STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 79 (2023)

Supporting information for article:

Crystal structure refinement, low- and high-temperature X-ray diffraction and Mössbauer spectroscopy study of oxoborate ludwigite $(Mg,Fe^{2+},Mn)_2(Fe^{3+},Al,Mg)O_2(BO_3)$ from the Iten'yurginskoe deposit (Eastern Chukotka, Russia)

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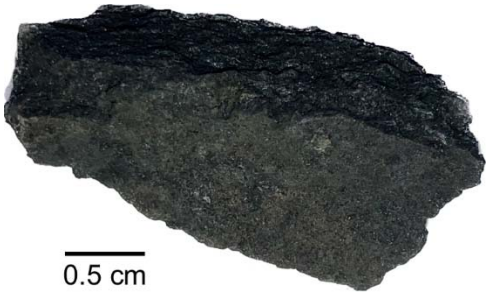

Figure S1 The investigated monomineralic sample of ludwigite.

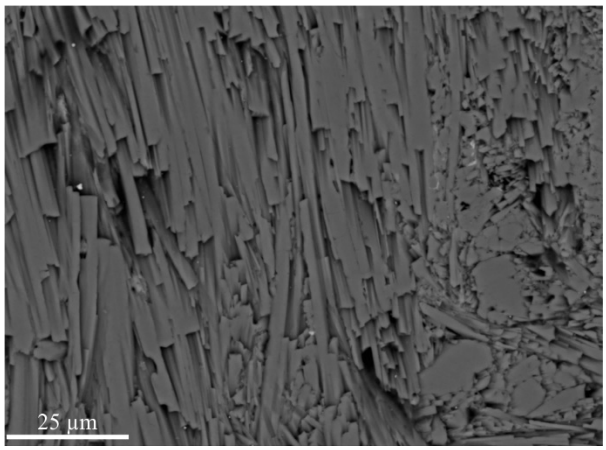

Figure S2 Backscattered electron (BSE) image of the studied ludwigite.

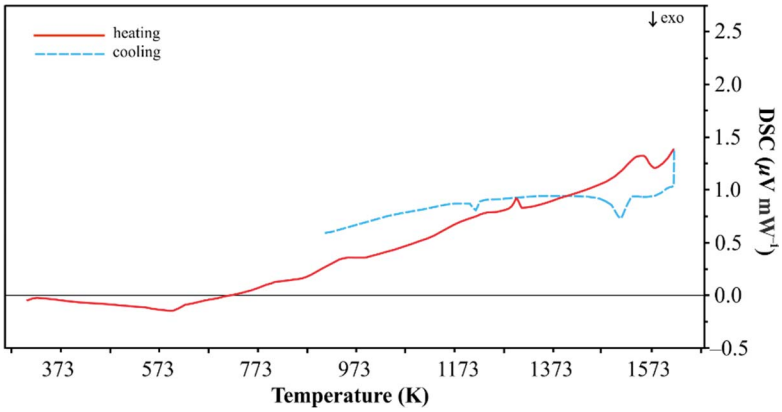

Figure S3 DSC curves of ludwigite recorded in heating and cooling regimes.

