

K<sub>2.5</sub>Na<sub>7.5</sub>Ba<sub>6</sub>Ca<sub>2</sub>Ti<sub>6</sub>Mn<sub>6</sub>Si<sub>36</sub>B<sub>12</sub>O<sub>119</sub>F<sub>4</sub>

hP212

(175) *P6/m* – 1<sup>13</sup>k<sup>5</sup>j<sup>3</sup>gdca(Na,K,□)<sub>10</sub>Ba<sub>6</sub>(Ca,Y,R)<sub>2</sub>(Mn,Fe,Zn)<sub>6</sub>(Ti,Nb)<sub>6</sub>Si<sub>36</sub>B<sub>12</sub>O<sub>119.5</sub>(OH,F)<sub>5.5</sub> [1], tienshanite

Structural features: Branched 6-rings formed by eighteen vertex-linked SiO<sub>4</sub> tetrahedra are interconnected via Ti(O,OH,F)<sub>6</sub> and (Ti,Nb)(O,OH,F)<sub>6</sub> octahedra and rings of edge-linked (Mn,Fe,Ti,Zn)O<sub>5</sub> square pyramids on one side and units of two vertex-linked BO<sub>4</sub> tetrahedra on the other side to form a 3D-framework; K, Na, (Na,K) and (Ca,Y) in the layers containing the O atoms belonging to two BO<sub>4</sub> tetrahedra; Ba and additional F in the (Ti,Nb,Mn,Fe,Zn) layers.

Cooper M.A. et al. (1998) [1]

B<sub>12</sub>Ba<sub>6</sub>Ca<sub>1.5</sub>F<sub>3.75</sub>Fe<sub>0.72</sub>H<sub>1.75</sub>K<sub>2.25</sub>Mn<sub>4.53</sub>Na<sub>7.09</sub>Nb<sub>1.8</sub>O<sub>121.25</sub>Si<sub>36</sub>Ti<sub>4.63</sub>Y<sub>0.5</sub>Zn<sub>0.32</sub>  
 $a = 1.6785$ ,  $c = 1.0454$  nm,  $c/a = 0.623$ ,  $V = 2.5507$  nm<sup>3</sup>,  $Z = 1$

site	Wyck.	sym.	<i>x</i>	<i>y</i>	<i>z</i>	occ.	atomic environment
O1	12l	1	0.0681	0.1785	0.1569		non-colinear Si <sub>2</sub>
O2	12l	1	0.0902	0.415	0.1619		non-colinear Si <sub>2</sub>
O3	12l	1	0.1536	0.5147	0.3733		single atom Si
Si4	12l	1	0.1792	0.5046	0.22784		tetrahedron O <sub>4</sub>
O5	12l	1	0.1877	0.0272	0.3713		non-coplanar triangle SiMn <sub>2</sub>
Si6	12l	1	0.19159	0.02836	0.2198		tetrahedron O <sub>4</sub>
O7	12l	1	0.2079	0.5953	0.1424		non-colinear BSi
O8	12l	1	0.289	0.0445	0.1619		non-colinear Si <sub>2</sub>
Si9	12l	1	0.36326	0.01531	0.21365		tetrahedron O <sub>4</sub>
O10	12l	1	0.3718	0.0205	0.3668		single atom Si
O11	12l	1	0.4598	0.077	0.1418		non-colinear BSi
O12	12l	1	0.485	0.2201	0.2269		non-colinear BSi
B13	12l	1	0.5125	0.1763	0.1272		tetrahedron O <sub>4</sub>
M14	6k	<i>m</i> ..	0.0596	0.4342	1/2	0.833	
Ti15	6k	<i>m</i> ..	0.0708	0.41959	1/2	0.167	
M16	6k	<i>m</i> ..	0.0848	0.22088	1/2		square pyramid O <sub>5</sub>
M17	6k	<i>m</i> ..	0.1311	0.3586	1/2		single atom Ti
Ba18	6k	<i>m</i> ..	0.50676	0.18579	1/2		single atom F
Na19	6j	<i>m</i> ..	0.018	0.5	0	0.5	
M20	6j	<i>m</i> ..	0.1544	0.3419	0	0.89	monocapped trigonal prism O <sub>7</sub>
O21	6j	<i>m</i> ..	0.5011	0.208	0		non-colinear B <sub>2</sub>
M22	3g	2/ <i>m</i> ..	1/2	0	1/2		colinear Ti <sub>2</sub>
F23	2d	-6..	1/3	2/3	1/2		coplanar triangle Ba <sub>3</sub>
M24	2c	-6..	1/3	2/3	0		tricapped trigonal prism O <sub>9</sub>
K25	1a	6/ <i>m</i> ..	0	0	0		hexagonal prism O <sub>12</sub>

M14 = 0.64Ti + 0.36Nb; M16 = 0.755Mn + 0.12Fe + 0.072Ti + 0.053Zn; M17 = 0.834O + 0.083F + 0.083OH; M20 = 0.766Na + 0.234K; M22 = 0.416F + 0.416OH + 0.168O; M24 = 0.75Ca + 0.25Y

Transformation from published data: *y*,*x*,*z*; origin shift 0 0 1/2

Experimental: single crystal, diffractometer, X-rays, R = 0.022

Remarks: KNa<sub>3</sub>(Na,K,□)<sub>6</sub>Ba<sub>6</sub>(Ca,Y,R)<sub>2</sub>(Mn,Fe,Zn,Ti)<sub>6</sub>(Ti,Nb)<sub>6</sub>Si<sub>36</sub>B<sub>12</sub>O<sub>114</sub>[O<sub>5.5</sub>(OH,F)<sub>3.5</sub>]F<sub>2</sub>. Natural specimen from Dara-i-Pioz, Tajikistan. Composition (Si<sub>36.19</sub>B<sub>12</sub>Ti<sub>4.17</sub>Nb<sub>1.77</sub>Ta<sub>0.03</sub>)(Mn<sub>4.50</sub>Fe<sub>0.72</sub>Zn<sub>0.32</sub>Ti<sub>0.42</sub>)<sub>6</sub>(Ba<sub>6.00</sub>Ca<sub>1.45</sub>Y<sub>0.37</sub>K<sub>2.24</sub>Na<sub>7.08</sub>)(F<sub>3.61</sub>OH<sub>1.89</sub>) from electron microprobe analysis. Partial occupation of site M24 by rare-earth elements (published 0.75Ca + 0.20Y + 0.05R) is ignored here. Short interatomic distances for partly occupied site(s). Hydrogen atoms are not taken into consideration for Pearson symbol, Wyckoff sequence and atomic environments. The basic structure without site splitting was reported in [2].

References: [1] Cooper M.A., Hawthorne F.C., Grew E.S. (1998), Can. Mineral. 36, 1305-1310. [2] Malinovskii I.A., Pobedinskaya E.A., Belov N.V. (1977), Dokl. Akad. Nauk SSSR 236, 863-865.