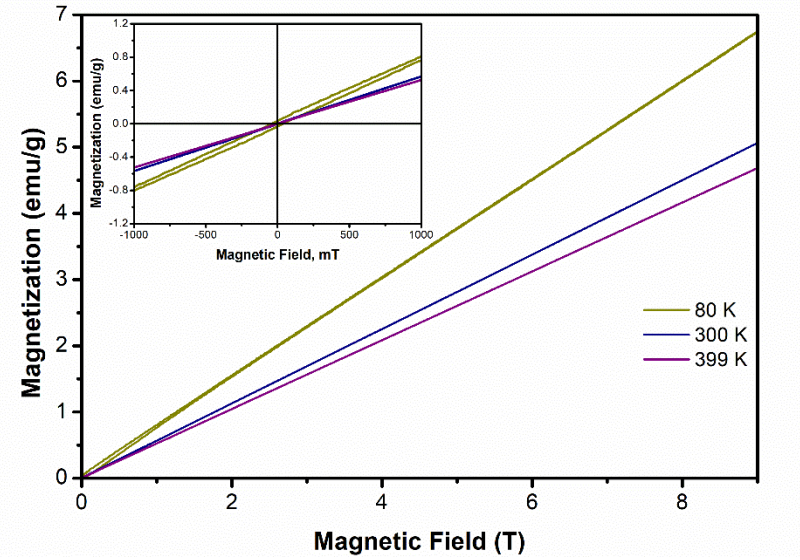

Figure S4 Field dependence of magnetization of hulsite recorded at 80, 300, and 399 K. Inset is the data in the region of low magnetic field.

Table S1 Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for hulsite and vonsenite (100 K).

Hulsite					
Atom	*x*	*y*	*z*	U_{iso}*/U_{eq} (Å^2)	Occupancy
Fe1	0	0	0	0.019 (2)	0.97 (2)
Sn1'	0	0	0	0.019 (2)	0.03 (2)
Fe2	0	0.5	0.5	0.030 (4)	0.6 (2)
Mg2'	0	0.5	0.5	0.030 (4)	0.4 (2)
Fe3	0.5	0	0	0.024 (2)	1
Fe4	0.5	0	0.5	0.021 (2)	1
Fe5	0.2726 (4)	0.5	0.2210 (6)	0.020 (2)	1
O1	−0.6908 (16)	−1	−0.499 (2)	0.019 (4)	1
O2	0.4659 (14)	0.5	0.242 (3)	0.019 (4)	1
O3	−0.6969 (16)	−1	−0.059 (2)	0.019 (4)	1
O4	−0.8872 (13)	−1	−0.291 (3)	0.019 (4)	1
O5	0.0922 (17)	0.5	0.182 (3)	0.019 (4)	1
Vonsenite (100K)					
Atom	*x*	*y*	*z*	U_{iso}*/U_{eq} (Å^2)	Occupancy
Fe1	0	0	0	0.0011 (4)*	0.76
Mg1'	0	0	0	0.0011 (4)*	0.24
Fe2	0.5	0	0.5	0.0168 (5)	1
Fe3	0.0020 (1)	0.2760 (1)	0	0.0106 (4)*	0.77
Mg3'	0.0020 (1)	0.2760 (1)	0	0.0106 (4)*	0.23
Fe4	0.7431 (1)	0.39731 (8)	0.5	0.0036 (3)	1
O1	0.8465 (6)	0.0439 (4)	0.5	0.0059 (10)*	1
O2	0.3871 (6)	0.0777 (4)	0	0.0067 (10)*	1
O3	0.6233 (6)	0.1410 (4)	0.5	0.0057 (10)*	1
O4	0.1122 (5)	0.1410 (4)	0	0.0026 (9)*	1
O5	0.3460 (5)	0.2622 (4)	0.5	0.0042 (9)*	1
B1	0.2714 (8)	0.3606 (6)	0.5	0.0014 (13)*	1

