SUPPLEMENTARY

Table S1. Starting phases (from Inorganic Crystal Structure Database, ICSD) used for the Rietveld refinements and results of phase proportions from the quantitative phase analyses

Run	Phase, No	Phase, Name	ICSD, No	Formula	Content, %
OV-4-2	1	Tourmaline	196351	$(Ca_{0.72}\square_{0.28})(Mg_{1.52}Al_{1.48})(Al_{4.90}Mg_{1.10})\times (Si_6O_{18})(BO_3)_3(OH)_3(O)$	74
	2	Lead feldspar	77512	$Pb(Al_2Si_2O_8)$	12
	3	Quartz	83849	SiO_2	8
	4	Diaspore	52349	$AlO(OH)$	3
OV-5-3	1	Tourmaline	196351	$(Ca_{0.72}\square_{0.28})(Mg_{1.52}Al_{1.48})(Al_{4.90}Mg_{1.10})\times (Si_6O_{18})(BO_3)_3(OH)_3(O)$	55
	2	Talc	26741	$Mg_3Si_4O_{10}(OH)_2$	20
	3	Mullite	99327	$Al_{4+2x}Si_{2-2x}O_{10-x} (x \approx 0.4)$	12
	4	Spinel	172280	$MgAl_2O_4$	9
	5	Quartz	83849	SiO_2	4

Table S2. Crystal parameters, data collection and structure refinement details for Pb-rich tourmaline

Crystal data	
Crystal system, space group	Trigonal, *R*3*m*
a (Å)	15.9508 (10)
c (Å)	7.2024 (6)
V (Å^3)	1587.0 (2)
Z	3
D_x (g cm^{-1})	3.341
Crystal size (mm)	0.08 × 0.05 × 0.04
Data collection and refinement	
Diffractometer	Bruker Kappa Apex DUO CCD
Radiation	Mo*K*α
μ (mm^{-1})	5.90
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12043, 1689, 1673
R_{int}, R_σ	0.038, 0.037
h, *k*, *l* min→max	-25→25, -25→25, -11→11
$2\Theta_{max}$ (°)	70
R_1, wR_2, *S*	0.031, 0.075, 1.23
No. of reflections, parameters, restrains	1689, 89, 1
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.63, -1.00

Table S3. Atomic coordinates and isotropic displacement parameters (Å^2) for Pb-rich tourmaline

Site	*x*	*y*	*z*	U_{iso}	Occupancy
X	2/3	1/3	0.66088(11)	0.0200(2)	$Pb_{0.63}\square_{0.37}$
Y	0.79030(14)	0.39515(7)	0.0808(3)	0.0091(3)	$Al_{0.57}Mg_{0.43}$
Z	0.96360(9)	0.70232(9)	0.71593(17)	0.0069(2)	$Al_{0.84}Mg_{0.16}$
T	0.85898(8)	0.52371(8)	0.43919(17)	0.0084(2)	$Si_{1.00}$
B	0.7766(2)	0.5532(4)	0.8937(9)	0.0082(9)	$B_{1.00}$
O1(*W*)	2/3	1/3	0.2118(12)	0.0180(16)	
O2	0.72699(16)	0.4540(3)	0.9297(7)	0.0131(8)	
O3(*V*)	0.87055(19)	0.7411(4)	0.6166(6)	0.0139(8)	
O4	0.8533(4)	0.42664(18)	0.5324(6)	0.0127(8)	
O5	0.76012(18)	0.5202(4)	0.5125(7)	0.0141(8)	
O6	0.8610(2)	0.5173(2)	0.2161(4)	0.0105(5)	
O7	0.9523(2)	0.6191(2)	0.5161(4)	0.0106(5)	
O8	0.8756(2)	0.6027(2)	0.8780(5)	0.0113(5)	

