

Tugtupite: High-temperature structures obtained from in situ synchrotron diffraction and Rietveld refinements

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ABSTRACT

The structural behavior of tugtupite, (ideally $\text{Na}_8[\text{Al}_2\text{Be}_2\text{Si}_8\text{O}_{24}]\text{Cl}_2$), a member of the sodalite-group minerals, at room pressure and from 33 to 982 °C on heating, was determined by using in situ synchrotron X-ray powder diffraction data [$\lambda = 0.91997(4)$ Å] and Rietveld refinement. The sample was heated at a rate of 9.5 °C/min and X-ray traces were collected at intervals of 16 °C. The unit-cell parameters for tugtupite increase smoothly and non-linearly to 982 °C. The percent volume change between 33 and 982 °C is 2.97(3)%. In tugtupite, large displacement parameters occur for the Na and Cl atoms, and the Na-Cl bond expands with temperature. The $[\text{Na}_4\text{Cl}]^{3+}$ clusters expand with increases of the Na-Cl bond length by 0.073(3) Å between 33 and 982 °C. This forces the Na atoms toward the plane of the framework six-membered rings, and causes the framework tetrahedra to rotate. The framework TO_4 (T = Al^{3+} , Be^{2+} , or Si^{4+}) tetrahedra distort slightly with temperature, but the T-O distances remain nearly constant. This mechanism causes a fairly high-rate of expansion in tugtupite. If the Na atom reaches approximately the plane of the six-membered ring, because of the increase in bonding to the Na atom, the expansion will be retarded, but tugtupite melts before this occurs. Tugtupite melts at 1029 °C. The NaCl component in tugtupite is lost in two main stages; 1.8 wt% NaCl is first lost at about 1007 °C, and 8.2 wt% NaCl is lost in several steps between 1019 and 1442 °C.

INTRODUCTION

The structure of tetragonal tugtupite (space group $I\bar{4}$), ideally $\text{Na}_8[\text{Al}_2\text{Be}_2\text{Si}_8\text{O}_{24}]\text{Cl}_2$, is isotypic with cubic sodalite, $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Cl}_2$, and the β -cages enclose $[\text{Na}_4\text{Cl}]^{3+}$ clusters (e.g., Danø 1966; Hassan and Grundy 1984, 1991). The framework of tugtupite, $[\text{Al}_2\text{Be}_2\text{Si}_8\text{O}_{24}]$, may be considered as intermediate in composition between the framework of sodalite, $[\text{Al}_6\text{Si}_6\text{O}_{24}]$, and helvite, $[\text{Be}_6\text{Si}_6\text{O}_{24}]$ (Hassan and Grundy 1985). The tetragonal symmetry of tugtupite arises from T cation ordering (T = Al^{3+} , Be^{2+} , and Si^{4+}). Interest in tugtupite arises mainly from the detailed structural effects that result from a framework that consists of three different cations. Previous high-temperature structural work was not done on tugtupite, so the present study was carried out to determine the structural behavior of tugtupite to 982 °C using in situ synchrotron X-ray powder diffraction data.

The general structural features of tugtupite are similar to those of sodalite. The tugtupite framework structure is characterized by four-membered rings (formed by T cations and ignoring O atoms) in the faces of the unit cell, and these rings are linked to form six-membered rings about the corners of the unit cell (Fig. 1). The four-membered rings parallel to (010) have an ordered distribution of T atoms consisting of one Al, one Be, and two Si atoms, whereas the four-membered rings parallel to (001) consists only of Si atoms. As a result of the linkage of the four-membered rings, all the six-membered rings have an ordered arrangement of T atoms consisting of one Al, one Be, and four Si atoms. The Al and Be atoms are diametrically opposite each other in the six-membered rings. The cages contain the Na and

Cl atoms; the Cl atoms are at the corners and center of the unit cell. The Na atoms tetrahedrally coordinate the Cl atom.

EXPERIMENTAL METHODS

The red tugtupite sample is from Ilímaussaq, Narssaq Kommune, South Greenland (Royal Ontario Museum, ROM no. M32790). This sample was previously studied by Hassan and Grundy (1991). The crystals of tugtupite were handpicked and crushed to a powder using an agate mortar and pestle. High-temperature synchrotron X-ray powder diffraction experiments were performed at beam-line X7B of the National Synchrotron Light Source at Brookhaven National Laboratory. The sample was loaded in a quartz capillary (diameter = 0.5 mm, open to air at one end) and was oscillated during the experiment over an angle of 15°. The raw high-temperature X-ray patterns were collected using in situ synchrotron radiation [$\lambda = 0.91997(4)$ Å] at room pressure and from 33 to 982 °C at regular intervals of 16 °C. The sample was heated at a rate of 9.5 °C/min using a horseshoe-shaped heater and controlled using a thermocouple element near the capillary. The data were collected to a maximum 2θ of 50° [$(\sin\theta/\lambda) < 0.46$ Å⁻¹]. An imaging plate (IP) detector (Mar345, 2300 × 2300 pixels) mounted perpendicular to the beam path was used to collect full circle Debye-Scherrer rings with an exposure time of 15 s. An external LaB_6 standard was used to determine the sample-to-detector distance, tilt angle, wavelength, and tilting angle of the IP. The diffraction patterns recorded by the IP were integrated using the Fit2d program (Hammersley 1996).