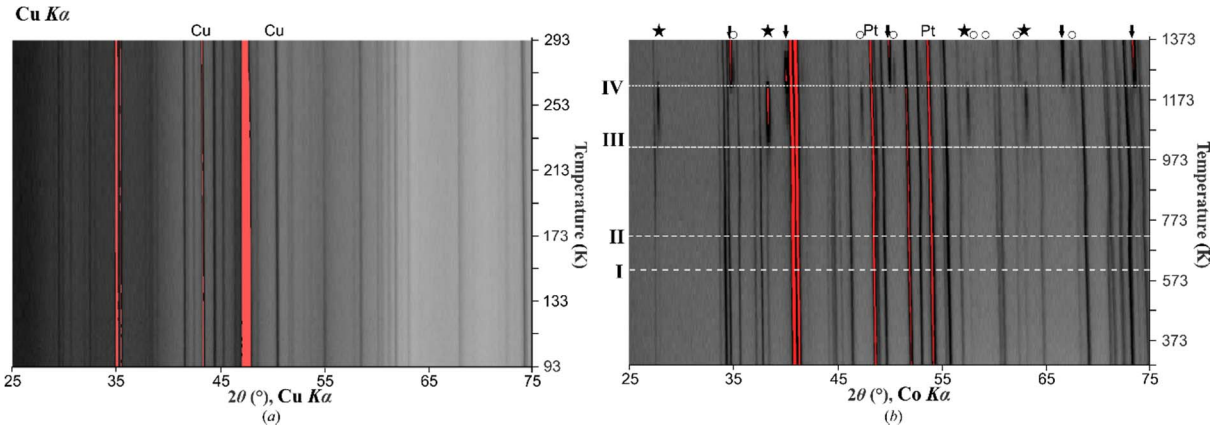

Figure S4 The 2D-image of X-ray diffraction patterns of ludwigite collected at (*a*) low- and (*b*) high temperatures (hematite α-Fe_2O_3 – by stars, warwickite $M_2O(BO_3)$ – by circles, magnetite Fe_3O_4 – by arrows, steps of the decomposition are shown by dashed horizontal lines).

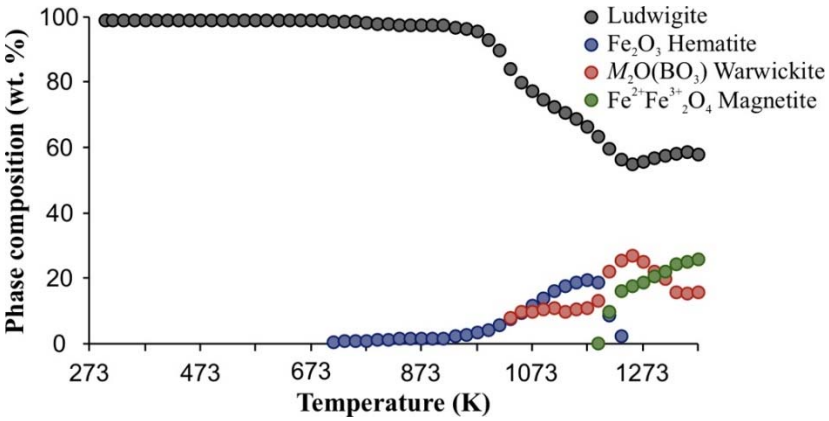

Figure S5 A change of quantitative phase composition (in wt. %) of ludwigite with an increase in temperature.

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

Constituent	Mean	Range	Stand. Dev.	Probe Standard
[FeO_{total}]	43.91	42.64 – 44.67	0.89	FeS_2
MgO	35.27	34.52 – 36.00	0.72	MgO
Al_2O_3	1.97	1.69 – 2.55	0.40	$NaAlSi_3O_8$
MnO	0.23	0.21 – 0.25	0.02	Mn
B_2O_3*	17.75	17.52 – 18.04	0.22	
[FeO]**	10.55	10.01 – 11.06	0.56	
[Fe_2O_3]**	37.07	36.27 – 37.62	0.59	
Total	99.12	98.29 – 100.16	0.78	

* – calculated from crystal structure

** – calculated by charge balance

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq} (Å^2)	Occupancy
Mg1	0	0	0	0.0077 (14)	1
Mg2	0.5	0	0.5	0.0089 (9)	0.48 (2)
Fe2'	0.5	0	0.5	0.0089 (9)	0.52 (2)
Mg3	0.0021 (4)	0.2796 (2)	0	0.0101 (11)	0.98 (1)
Fe3'	0.0021 (4)	0.2796 (2)	0	0.0101 (11)	0.02 (1)
Fe4	0.73942 (19)	0.38552 (11)	0.5	0.0065 (5)	0.90
Al4	0.73942 (19)	0.38552 (11)	0.5	0.0065 (5)	0.08
Mg4	0.73942 (19)	0.38552 (11)	0.5	0.0065 (5)	0.02
O1	0.8499 (8)	0.0442 (5)	0.5	0.010 (2)	1
O2	0.3843 (7)	0.0769 (5)	0	0.012 (2)	1
O3	0.6253 (7)	0.1418 (5)	0.5	0.011 (2)	1
O4	0.1104 (7)	0.1418 (5)	0	0.011 (2)	1
O5	0.3498 (8)	0.2624 (5)	0.5	0.008 (7)	1
B1	0.2733 (14)	0.3588 (8)	0.5	0.010 (3)	1