Table S4. Anisotropic displacement parameters (Å^2) for Pb-rich tourmaline

Site	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
X	0.0158(2)	0.0158(2)	0.0284(4)	0.00788(11)	0	0
Y	0.0082(8)	0.0068(6)	0.0126(8)	0.0041(4)	-0.0022(6)	-0.0011(3)
Z	0.0069(5)	0.0062(5)	0.0076(5)	0.0033(4)	0.0005(4)	0.0003(4)
T	0.0083(5)	0.0073(5)	0.0093(4)	0.0037(4)	-0.0003(4)	-0.0009(4)
B	0.0066(16)	0.002(2)	0.015(2)	0.0009(10)	0.0009(9)	0.0019(17)
O1(*W*)	0.019(2)	0.019(2)	0.015(4)	0.0096(12)	0	0
O2	0.0124(14)	0.0061(16)	0.019(2)	0.0030(8)	0.0010(7)	0.0021(14)
O3(*V*)	0.0145(14)	0.023(2)	0.0072(17)	0.0114(12)	0.0009(8)	0.0019(16)
O4	0.017(2)	0.0108(13)	0.0122(18)	0.0086(10)	0.0008(15)	0.0004(7)
O5	0.0107(13)	0.018(2)	0.016(2)	0.0092(10)	-0.0005(8)	-0.0010(16)
O6	0.0115(12)	0.0118(13)	0.0100(12)	0.0073(10)	0.0007(9)	-0.0007(9)
O7	0.0085(11)	0.0071(12)	0.0117(12)	0.0006(10)	-0.0012(10)	-0.0005(10)
O8	0.0072(12)	0.0098(13)	0.0166(13)	0.0041(10)	0.0000(10)	0.0014(11)

Table S5. Bond lengths (Å) in main polyhedrons and polyhedral volumes (Å^3) of Pb-rich tourmaline (our data) in comparison with published data

	Our data	Pertlik et al., 2003	Berryman et al., 2016			Our data	Pertlik et al., 2003	Berryman et al., 2016	
			MF2	CN11				MF2	CN11
X - O2 [3]	2.555(5)	2.498(3)		2.523(1)	*Z* - O3(*V*) [1]	2.004(6)	1.979(1)	2.000(1)	1.995(1)
- O4 [3]	2.739(6)	2.784(1)		2.768(1)	- O6 [1]	1.910(3)	1.870(1)	1.884(1)	1.907(1)
- O5 [3]	2.794(6)	2.709(1)	-	2.677(1)	- O7 [1]	1.904(4)	1.962(1)	1.890(1)	1.907(1)
Mean	2.696	2.663		2.656	- O7 [1]	1.952(4)	1.893(1)	1.942(1)	1.957(1)
V(XO_9)	32.36	31.25		30.98	- O8 [1]	1.930(4)	1.888(1)	1.888(1)	1.900(1)
Y - O1(*W*) [1]	1.951(5)	2.041(1)	2.029(1)	1.965(1)	- O8 [1]	1.905(4)	1.918(1)	1.917(1)	1.924(1)
- O2 [2]	2.008(6)	2.018(1)	1.951(1)	1.999(1)	*Mean*	1.934	1.918	1.920	1.932
- O3v [1]	2.093(6)	2.129(1)	2.056(1)	2.092(1)	V(ZO_6)	9.42	9.24	9.23	9.40
- O6 [2]	1.955(4)	2.028(1)	1.983(1)	1.970(1)	*T* - O4 [1]	1.648(5)	1.631(1)	1.616(1)	1.627(1)
Mean	1.995	2.044	1.992	1.999	- O5 [1]	1.638(5)	1.645(1)	1.632(1)	1.645(1)
V(YO_6)	10.25	11.00	10.14	10.34	- O6 [1]	1.611(4)	1.594(1)	1.610(1)	1.603(1)
B - O2 [1]	1.395(7)	1.359(1)	1.367(1)	1.381(3)	- O7 [1]	1.604(3)	1.609(1)	1.606(1)	1.600(1)
- O8 [2]	1.372(4)	1.386(3)	1.380(1)	1.373(1)	*Mean*	1.625	1.620	1.616	1.619
Mean	1.380	1.377	1.376	1.375	V(TO_4)	2.20	2.17	2.17	2.17

Table S6. Bond valence (BV) table for Pb-rich tourmaline

	<*X*-O>			<*Y*-O>			<Z-O>			<*T*-O>			Constant
	ΣBV	IC	|Δ|	ΣBV	IC	|Δ|	ΣBV	IC	|Δ|	ΣBV	IC	|Δ|	
$^{X}(Pb^{2+}_{0.60})$	1.159 1.236	1.200	0.041 0.036										1 2
$^{X}(Pb^{4+}_{0.60})$	0.959 0.589	2.400	1.441 1.811										1 2
$^{Y}(Al^{3+}_{1.71}Mg^{2+}_{1.29})$				2.512 2.443	2.570	0.058 0.127							1 2
$^{Z}(Al^{3+}_{5.04}Mg^{2+}_{0.96})$							2.857 2.803	2.840	0.017 0.037				1 2
$^{T}(Si^{4+}_{1.00})$										3.992 3.991	4.000	0.008 0.009	1 2

Note: ΣBV – sum of bond valences; IC – average ionic charge of atoms occupying the site; $|\Delta| = |IC - \Sigma BV|$;
1 – Brese and O'Keeffe, 1991; 2 - Gagné and Hawthorne, 2015.