Of the numerous diffraction traces collected, sixteen patterns were chosen at regular temperature intervals for treatment with the Rietveld method using the *GSAS* and *EXPGUI* programs (Larson and Von Dreele 2000; Toby 2001). For the room-temperature structure, the starting atomic coordinates, cell parameters, isotropic displacement parameters, and space group, $I\bar{4}$, were those of Hassan and Grundy (1991). The refined atomic coordinates were then used as input for the next higher-temperature structure. The site occupancies were fixed to the idealized chemical formula for tugtupite. Refinement of the occupancy factors for the Na and Cl atoms indicate this formula to be appropriate.

In the initial stages, the background was fitted using a Chebyshev polynomial with twenty-four coefficients, and the profiles were fitted using the pseudo-Voigt function and an asymmetry correction term (GV, GW, LY, and Asym terms). The zero-shift was set to zero at all temperatures. A full-matrix least-squares refinement made by varying a scale factor, cell parameters, atomic coordinates, and isotropic

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displacement parameters converged rapidly. Isotropic displacement parameters were used for all atoms. The Al and Si atoms were constrained to have equal isotropic displacement parameters, and the O atoms were set to have equal isotropic values. Finally, the background and profile parameters were also allowed to vary, and the refinement proceeded to convergence. The total number of variables [including structural (23), background (24), profile (4), and a scale factor] was 52 at the end of the refinement, the number of observations (data points) was 2120, and the number of observed reflections was 154 (see footnote in Table 1). The structures refined well at all temperatures. A synchrotron powder X-ray diffraction pattern is shown in Figure 2 as an example. The cell parameters and the Rietveld refinement statistics at various temperatures are listed in Table 1. The atomic coordinates and isotropic displacement parameters are given in Table 2, and the bond distances and angles are listed in Table 3.

RESULTS OF THE STRUCTURE REFINEMENTS AND DISCUSSION

Structure of tugtupite

The general structural features of tugtupite have been described in the introduction and the structure obtained at 33 °C is shown in Figure 1. The BeO_4 and AlO_4 tetrahedra in tugtupite are

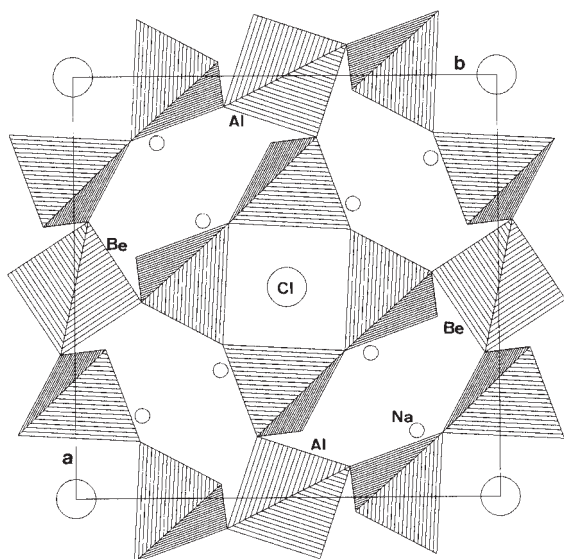


FIGURE 1. Projection of the lower half of the unit-cell structure of tugtupite down [001]. The SiO_4 tetrahedra are unlabeled. The TO_4 tetrahedra are ordered.

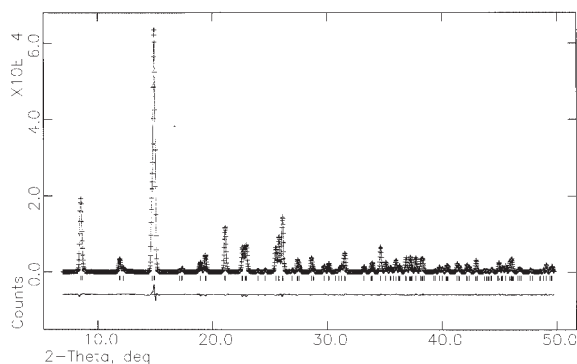


FIGURE 2. Synchrotron X-ray powder diffraction trace for tugtupite at 33 °C, together with the calculated and difference plot from Rietveld refinement.

close to being regular; the Be-O and Al-O distances are 1.640(4) and 1.705(4) Å, respectively (Table 3). The SiO_4 tetrahedra are distorted; in the pure Si-O1-Si linkage, the Si-O distances are 1.620(5) and 1.666(5) Å. The Si-O distance is 1.560(5) Å with a Be linkage, and it is 1.645(5) Å with an Al linkage. The mean $\langle\text{Si-O}\rangle$ distance is 1.623(3) Å. The individual Si-O bond length varies with other T cations in the Si-O-T linkage, but the mean $\langle\text{Si-O}\rangle$ bond length appears constant (see Hassan and Grundy 1991).