Table S2 Anisotropic atomic displacement parameters (Å^2) of hulsite and vonsenite (100 K).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hulsite						
Fe1	0.037 (5)	0.015 (3)	0.003 (6)	0	−0.001 (2)	0
Sn1'	0.037 (5)	0.015 (3)	0.003 (6)	0	−0.001 (2)	0
Fe2	0.045 (7)	0.026 (6)	0.019 (5)	0	−0.005 (3)	0
Mg2'	0.045 (7)	0.026 (6)	0.019 (5)	0	−0.005 (3)	0
Fe3	0.042 (4)	0.010 (3)	0.020 (3)	0	0.004 (3)	0
Fe4	0.024 (4)	0.024 (4)	0.015 (3)	0	0.000 (3)	0
Fe5	0.038 (3)	0.016 (2)	0.007 (3)	0	0.001 (2)	0
O1	0.031 (8)	0.018 (7)	0.006 (8)	0	−0.001 (3)	0
O2	0.031 (8)	0.018 (7)	0.006 (8)	0	−0.001 (3)	0
O3	0.031 (8)	0.018 (7)	0.006 (8)	0	−0.001 (3)	0
O4	0.031 (8)	0.018 (7)	0.006 (8)	0	−0.001 (3)	0
O5	0.031 (8)	0.018 (7)	0.006 (8)	0	−0.001 (3)	0
Vonsenite (100K)						
Fe2	0.0174 (9)	0.0146 (9)	0.0184 (9)	−0.0007 (7)	0	0
Fe4	0.0041 (5)	0.0037 (5)	0.0028 (5)	−0.0008 (4)	0	0

Table S3 Selected bond lengths (Å) of hulsite and vonsenite (100 K).

Bond	Distance (Å)	BVS (v.u.)	Bond	Distance (Å)	BVS (v.u.)
Hulsite					
Fe1—O4^{i}	2.04 (2)	0.46	Fe4—O1^{vi}	2.03 (2)	0.46
Fe1—O4^{ii}	2.04 (2)	0.46	Fe4—O1^{xii}	2.03 (2)	0.46
Fe1—O5^{iii}	2.05 (1)	0.46	Fe4—O2^{iii}	2.10 (1)	0.38
Fe1—O5	2.05 (1)	0.46	Fe4—O2	2.10 (1)	0.38
Fe1—O5^{iv}	2.05 (1)	0.46	Fe4—O2^{xiii}	2.10 (1)	0.38
Fe1—O5^{v}	2.05 (1)	0.46	Fe4—O2^{xiv}	2.10 (1)	0.38
<Fe1—O>$_6$	2.04	2.76	<Fe4—O>$_6$	2.07	2.46
Fe2—O4^{vi}	2.22 (1)	0.26	Fe5—O1^{vi}	2.18 (1)	0.30
Fe2—O4^{vii}	2.22 (1)	0.26	Fe5—O1^{vii}	2.18 (1)	0.30
Fe2—O4^{ii}	2.22 (1)	0.26	Fe5—O2	2.05 (2)	0.43
Fe2—O4^{viii}	2.22 (1)	0.26	Fe5—O3^{i}	2.20 (1)	0.28
Fe2—O5	2.04 (2)	0.42	Fe5—O3^{xv}	2.20 (1)	0.28
Fe2—O5^{ix}	2.04 (2)	0.42	Fe5—O5	1.92 (2)	0.60
<Fe2—O>$_6$	2.16	1.88	<Fe5—O>$_6$	2.12	2.20
Fe3—O2^{iii}	2.07 (1)	0.42	B1—O1	1.36 (2)	1.03
Fe3—O2	2.07 (1)	0.42	B1—O3	1.41 (2)	0.90
Fe3—O2^{x}	2.07 (1)	0.42	B1—O4	1.37 (2)	1.00
Fe3—O2^{xi}	2.07 (1)	0.42	<B1—O>$_3$	1.38	2.92
Fe3—O3^{i}	2.10 (2)	0.38			
Fe3—O3^{xii}	2.10 (2)	0.38			
<Fe3—O>$_6$	2.08	2.43			
Vonsenite (100K)					
Fe1—O3	2.077(6)	0.41	Fe2—O4	2.022(5)	0.49
Fe1—O3	2.077(6)	0.41	Fe2—O4	2.022(5)	0.49
Fe1—O2	2.084(4)	0.40	Fe2—O1	2.160(4)	0.34
Fe1—O2	2.084(4)	0.40	Fe2—O1	2.160(4)	0.34
Fe1—O2	2.084(4)	0.40	Fe2—O1	2.160(4)	0.34
Fe1—O2	2.084(4)	0.40	Fe2—O1	2.160(4)	0.34
< Fe1—O>$_6$	2.08	2.41	< Fe2—O>$_6$	2.11	2.34

