STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 78 (2022)

Supporting information for article:

X-ray diffraction and Mössbauer spectroscopy study of oxoborate azoproite (Mg,Fe^{2+})2(Fe^{3+},Ti,Mg,Al)O2(BO3): an *in situ* temperature-dependent investigation (5 ≤ *T* ≤ 1650 K)

Yaroslav P. Biryukov, Almaz L. Zinnatullin, Irina O. Levashova, Andrey P. Shablinskii, Mikhail A. Cherosov, Rimma S. Bubnova, Farit G. Vagizov, Maria G. Krzhizhanovskaya, Stanislav K. Filatov, Vladimir V. Shilovskikh and Igor V. Pekov

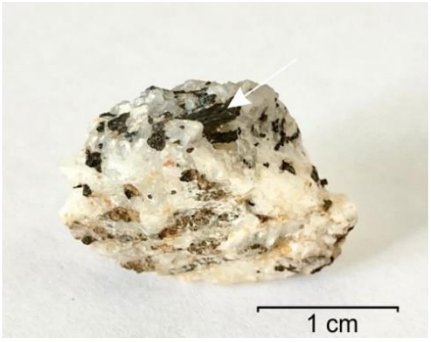

Figure S1 The investigated sample of azoproite shown by white arrow.

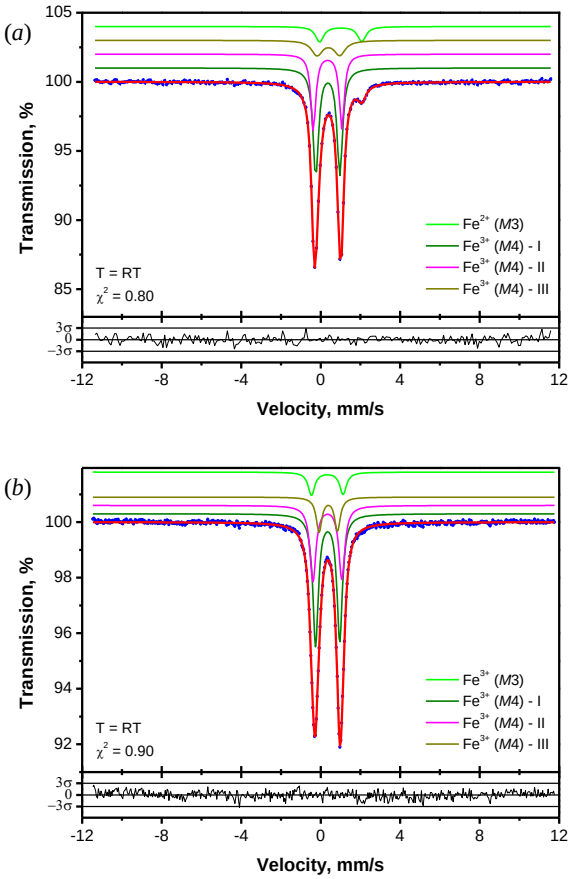

Figure S2 The ^{57}Fe Mössbauer spectra in a wide-velocity range of (*a*) initial azoproite and (*b*) azoproite calcined at 1023 K for 1 hour in air.

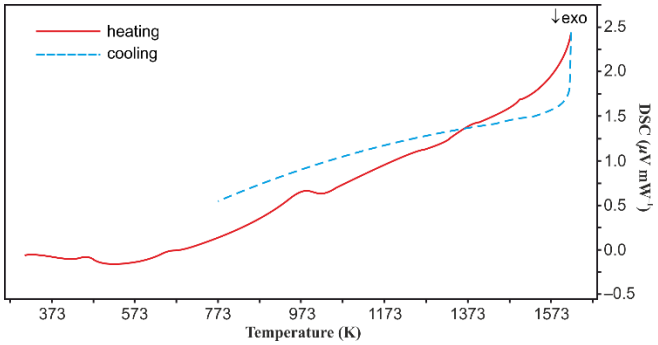

Figure S3 DSC curves of azoproite in heating and cooling regimes.

Table S1 Chemical composition (in wt. %) of azoproite.

Constituent	Mean	Range	Stand. Dev.	Probe Standard
[FeO_{total}]	21.32	20.63 – 22.00	0.97	FeS_2
MgO	45.23	45.01 – 45.45	0.31	MgO
Al_2O_3	3.38	2.97 – 3.78	0.57	$NaAlSi_3O_8$
TiO_2	11.22	11.20 – 11.24	0.03	Ti
B_2O_3*	18.93	18.78 – 19.07	0.20	
[FeO]**	4.00	3.00 – 5.00	1.41	
[Fe_2O_3]**	23.69	23.34 – 24.04	0.49	
Total	100.07	99.03 – 101.10	1.46	

* – calculated from crystal structure

** – calculated from charge balance

Table S2 Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for azoproite (293 K).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq} (Å^2)	Occupancy
Mg1	0	0	0	0.0030 (4)	1
Mg2	0.5	0	0.5	0.0137 (5)	1
Mg3	0.00090 (12)	0.28056 (11)	0	0.0162 (4)	0.95
Fe3	0.00090 (12)	0.28056 (11)	0	0.0162 (4)	0.05
Fe4	0.73794 (7)	0.38401 (6)	0.5	0.0090 (2)	0.4
Ti4	0.73794 (7)	0.38401 (6)	0.5	0.0090 (2)	0.3
Mg4	0.73794 (7)	0.38401 (6)	0.5	0.0090 (2)	0.2
Al4	0.73794 (7)	0.38401 (6)	0.5	0.0090 (2)	0.1
O1	0.8503 (3)	0.0423 (2)	0.5	0.0090 (7)	1
O2	0.3832 (3)	0.0757 (2)	0	0.0109 (7)	1
O3	0.6248 (3)	0.1420 (2)	0.5	0.0097 (7)	1
O4	0.1089 (3)	0.1432 (2)	0	0.0101 (7)	1
O5	0.3495 (3)	0.2628 (2)	0.5	0.0093 (7)	1
B1	0.2735 (4)	0.3608 (3)	0.5	0.0082 (9)	1

Table S3 Refined site-scattering factors and assignment for cation sites in the structure of azoproite (293 K).