The Na atom is fivefold coordinated by one Cl and four O atoms that are less than 2.6 Å away (Table 3), in contrast to its fourfold coordination in sodalite (see Hassan and Grundy 1991). In tugtupite, there is an O1* atom at a further distance, [3.051(3) Å], which plays an important role in the thermal behavior of tugtupite. When the O1* atom is included, the average $\langle\text{Na-O}\rangle$ distance is 2.538(2) Å, and this average is nearly constant with temperature (see below). In addition, there is an O3* atom that is about 3.3 Å away from the Na atom, but because of this long distance, it is not included in the

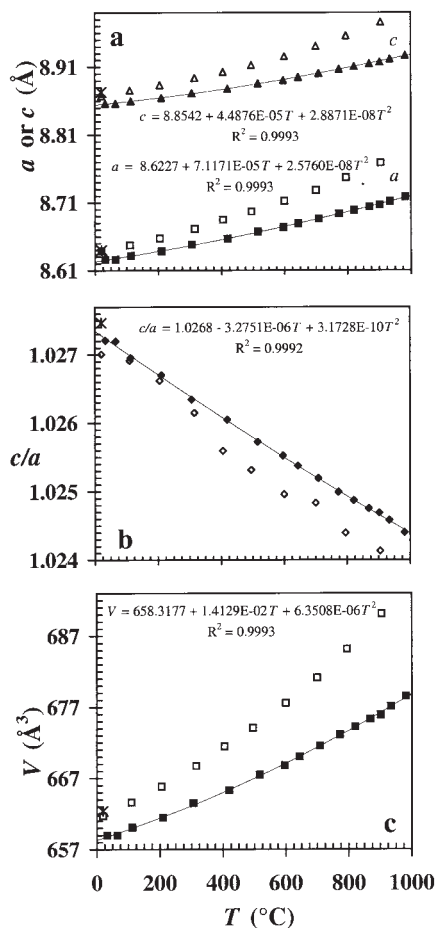


FIGURE 3. Unit-cell parameters variation with temperature: (a) The expansion of the a parameter is higher than that of c . (b) The ratio c/a decreases smoothly with temperature. (c) The V parameter increases smoothly with temperature. Equations of least-squares fits to the data are given as inserts. Error bars are smaller than the symbols. Data from Henderson and Taylor (1977; open symbols) and Hassan and Grundy (1991; shown as X at 20 °C) are included for comparison.

TABLE 1. Tugtupite: Rietveld refinement* and unit-cell data at different temperatures (°C)

T (°C)	a (Å)	c (Å)	c/a	V (Å ³)	R _p	R _{wp}	Exp. R _{wp}	R _f ²	χ ²
20*	8.640(1)	8.873(1)	1.0270(166)	662.4					
33	8.62597(7)	8.8564(1)	1.0267(14)	658.98(1)	0.0180	0.0231	0.0175	0.0268	1.774
65	8.62591(7)	8.8562(1)	1.0267(14)	658.96(1)	0.0181	0.0233	0.0176	0.0273	1.788
113	8.63144(7)	8.8598(1)	1.0265(14)	660.07(1)	0.0181	0.0234	0.0177	0.0325	1.790
210	8.63812(7)	8.8644(1)	1.0262(14)	661.44(1)	0.0175	0.0225	0.0179	0.0283	1.622
306	8.64804(7)	8.8715(1)	1.0258(15)	663.49(1)	0.0178	0.0229	0.0180	0.0320	1.652
419	8.65669(7)	8.8778(1)	1.0256(16)	665.29(1)	0.0184	0.0238	0.0181	0.0343	1.771
516	8.66710(8)	8.8857(1)	1.0252(17)	667.48(1)	0.0180	0.0236	0.0182	0.0364	1.726
596	8.67339(8)	8.8904(1)	1.0250(18)	668.81(1)	0.0188	0.0249	0.0183	0.0356	1.901
644	8.67908(8)	8.8950(1)	1.0249(18)	670.03(1)	0.0181	0.0240	0.0183	0.0402	1.767
709	8.68613(8)	8.9006(1)	1.0247(18)	671.54(1)	0.0175	0.0230	0.0185	0.0366	1.572
773	8.69349(8)	8.9064(1)	1.0245(19)	673.12(1)	0.0176	0.0235	0.0187	0.0533	1.614
821	8.69872(8)	8.9107(1)	1.0244(19)	674.25(1)	0.0176	0.0233	0.0188	0.0526	1.571
869	8.70359(8)	8.9147(1)	1.0243(19)	675.31(1)	0.0174	0.0230	0.0189	0.0467	1.518
902	8.70633(9)	8.9169(1)	1.0242(20)	675.90(2)	0.0177	0.0236	0.0189	0.0472	1.591
934	8.71168(9)	8.9214(1)	1.0241(20)	677.08(2)	0.0176	0.0234	0.0190	0.0451	1.556
982	8.71853(9)	8.9269(1)	1.0239(20)	678.56(2)	0.0173	0.0232	0.0190	0.0551	1.515

* R_p = pattern R factor = $\{\sum |I_o - I_c| / \sum I_o\}$; R_{wp} = weighted pattern R factor = $\{\sum [w(I_o - I_c)^2] / \sum [wI_o^2]\}^{1/2}$, where I_o = observed intensity, I_c = calculated intensity, and w = 1/I_o; R_p and R_{wp} are the fitted values obtained without background subtraction. Exp. R_{wp} = expected value of R_{wp} = R_e. R_f² = R-structure factor based on observed and calculated structure amplitudes = $\{\sum [(F_o^2 - F_c^2) / \sum F_o^2]\} / \sum F_o^2$; χ² = [R_{wp} / R_e]; where R_e = $[(N - P) / (\sum wI_o^2)]^{1/2}$, where N is the number of observations (data points = 2120) and P is the total number of variables [including structural (22), background (24), and profile terms (4), scale, total = 51]; N_{obs.} = number of observed reflections = 154 for all patterns at different temperatures.

