Tables and figures

Table 1. Crystal structures and lattice parameters.

Silicate	*T* [K]	Space group	Lattice parameters [Å]			Refs.
			a	*b*	*c*	
Green dioptase[1)]	RT	$R\bar{3}$	14.570		7.780	89B1
Green dioptase[2)]	RT	$R\bar{3}$	14.569		7.779	78B1
Green dioptase[2)]	RT	$R\bar{3}$	14.597(2)		7.796(1)	02B1
Green dioptase[3)]	RT	$R\bar{3}$	14.566		7.778	77R1
Green dioptase	RT	$R\bar{3}$	14.61		7.80	55H1
Blue dioptase[4)]	RT	$R\bar{3}$	14.519		7.785	89B1
Blue dioptase[5)]	RT	$R\bar{3}$	14.506		7.783	88B1
Blue dioptase[6)]	RT	$R\bar{3}$	14.506		7.790	88B1
Black dioptase[7)]	1.5	$R\bar{3}$	14.40		7.73	93W1
Black dioptase[8)]	RT	$R\bar{3}$	14.427		7.741	89B1
$CuSiO_3$[9)]	5		4.6227(4)	8.7448(7)	2.8338(2)	04W1
	15		4.6224(4)	8.7464(7)	2.8338(2)	
	295	Pbnm	4.6343(4)	8.7802(7)	2.8330(2)	
$CuSiO_3$[9)]	RT	Pbnm	4.6357(6)	8.7435(9)	2.8334(4)	99O1, 02O1
$CuGeO_3$	5		4.7894(2)	8.402(5)	2.9445(13)	96B1
	295	Pbnm	4.7956(13)	8.466(2)	2.9404(13)	

1) Natural sample, Tsumeb, Namibia;
2) Natural sample, Altyn-Tybe, Kazakstan;
3) Natural sample, Reneville, Kongo;
4) Synthetic, hydrothermal annealing 48 h at 400ºC, 0.5 kbar, produced from green dioptase;
5) Synthetic, hydrothermal annealing 21 days at 250ºC, 2 kbar, produced from black dioptase;
6) Synthetic, hydrothermal annealing 21 days at 220ºC, 1.8 kbar, produced from black dioptase;
7) Heating natural green dioptase[3)] at 500ºC and then at 600ºC;
8) Synthetic, hydrothermal annealing 24 h at 600ºC, 1 bar (air), produced from green dioptase;
9) Synthetic.

Table 2. Atomic coordinates and thermal parameters.

a) Green dioptase, $Cu_6[Si_6O_{18}] \cdot 6H_2O$, having space group $R\bar{3}$ [77R1].

Atom	*x*	*y*	*z*	B_{eq} [Å^2]
Cu	0.40646(4)	0.40251(4)	0.06303(6)	0.41
Si	0.17563(8)	0.21741(8)	0.04130(13)	0.28
O1	0.07147(21)	0.18088(22)	–0.08273(35)	0.64
O2	0.28070(20)	0.29949(21)	–0.06410(34)	0.48
O3	0.15994(21)	0.26776(21)	0.21385(35)	0.50
Ow	0.14217(29)	0.18201(29)	0.57848(42)	1.5
H1	0.146(5)	0.106(5)	0.559(9)	1.0
H2	0.109(6)	0.162(6)	0.68(1)	1.3

Table 2 (cont.)

b) Black dioptase, $Cu_6Si_6O_{18}$, having space group $R\bar{3}$ [89B1].

Atom	*x*	*y*	*z*	B_{eq} [Å^2]
Cu	0.4095(2)	0.3992(2)	0.0564(3)	0.77(5)
Si	0.1761(4)	0.2154(4)	0.0384(6)	0.91(9)
O1	0.0728(3)	0.1810(3)	-0.0854(6)	0.82(6)
O2	0.2844(2)	0.2978(2)	-0.0675(5)	0.48(5)
O3	0.1631(3)	0.2734(3)	0.2088(4)	1.12(7)

c) $CuSiO_3$, having orthorhombic-type structure, space group Pbnm [99O1] (at 295 K).

Atom	*x*	*y*	*z*	Displacement factors[1] [Å^2]·10^3				
				β	β_{11}	β_{22}	β_{33}	β_{12}
Cu	0.5	0	0		59(4)	42(4)	12(3)	27(3)
Si	0.0962(2)	0.25	0.5	26(3)				
O1	0.918(3)	0.25	0	9(5)				
O2	0.285(2)	0.0999(9)	0.5		30(9)	45(10)	6(4)	4(8)

[1] The displacement coefficients β (isotropic) or β_{ij} (anistropic), where $\beta_{13} = \beta_{23} = 0$.