Fe3—O4	1.949(6)	0.50	Fe4—O4	1.985(4)	0.54
Fe3—O2	2.091(6)	0.34	Fe4—O4	1.985(4)	0.54
Fe3—O3	2.155(4)	0.29	Fe4—O5	2.075(5)	0.43
Fe3—O3	2.155(4)	0.29	Fe4—O2	2.076(5)	0.42
Fe3—O5	2.159(4)	0.28	Fe4—O2	2.076(5)	0.42
Fe3—O5	2.159(4)	0.28	Fe4—O1	2.091(6)	0.41
< Fe3—O>$_6$	2.11	1.98	< Fe4—O>$_6$	2.05	2.77
B1—O3	1.365(9)	1.01			
B1—O5	1.380(10)	0.97			
B1—O1	1.394(9)	0.94			
<B1—O>$_3$	1.38	2.92			

BVS – bond valence sum

Table S4 Equations of approximation of temperature dependencies of unit cell parameters of vonsenite.

T **(K)**	**Equation** $l(t) = l_0 + l_1t + l_2t^2$			
	a**(*****t*****) (Å)**	***b*****(*****t*****) (Å)**	***c*****(*****t*****) (Å)**	***V*****(*****t*****) (Å^3)**
93–115	9.3771(1) – 0.001221(2)×t + 0.0000052(1)×t^2	12.3791(2) – 0.00179(3)×t + 0.0000079(2)×t^2	3.0555(3) + 0.000043(6)×t – 0.00000016(3)×t^2	354.66(9) – 0.0921(2)×t + 0.000404(8)×t^2
115–313	9.3051(6) – 0.000027(6)×t + 0.00000027(2)× t^2	12.2758(7) – 0.000016(7)×t + 0.00000028 (2)×t^2	3.0599(1) – 0.000021(1)×t – 0.000000077(3)×t^2	349.53(3) – 0.0039(4)×t + 0.000027(1)×t^2

Table S5 Coefficients of approximation of temperature dependencies of unit cell parameters of hulsite.

T **(K)**	**Equation** $l(t) = l_0 + l_1t + l_2t^2$				
	a**(*****t*****) (Å)**	***b*****(*****t*****) (Å)**	***c*****(*****t*****) (Å)**	***β*****(*****t*****) (°)**	***V*****(*****t*****) (Å^3)**
93–120	10.6773(2) – 0.000173(3)×t	3.0759(9) – 0.000052(9)×t	5.4655(2) – 0.000091(2)×t	93.635(3) + 0.86(2)×t	179.14(1) – 0.0091(1)×t
120–390	10.6521(6) + 0.000016(6)×t + 0.00000018(3) ×t^2	3.0673(4) + 0.000018(4)×t + 0.000000012(7)×t^2	5.4506(9) + 0.000028(8)×t + 0.000000032(1)×t^2	93.778(9) – 0.51(9)×t + 1.03(2)×t^2	177.71(5) + 0.0024(4)×t + 0.0000047(8)×t^2
390–523	10.5721(5) + 0.000391(2)×t – 0.00000026(2) ×t^2	3.0781(1) – 0.000033(5)×t + 0.000000012(7)×t^2	5.4506(9) + 0.000028(8)×t + 0.000000077(6)×t^2	93.523(2) + 0.56(5)×t	176.41(2) + 0.0077(9)×t – 0.0000011(1)×t^2