† Single-crystal data from Hassan and Grundy (1991).

TABLE 2. Positional and isotropic displacement parameters (U × 100 Å²) at various temperatures (°C)

Atom/T	20‡	33	65	113	210	306	419	516	596
*Al	U	0.75(3)	1.25(4)	1.26(4)	1.35(4)	1.43(4)	1.53(4)	1.60(5)	1.75(5)
*Be	U	0.98(14)	0.7(4)	0.6(4)	0.5(4)	0.7(4)	0.9(4)	1.0(5)	1.3(5)
†Si	x	0.0127(1)	0.0133(2)	0.0133(3)	0.0131(3)	0.0129(3)	0.0127(3)	0.0124(3)	0.0122(3)
	y	0.2533(1)	0.2539(2)	0.2541(1)	0.2540(1)	0.2541(1)	0.2541(2)	0.2541(2)	0.2544(2)
	z	0.4958(1)	0.4949(3)	0.4947(3)	0.4947(3)	0.4948(3)	0.4948(3)	0.4949(4)	0.4946(4)
O1	x	0.1504(3)	0.1501(5)	0.1502(5)	0.1502(5)	0.1502(5)	0.1500(5)	0.1501(5)	0.1501(6)
	y	0.1343(2)	0.1367(4)	0.1363(4)	0.1366(4)	0.1368(4)	0.1372(5)	0.1374(5)	0.1384(6)
	z	0.4417(2)	0.4433(3)	0.4427(2)	0.4433(2)	0.4437(2)	0.4445(3)	0.4454(3)	0.4467(3)
	U	1.21(4)	1.11(5)	1.11(5)	1.20(5)	1.34(5)	1.57(5)	1.72(5)	2.08(6)
†O2	x	0.3472(2)	0.3438(5)	0.3436(5)	0.3436(5)	0.3433(5)	0.3434(5)	0.3436(5)	0.3427(6)
	y	0.0385(3)	0.0359(5)	0.0354(5)	0.0352(5)	0.0348(5)	0.0343(5)	0.0340(5)	0.0329(6)
	z	0.6488(2)	0.6503(4)	0.6505(4)	0.6506(4)	0.6507(4)	0.6512(4)	0.6515(5)	0.6520(5)
†O3	x	0.4256(2)	0.4249(4)	0.4250(4)	0.4257(4)	0.4266(4)	0.4277(4)	0.4291(4)	0.4310(4)
	y	0.1486(2)	0.1430(5)	0.1434(5)	0.1439(5)	0.1439(5)	0.1442(6)	0.1447(6)	0.1444(6)
	z	0.1377(3)	0.1391(4)	0.1391(4)	0.1390(4)	0.1391(4)	0.1391(5)	0.1392(5)	0.1393(5)
Na	x	0.1563(2)	0.1571(3)	0.1573(3)	0.1577(3)	0.1582(3)	0.1589(3)	0.1595(3)	0.1602(3)
	y	0.1972(2)	0.1970(3)	0.1967(3)	0.1969(3)	0.1969(3)	0.1972(3)	0.1976(3)	0.1974(4)
	z	0.1818(2)	0.1824(2)	0.1824(2)	0.1824(2)	0.1826(2)	0.1827(2)	0.1828(2)	0.1830(2)
	U	1.88(3)	2.68(7)	2.76(7)	3.01(8)	3.36(7)	3.85(8)	4.24(9)	5.18(10)
*Cl	U	2.34(3)	3.02(6)	3.04(6)	3.44(6)	3.89(6)	4.58(7)	5.16(7)	6.38(9)
Atom/T		644	709	773	821	869	902	934	982
*Al	U	1.82(5)	1.87(5)	1.95(5)	2.00(5)	2.05(5)	2.08(5)	2.10(5)	2.18(5)
*Be	U	1.4(5)	1.3(5)	1.4(5)	1.3(5)	1.4(5)	1.5(5)	1.5(6)	1.5(6)
†Si	x	0.0121(3)	0.0119(3)	0.0118(3)	0.0118(3)	0.0117(3)	0.0116(3)	0.0117(3)	0.0115(3)
	y	0.2544(2)	0.2541(2)	0.2541(2)	0.2541(2)	0.2540(2)	0.2541(2)	0.2540(2)	0.2540(2)
	z	0.4945(4)	0.4949(4)	0.4949(4)	0.4949(4)	0.4948(4)	0.4949(4)	0.4949(4)	0.4949(4)
O1	x	0.1501(6)	0.1496(6)	0.1496(6)	0.1496(6)	0.1492(6)	0.1494(6)	0.1492(6)	0.1491(6)
	y	0.1386(6)	0.1380(5)	0.1383(6)	0.1385(6)	0.1388(6)	0.1387(6)	0.1389(6)	0.1393(6)
	z	0.4473(3)	0.4483(3)	0.4492(3)	0.4497(3)	0.4502(3)	0.4505(3)	0.4511(3)	0.4518(3)
	U	2.19(6)	2.28(6)	2.46(6)	2.56(6)	2.66(6)	2.72(6)	2.82(6)	2.97(6)
†O2	x	0.3427(5)	0.3433(5)	0.3434(6)	0.3435(6)	0.3432(6)	0.3433(6)	0.3432(6)	0.3432(6)
	y	0.0324(6)	0.0325(6)	0.0320(6)	0.0321(6)	0.0316(6)	0.0315(6)	0.0313(6)	0.0308(6)
	z	0.6521(5)	0.6522(5)	0.6524(5)	0.6526(5)	0.6526(5)	0.6528(6)	0.6527(6)	0.6529(6)
†O3	x	0.4316(4)	0.4327(4)	0.4337(5)	0.4344(5)	0.4351(5)	0.4355(5)	0.4363(5)	0.4373(5)
	y	0.1445(6)	0.1456(6)	0.1457(7)	0.1459(7)	0.1458(7)	0.1460(7)	0.1462(7)	0.1462(7)
	z	0.1397(6)	0.1396(6)	0.1399(6)	0.1400(6)	0.1399(6)	0.1400(6)	0.1401(6)	0.1400(6)
Na	x	0.1612(3)	0.1618(3)	0.1622(4)	0.1626(4)	0.1628(4)	0.1631(4)	0.1634(4)	0.1640(4)
	y	0.1975(4)	0.1978(4)	0.1980(4)	0.1983(4)	0.1984(4)	0.1985(4)	0.1986(4)	0.1988(4)
	z	0.1830(2)	0.1831(2)	0.1832(3)	0.1832(3)	0.1834(3)	0.1834(3)	0.1836(3)	0.1837(3)
	U	5.50(10)	5.71(10)	6.15(11)	6.34(11)	6.56(11)	6.74(11)	6.98(11)	7.37(12)
*Cl	U	6.81(9)	7.31(9)	7.89(9)	8.34(10)	8.74(10)	8.99(10)	9.40(11)	10.02(11)