Table 3. Magnetic properties.

a) Dioptase and related compounds.

Silicate	T_N [K]	Θ [K]	p_{eff} [μ_B/Cu atom]	Refs.
$Cu_6Si_6O_{18}\cdot 6H_2O$	70	–70	1.86	67N1
$Cu_6Si_6O_{18}\cdot 6H_2O$	20			58S1
$Cu_6Si_6O_{18}\cdot 6H_2O$		–42		21F1
$Cu_6Si_6O_{18}\cdot 6H_2O$	40…50[1]	–45	1.85	93W1
$Cu_6Si_6O_{18}\cdot 6H_2O$	15.9(1)			02B1
$Cu_6Si_6O_{18}$	110[1]	–180	1.9	93W1
$CuSiO_3$	7.9	–7.2	1.79 (after correction for impurity content) $200 \le T \le 300$ K	00B1
$CuGe_{0.5}Si_{0.5}O_3$		–80	1.80	97W1

[1] Maximum in χ values were identified with T_N; really T_N values given by [02G1] and [02B1] seem to be correct.

b) $CuGe_{1-x}Si_xO_3$ ($x \le 0.03$) [98L1].

Composition (x)	p [μ_B]	T_N[1] [K]			T_{SP}[1] [K]		
		χ	C_p	N	χ	C_p	N
0.004	–	–	0.8	–	13.2	13.1	13.6
0.006	–	–	–	–	12.9	–	–
0.011	0.20	3.8	3.3	3.6	11(1)	10(1)	11(1)
0.019	0.27	5.2	–	4.9			–
0.03	0.23	4.5	–	4.6			–

[1] The Néel and spin-Peierls temperatures, determined from susceptibilities (χ), specific heats (C_p) and neutron (N) studies.

Table 4. Observed and calculated frequencies for $Cu_6[Si_6O_{18}] \cdot 6H_2O$ [95M1].

a) A_g fundamental frequencies.

$\bar{\nu}$ (experimental) [cm^{-1}]		$\bar{\nu}$ (calculated) [cm^{-1}]	Assignment
x(zz)y [95M1]	[74A1]		
72	73	75	Ring rotation and minor Cu–O stretch
99	98	98	
125[a)]	–	123	
131	132	140	
178	178	176	Cu–O stretch, O–Cu–O bend, and ring puckering
225	226	220	
265	267	247	
291	285	281	Cu–Ow stretch
357	356	350	Cu–Ow stretch
399	398	375	
426	428	423	
489	488	473	
561	–	537	
659	660	694	O1 breathing
938	–	899	
957	956	945	O1–Si–O1 bend and Si–O2 stretch
1015	1008[b)]	1024	Si–O1 stretch

[a)] Shoulder; [b)] Doubtful.

b) E_g fundamental frequencies.

$\bar{\nu}$ (experimental) [cm^{-1}]		$\bar{\nu}$ (calculated) [cm^{-1}]	Assignment
x(zz)y [95M1]	[74A1]		
72	73	70	Lattice: Cu motion and ring deformation
99	98	93	Ring rotation and O–Cu–O
115	116	117	O–Cu–O and ring rotation
160	160	171	Ring rotation and Cu–Ow
195	196	203	
222	221	220	
241	241	251	
294	295	290	
327	324	319	Cu–O stretch
399	398	398	Cu–Ow stretch
433[a)]	428	426	
453	454	467	
523	524	504	
660	660	661	
743	744	–	Combination
800[b)]	–	815	O1–Si–O1 bend and Si–O2 stretch
915	913	920	
1005	1008	1013	O1–Si–O1 bend

[a)] Broad; [b)] Broad, weak.

Table 4 (cont.)

c) Infrared active A_u and E_u modes.

A_u modes [cm^{-1}]		E_u modes [cm^{-1}]	
$\bar{\nu}$ (experimental) [74A1]	$\bar{\nu}$ (calculated)	$\bar{\nu}$ (experimental) [74A1]	$\bar{\nu}$ (calculated)
	63		44
78	70		115
	134	140	160
	193		190
	209		216
256	247		231
	308		285
	314		336
344	373	372	394
	437	412	
	458	440	444
	483		480
	715	500	
774	750	564	546
876	918	642	667
978	1008	760	
			880
		932	926
		986	1021