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

Site	SC	SOF	$SSF_{exp}[e^-]$	Assigned occupancy	$SSF_{calc}[e^-]$
(*M*)4	Mg	2.016	24.19	$Fe_{0.90}Al_{0.08}Mg_{0.02}$	24.68

*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 ludwigite (293 K).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg1	0.010 (3)	0.008 (2)	0.005 (2)	−0.001 (2)	0	0
Mg2	0.0134 (19)	0.0055 (14)	0.0077 (16)	−0.0005 (12)	0	0
Fe2'	0.0134 (19)	0.0055 (14)	0.0077 (16)	−0.0005 (12)	0	0
Mg3	0.012 (2)	0.0090 (17)	0.0094 (19)	0.0011 (16)	0	0
Fe3'	0.012 (2)	0.0090 (17)	0.0094 (19)	0.0011 (16)	0	0
Fe4	0.0051 (9)	0.0075 (8)	0.0071 (8)	0.0021 (7)	0	0
Al4	0.0051 (9)	0.0075 (8)	0.0071 (8)	0.0021 (7)	0	0
Mg4	0.0051 (9)	0.0075 (8)	0.0071 (8)	0.0021 (7)	0	0
O1	0.006 (4)	0.012 (3)	0.012 (4)	0.002 (3)	0	0
O2	0.014 (4)	0.007 (3)	0.016 (4)	0.003 (3)	0	0
O3	0.008 (4)	0.015 (3)	0.010 (3)	−0.004 (3)	0	0
O4	0.016 (4)	0.007 (3)	0.009 (4)	0.000 (3)	0	0
O5	0.011 (4)	0.009 (3)	0.006 (4)	−0.003 (3)	0	0
B1	0.024 (8)	0.006 (4)	0.001 (5)	−0.004 (5)	0	0

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

Bond	Distance (Å)	BVS (v.u.)	Bond	Distance (Å)	BVS (v.u.)
M(1)—O1^{ix}	2.124 (5)	0.31	*M*(4)—O2^{ii}	2.074 (5)	0.42
M(1)—O1^{x}	2.124 (5)	0.31	*M*(4)—O2^{iii}	2.074 (5)	0.42
M(1)—O4	2.023 (6)	0.41	*M*(4)—O5^{ii}	2.087 (7)	0.40
M(1)—O4^{xii}	2.023 (6)	0.41	*M*(4)—O1^{i}	2.120 (7)	0.37
M(1)—O1^{xi}	2.124 (5)	0.31	*M*(4)—O4^{iii}	1.956 (4)	0.57
M(1)—O1^{iv}	2.124 (5)	0.31	*M*(4)—O4^{ii}	1.956 (4)	0.57
<*M*(1)—O>$_6$	2.09	2.07	<*M*(4)—O>$_6$	2.04	2.74
M(2)—O2	2.081 (4)	0.37	B1—O5	1.381 (13)	0.97
M(2)—O2^{iv}	2.081 (4)	0.37	B1—O3^{viii}	1.369 (14)	1.01
M(2)—O3	2.095 (6)	0.36	B1—O1^{viii}	1.388 (13)	0.96
M(2)—O3^{iv}	2.095 (6)	0.36	<B1—O>$_3$	1.38	2.93
M(2)—O2^{vi}	2.081 (4)	0.37			
M(2)—O2^{v}	2.081 (4)	0.37			
<*M*(2)—O>$_6$	2.09	2.20			
M(3)—O3^{vii}	2.127 (5)	0.31			
M(3)—O3^{viii}	2.127 (5)	0.31			
M(3)—O4	1.968 (7)	0.48			
M(3)—O2^{vii}	2.075 (7)	0.36			
M(3)—O5^{vii}	2.131 (6)	0.31			
M(3)—O5^{viii}	2.131 (6)	0.31			
<*M*(3)—O>$_6$	2.09	2.07			