* Al is at (0, 1/2, 3/4); Be at (0, 1/2, 1/4); Cl at (0, 0, 0).

† Constraints: U(Si) = U(Al) and U(O1) = U(O2) = U(O3).

‡ Single-crystal data from Hassan and Grundy (1991).

TABLE 3. Bond distances (Å) and angles (°) at various temperatures (°C)

Bond or angle/T	20*	33	65	113	210	306	419	516	596
Al-O3 ×4	1.748(2)	1.705(4)	1.707(4)	1.709(4)	1.707(4)	1.707(5)	1.707(5)	1.706(5)	1.700(6)
Be-O2 ×4	1.631(2)	1.640(4)	1.640(4)	1.640(4)	1.642(4)	1.641(4)	1.638(5)	1.639(5)	1.644(5)
Si-O1	1.644(2)	1.620(5)	1.625(5)	1.624(5)	1.624(5)	1.622(6)	1.624(6)	1.623(6)	1.620(7)
Si-O1*	1.647(2)	1.666(5)	1.666(5)	1.665(5)	1.666(5)	1.668(5)	1.664(6)	1.664(6)	1.672(6)
Si-O2	1.581(2)	1.560(5)	1.557(5)	1.560(5)	1.558(5)	1.561(5)	1.567(6)	1.568(6)	1.562(6)
Si-O3	1.609(2)	1.645(5)	1.643(5)	1.639(5)	1.639(5)	1.636(5)	1.633(6)	1.631(6)	1.636(6)
<Si-O>	1.620(1)	1.623(3)	1.623(3)	1.622(3)	1.622(3)	1.622(3)	1.622(3)	1.622(3)	1.623(3)
Si-O1-Si	140.8(2)	141.6(2)	141.4(2)	141.6(2)	141.8(2)	142.3(2)	142.7(2)	143.3(2)	143.4(2)
Si-O2-Be	143.6(1)	143.2(2)	143.2(3)	143.4(3)	143.4(3)	143.6(3)	143.6(3)	143.7(3)	143.7(4)
Si-O3-Al	135.3(1)	135.7(2)	135.6(2)	135.9(2)	136.3(2)	136.8(2)	137.3(2)	137.8(2)	138.1(3)
Na-O1	2.370(3)	2.369(3)	2.365(3)	2.370(3)	2.373(2)	2.382(3)	2.391(3)	2.401(3)	2.402(3)
Na-O1*	3.074(2)	3.051(3)	3.055(3)	3.050(3)	3.047(3)	3.041(3)	3.034(3)	3.027(3)	3.022(4)
Na-O2*	2.603(3)	2.563(4)	2.560(4)	2.562(4)	2.562(4)	2.561(4)	2.565(5)	2.568(5)	2.561(5)
Na-O2	2.303(3)	2.321(5)	2.328(5)	2.330(5)	2.335(5)	2.339(5)	2.338(6)	2.342(6)	2.356(6)
Na-O3	2.396(3)	2.388(4)	2.385(4)	2.389(5)	2.394(4)	2.401(5)	2.410(5)	2.417(5)	2.421(6)
<Na-O>	2.549(1)	2.538(2)	2.539(2)	2.540(2)	2.542(2)	2.545(2)	2.548(2)	2.551(2)	2.552(2)
Na-Cl	2.707(1)	2.708(2)	2.707(2)	2.712(2)	2.717(2)	2.725(2)	2.732(2)	2.739(2)	2.742(2)
Bond or angle/T	644	709	773	821	869	902	934	982	
Al-O3 ×4	1.700(5)	1.705(5)	1.702(6)	1.702(6)	1.701(6)	1.701(6)	1.700(6)	1.699(6)	
Be-O2 ×4	1.644(5)	1.64(5)	1.639(5)	1.638(5)	1.641(5)	1.639(5)	1.642(5)	1.641(5)	
Si-O1	1.619(7)	1.618(7)	1.617(7)	1.615(7)	1.611(7)	1.614(7)	1.611(7)	1.608(8)	
Si-O1*	1.672(6)	1.666(6)	1.667(7)	1.667(7)	1.670(7)	1.668(7)	1.669(7)	1.671(7)	
Si-O2	1.561(6)	1.569(6)	1.571(6)	1.574(6)	1.572(6)	1.574(7)	1.575(7)	1.575(7)	
Si-O3	1.636(6)	1.628(6)	1.628(6)	1.628(6)	1.627(6)	1.626(7)	1.625(7)	1.623(7)	
<Si-O>	1.622(3)	1.620(3)	1.621(3)	1.621(3)	1.620(3)	1.621(4)	1.620(4)	1.619(4)	
Si-O1-Si	143.7(2)	144.3(2)	144.7(2)	145.0(2)	145.2(2)	145.4(2)	145.7(2)	146.0(2)	
Si-O2-Be	143.9(3)	144.1(3)	144.3(4)	144.3(4)	144.3(4)	144.4(4)	144.4(4)	144.6(4)	
Si-O3-Al	138.3(3)	138.8(3)	139.2(3)	139.4(3)	139.8(3)	140.0(3)	140.3(3)	140.8(3)	
Na-O1	2.408(3)	2.419(3)	2.428(3)	2.433(3)	2.437(3)	2.441(3)	2.445(3)	2.452(3)	
Na-O1*	3.017(4)	3.014(3)	3.007(4)	3.003(4)	3.001(4)	2.998(4)	2.996(4)	2.990(4)	
Na-O2*	2.562(5)	2.568(5)	2.568(6)	2.569(6)	2.567(6)	2.568(6)	2.568(6)	2.569(6)	