Site	SC	SOF	SSF_{exp}[e^-]	Assigned occupancy	SSF_{calc}[e^-]
M4	Ti	0.99308	21.85	$Fe_{0.4}Ti_{0.3}Mg_{0.2}Al_{0.1}$	20.70

*SC – scattering curve used to refine site occupancy; SOF – refined site-occupation factor; SSF_{exp} and SSF_{calc} – experimental and calculated site-scattering factors.

Table S4 Anisotropic atomic displacement parameters (Å^2) of azoproite (293 K).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg1	0.0044 (8)	0.0020 (7)	0.0026 (7)	−0.0001 (4)	0	0
Mg2	0.0124 (9)	0.0141 (9)	0.0146 (10)	0.0013 (6)	0	0
Mg3	0.0157 (7)	0.0155 (7)	0.0174 (7)	−0.0008 (4)	0	0
Fe3	0.0157 (7)	0.0155 (7)	0.0174 (7)	−0.0008 (4)	0	0
Fe4	0.0087 (3)	0.0092 (3)	0.0091 (3)	0.0010 (2)	0	0
Ti4	0.0087 (3)	0.0092 (3)	0.0091 (3)	0.0010 (2)	0	0
Mg4	0.0087 (3)	0.0092 (3)	0.0091 (3)	0.0010 (2)	0	0
Al4	0.0087 (3)	0.0092 (3)	0.0091 (3)	0.0010 (2)	0	0
O1	0.0083 (11)	0.0096 (12)	0.0090 (11)	−0.0002 (8)	0	0
O2	0.0079 (11)	0.0103 (12)	0.0146 (12)	0.0005 (9)	0	0
O3	0.0085 (11)	0.0098 (12)	0.0107 (12)	0.0009 (8)	0	0
O4	0.0094 (12)	0.0067 (11)	0.0141 (13)	0.0007 (8)	0	0
O5	0.0088 (11)	0.0077 (11)	0.0114 (12)	−0.0005 (8)	0	0
B1	0.0070 (16)	0.0102 (17)	0.0072 (16)	0.0024 (12)	0	0

Table S5 Selected bond lengths (Å) of of azoproite (293 K).

Bond	Distance (Å)	BVS (v.u.)	Bond	Distance (Å)	BVS (v.u.)
Mg1—O1^{ix}	2.109 (2)	0.32	M4—O5^{i}	2.076 (3)	0.42
Mg1—O1^{x}	2.109 (2)	0.32	M4—O1^{ii}	2.107 (3)	0.38
Mg1—O1^{xi}	2.109 (2)	0.32	M4—O4^{iii}	1.949 (2)	0.59
Mg1—O1^{iv}	2.109 (2)	0.32	M4—O4^{i}	1.949 (2)	0.59
Mg1—O4	2.026 (3)	0.41	M4—O2^{iii}	2.077 (2)	0.42
Mg1—O4^{xii}	2.026 (3)	0.41	M4—O2^{i}	2.077 (2)	0.42
<M1—O>$_6$	2.08	2.11	<M4—O>$_6$	2.04	2.81
Mg2—O3	2.090 (3)	0.34	B1—O5	1.393 (5)	0.94
Mg2—O3^{iv}	2.090 (3)	0.34	B1—O3^{viii}	1.375 (5)	0.99
Mg2—O2	2.072 (2)	0.36	B1—O1^{viii}	1.385 (5)	0.96
Mg2—O2^{v}	2.072 (2)	0.36	<B1—O>$_3$	1.38	2.89
Mg2—O2^{iv}	2.072 (2)	0.36			
Mg2—O2^{vi}	2.072 (2)	0.36			
<M2—O>$_6$	2.08	2.12			
Mg3—O5^{vii}	2.123 (2)	0.31			
Mg3—O5^{viii}	2.123 (2)	0.31			
Mg3—O3^{vii}	2.117 (2)	0.32			
Mg3—O3^{viii}	2.117 (2)	0.32			
Mg3—O4	1.959 (3)	0.49			
Mg3—O2^{vii}	2.073 (3)	0.36			
<M3—O>$_6$	2.09	2.12			

BVS – bond valence sum

Table S6 Equations of approximation of temperature dependencies of unit cell parameters of azoproite.

T **(K)**	**Equation** $l(t) = l_0 + l_1 t + l_2 t^2$			
	a**(*****t*****) (Å)**	***b*****(*****t*****) (Å)**	***c*****(*****t*****) (Å)**	***V*****(*****t*****) (Å^3)**
93–293	9.2551(1) + 0.000057(3)×t + 0.000000048(1)×t^2	12.2814(2) + 0.000061(6)×t + 0.000000015(3)×t^2	3.0108(3) + 0.000027(1)×t + 0.000000041(5)×t^2	342.23(1) + 0.0069(3)×t + 0.0000069(2)×t^2
293–1373	9.2534(3) + 0.000087(1)×t + 0.000000016(1)×t^2	12.2765(1) + 0.000068(1)×t + 0.000000043(1)×t^2	3.01591(4) + 0.000039(1)×t + 0.000000085(1)×t^2	343.83(1) + 0.0094(7)×t + 0.0000029(6)×t^2