BVS – bond valence sum

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

T (K)	**Equation** $l(t) = l_0 + l_1t + l_2t^2 + l_3t^3$			
	$a(t)$ (Å)	$b(t)$ (Å)	$c(t)$ (Å)	$V(t)$ (Å^3)
93–293	9.24966(21) + 0.0000935(57)×t + 0.000000158(31)×t^2	12.29774(24) + 0.0001103(64)×t + 0.000000220(35)×t^2	3.025677(72) + 0.0000316(19)×t − 0.000000085(11)×t^2	344.171(14) + 0.01016(39)×t + 0.0000218(22)×t^2
	Equation $l(t) = l_0 + l_1t + l_2t^2$			
	$a(t)$ (Å)	$b(t)$ (Å)	$c(t)$ (Å)	$V(t)$ (Å^3)
293–600	9.23899(24) + 0.0000772(33)×t + 0.0000000577(97)×t^2	12.28306(35) + 0.0000918(49)×t − 0.000000035(14)×t^2	3.022538(69) + 0.00002645(98)×t − 0.0000000200(28)×t^2	343.007(21) + 0.00843(31)×t + 0.00000551(90)×t^2

Table S7 Chemical composition of ludwigite, azoproite and vonsenite.

Mineral	Constituent	Mean
Ludwigite $(Mg_{1.70}Fe^{2+}_{0.29}Mn_{0.01})_{\Sigma 2.00}(Fe^{3+}_{0.90}Al_{0.08}Mg_{0.02})_{\Sigma 1.00}O_2(BO_3)$ (this work)	$[FeO_{total}]$	43.91
	MgO	35.27
	Al_2O_3	1.97
	MnO	0.23
	B_2O_3*	17.75
	[FeO]**	10.55
	$[Fe_2O_3]$**	37.07
	Total	99.12
Azoproite $(Mg_{1.81}Fe^{2+}_{0.19})_{\Sigma 2.00}(Fe^{3+}_{0.36}Ti_{0.26}Mg_{0.26}Al_{0.12})_{\Sigma 1.00}O_2(BO_3)$ (Biryukov *et al*., 2022)	$[FeO_{total}]$	21.32
	MgO	45.23
	Al_2O_3	3.38
	TiO_2	11.22
	B_2O_3*	18.93
	[FeO]**	4.00
	$[Fe_2O_3]$**	23.69
	Total	100.07
Vonsenite $(Fe^{2+}_{1.86}Mg_{0.13})_{\Sigma 1.99}(Fe^{3+}_{0.92}Mn^{2+}_{0.05}Sn^{4+}_{0.02}Al_{0.02})_{\Sigma 1.01}O_2(BO_3)$ (Biryukov *et al*., 2020)	$[FeO_{total}]$	77.88
	MgO	1.87
	MnO	1.56
	Al_2O_3	0.38
	TiO_2	0.02
	SnO_2	2.85
	B_2O_3*	13.38
	[FeO]**	52.71
	$[Fe_2O_3]$**	27.99
	Total	97.93

* – calculated from crystal structure

** – calculated by charge balance

Table S8 Site occupancies and $<^{VI}r_{ion}>$ in ludwigite, azoproite and vonsenite (at 293 K).

Atom	Occupancy	$^{VI}r_{ion}$ (Å) (Shannon, 1976)	$<^{VI}r_{ion}>$ (Å)
Ludwigite (this work)			
Mg(1)	1	0.72	0.72
Mg(2)	0.48	0.72	0.75
$Fe(2)^{2+}$	0.52	0.78	
Mg(3)	0.98	0.72	0.72
$Fe(3)^{2+}$	0.02	0.78	
$Fe(4)^{3+}$	0.90	0.645	0.64
$Al(4)^{3+}$	0.08	0.535	
Mg(4)	0.02	0.72	
Azoproite (Biryukov *et al*., 2022)			
Mg(1)	1	0.72	0.72
Mg(2)	1	0.72	0.72
Mg(3)	0.95	0.72	0.72
$Fe(3)^{2+}$	0.05	0.78	
Mg(4)	0.2	0.72	0.64
$Ti(4)^{4+}$	0.3	0.605	
$Fe(4)^{3+}$	0.4	0.645	
$Al(4)^{3+}$	0.1	0.535	
Vonsenite (Biryukov *et al*., 2020)			
$Fe(1)^{2+}$	0.76	0.78	0.77
Mg(1)	0.24	0.72	
$Fe(2)^{2.5+}$	1	0.71	0.71
$Fe(3)^{2+}$	0.77	0.78	0.77
Mg(3)	0.23	0.72	
$Fe(4)^{3+}$	1	0.645	0.645