Na-O2	2.361(6)	2.359(6)	2.363(7)	2.362(7)	2.366(7)	2.367(7)	2.369(7)	2.375(7)	
Na-O3	2.422(6)	2.428(6)	2.434(6)	2.438(6)	2.444(6)	2.446(6)	2.452(6)	2.457(7)	
<Na-O>	2.554(2)	2.558(2)	2.560(2)	2.561(2)	2.563(2)	2.564(2)	2.566(2)	2.569(3)	
Na-Cl	2.747(2)	2.754(2)	2.759(2)	2.764(2)	2.769(2)	2.771(2)	2.776(2)	2.782(2)	

* Single-crystal data from Hassan and Grundy (1991).

<Na-O> average (Table 3). The Cl atom is tetrahedrally coordinated by Na atoms with a Na-Cl distance of 2.708(2) Å.

Cell parameters

The variations of the unit-cell parameters for tugtupite with temperature are shown in Figure 3, together with the least-squares fits to the data, which are given as inserts. The *a* and *c* unit-cell parameters increase non-linearly with temperature (Fig. 3a). When the *a* and *c* parameters are plotted on the same scale the expansion is seen to be anisotropic, being higher along *a* than along *c* (Fig. 3a), which results in a decrease in the *c/a* ratio with increasing temperature (Fig. 3b). The unit-cell volume, *V*, also increases smoothly with temperature (Fig. 3c). The data yield smooth expansion curves without changes or discontinuities that may indicate changes in the tugtupite sample up to 982 °C. The percent volume change between 33 and 982 °C is 2.97(3)%. In sodalite, the percent volume change between 28 and 982 °C is 4.8(2)% (Hassan et al. 2004). Tugtupite begins to lose NaCl at about 926 °C (the total mass change to 1019 °C is -1.8%), and melts at about 1029 °C (Antao and Hassan 2002); therefore, tugtupite did not change composition significantly in the temperature range used in this study. The unit-cell parameters for tugtupite at 33 °C obtained in this study [*a* = 8.62597(7) Å, *c* = 8.8564(1) Å] are similar to those obtained at 20 °C by Hassan and Grundy [1991; *a* = 8.640(1) Å, *c* = 8.873(1) Å], and Henderson and Taylor [1977; *a* = 8.6384(6) Å, *c* = 8.8674(8) Å]. The atomic coordinates at 33 °C are nearly identical to those obtained by Hassan and Grundy (1991), as are the bond lengths, except for

the Al-O3 distance (Table 3, Fig. 4a). The thermal-expansion data for tugtupite from Henderson and Taylor (1977) are different from those obtained in this study, but the trend in their data is similar (Fig. 3). The reason for the difference in results from the two studies is not clear as the room temperature data are similar, but large differences occur at high temperatures. We tried to duplicate the room-temperature data of Hassan and Grundy (1991) and Henderson and Taylor (1977) by fixing the zero-shift to produce their cell parameters and using soft-bond constraints, but the structure refinements were poor. Consequently, the zero-shift was set to zero at all temperatures. The successful structure refinements of our data at all temperatures give us confidence that our data is essentially accurate.

Framework

The framework of tugtupite consists of corner linked TO₄ tetrahedra (T = Si, Al, and Be). The structure refinements indicate that these tetrahedra are fully ordered. Both the AlO₄ and BeO₄ tetrahedra contain one independent T-O bond (e.g., all four Al-O bonds are of equal length), while the SiO₄ tetrahedron contains four independent Si-O bonds. The variations of the T-O distances and the average <Si-O> distances are shown in Figure 4a, and they are essentially constant with temperature, as expected. The Al-O3 bond distance decreases slightly with temperature. The variations of the T-O-T angles are shown in Figure 4b, and these angles increase with temperature. The Si-O2-Be angle, which is the largest at room temperature, increases less than the two smaller angles.

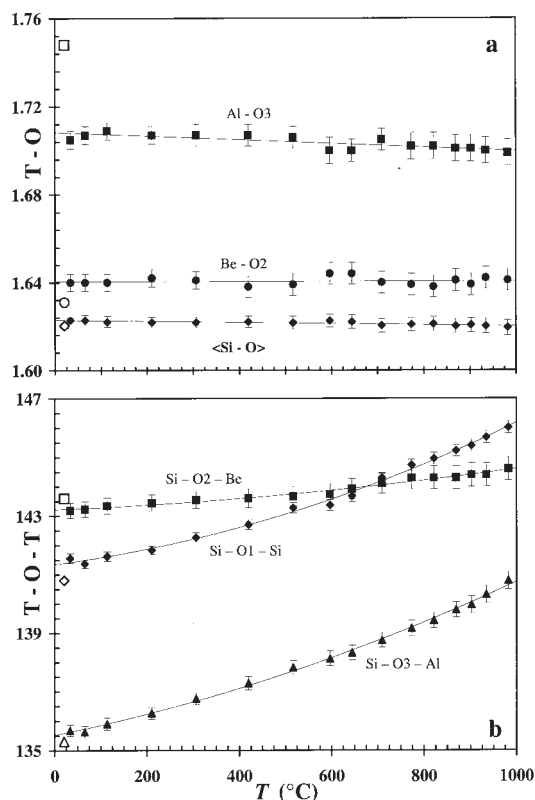


FIGURE 4. (a) Variation of the framework T-O distance with temperature. (b) Variation of the framework T-O-T angle with temperature. Data at 20 °C from Hassan and Grundy (1991) are included for comparison.

Cage clusters

The sodalite or β -cage enclose $[\text{Na}_4\text{Cl}]^{3+}$ clusters. The orientation of these clusters is fixed by Na-O bonds to the framework O atoms. The long Na-O1* bond decreases significantly, while all the short Na-O bonds increase slightly with temperature, and the Na-O2* bond is nearly constant. This results in a constant average $\langle\text{Na-O}\rangle$ bond distance with increasing temperature (Fig. 5a). The Na atom, therefore, moves toward the plane of the six-membered rings, where it comes into bonding distance with the framework oxygen atom, O1*, that was further away at room temperature (see Fig. 6). The migration of the Na atom occurs because the weaker Na-Cl bond distance increases with temperature.

Isotropic displacement parameters

Figure 5b shows the variations of the isotropic displacement parameters for the atoms in tugtupite. The Be, Si/Al, and O atoms have the lowest U values and they increase slightly with temperature. The isotropic displacement parameter for the Na atom, and in particular, that for the Cl atom increases considerably with temperature. The Na and Cl atoms, therefore, play a crucial role in the thermal expansion of tugtupite. The $[\text{Na}_4\text{Cl}]^{3+}$ clusters expand as the Na-Cl bond length increases by 0.073(3) Å between 33 and 982 °C. In sodalite, the Na-Cl bond length increases by 0.182(4) Å between 28 and 982 °C (Hassan et al. 2004).

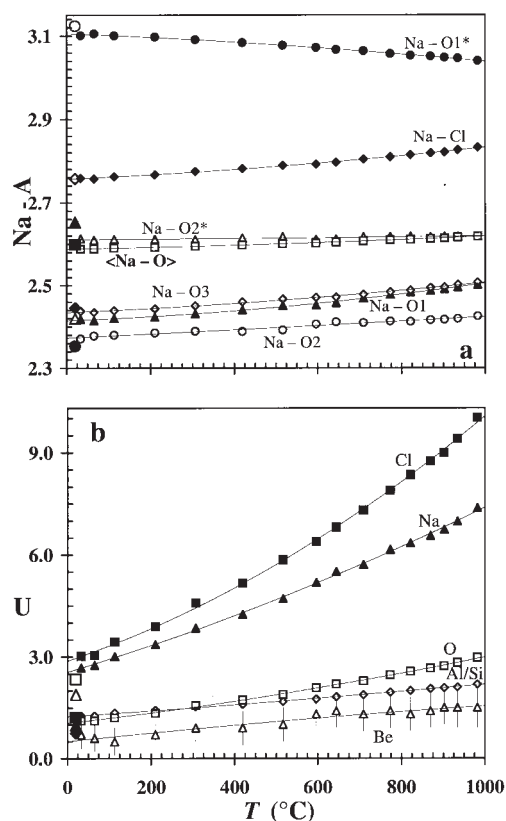


FIGURE 5. (a) Variation of the Na-A (A = O or Cl) distance with temperature. The Na-Cl distance increases with temperature, while the long Na-O1* distance decreases. The other Na-O distances increase slightly with temperature, but the average $\langle\text{Na-O}\rangle$ and Na-O2* distances are nearly constant. (b) Variation of the isotropic displacement parameters, U, with temperature. The U values for Na and Cl increase significantly, while Be, O, and Al/Si values increase slightly with temperature. Error bars are not seen if smaller than the symbols. Data at 20 °C from Hassan and Grundy (1991) are included for comparison.

The thermal-expansion mechanism for tugtupite

The geometrical model for sodalite (Hassan and Grundy 1984) is now combined with the thermal analyses of tugtupite (Antao and Hassan 2002) and the present results to give a complete picture of the thermal behavior of tugtupite. In the thermal expansion of sodalite, the Na-Cl bond expands and forces the Na atom toward the plane of the six-membered ring, which causes the framework tetrahedra to rotate. This mechanism causes a high rate of expansion. If the Na atom reaches (1/4, 1/4, 1/4), then it is midway between two Cl atoms and approximately in the plane of the six-membered ring. The Cl is then eightfold coordinated by eight Na atoms, and the Na atom is eightfold coordinated by two Cl and six framework O atoms. The expansion rate would, therefore, decrease. In sodalite, melting occurs before the Na atom reaches (1/4, 1/4, 1/4) because the thermal-expansion curve for sodalite increases smoothly to 982 °C (Hassan et al. 2004).

Hassan and Grundy (1991) modeled the thermal expansion of tugtupite using the distance least-squares (DLS) method and indicated that the expansion is similar to that in sodalite. In tugtupite, the Na-Cl bond expands, which is also indicated by

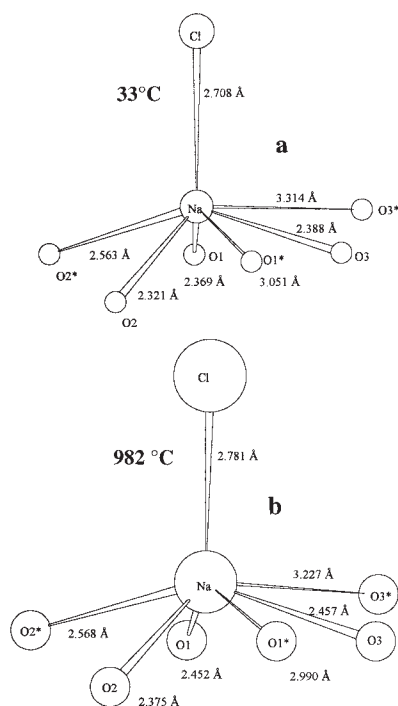


FIGURE 6. Comparison of the Na coordination in tugtupite at (a) 33 °C and (b) 982 °C. The displacement parameters are drawn to scale at the 50% probability level. The bond distances and the six O atoms of a six-membered ring are shown. The O1* and O3* do not form typical Na-O bonds as they are too far away from the Na atom, but these long distances decrease with temperature as the Na atom migrates toward the six-membered ring.

large displacement parameters for the Na and Cl atoms (Figs. 5b and 6). This forces the Na atom to migrate toward the plane of the six-membered ring, which causes the framework tetrahedra to rotate, as the average $\langle \text{Na-O} \rangle$ bond distance remains nearly

constant with temperature. In addition, the framework TO_4 tetrahedra distorts slightly with temperature. This mechanism causes a high rate of expansion. In tugtupite, melting occurs before the Na atom reaches approximately the plane of the six-membered ring. The thermal-expansion curves for tugtupite, therefore, increase quite smoothly to 982 °C. Tugtupite begins to lose NaCl at 844 °C and melts at 1029 °C. The NaCl component is lost in several stages: NaCl is lost slowly at 1007 °C, but the loss is faster and occurs in several steps at temperatures beyond 1019 °C, and continues beyond 1440 °C (Antao and Hassan 2002).

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REFERENCES CITED

- Antao, S.M. and Hassan, I. (2002) Thermal analyses of sodalite, tugtupite, danalite, and helvite. *Canadian Mineralogist*, 40, 163–172.
- Danø, M. (1966) The crystal structure of tugtupite - a new mineral, $\text{Na}_8[\text{Al}_2\text{Be}_2\text{Si}_8\text{O}_{24}](\text{Cl},\text{S})_2$. *Acta Crystallographica*, 20, 812–816.
- Hammersley, J. (1996) Fit2d user manual. ESRF publication, Grenoble, France.
- Hassan, I. and Grundy, H.D. (1984) The crystal structures of sodalite-group minerals. *Acta Crystallographica*, B40, 6–13.
- (1985) The crystal structures of helvite-group minerals, $(\text{Mn},\text{Fe},\text{Zn})_8[\text{Be}_6\text{Si}_6\text{O}_{24}]_2$. *American Mineralogist*, 70, 186–192.
- (1991) The crystal structure and thermal expansion of tugtupite, $\text{Na}_8[\text{Al}_2\text{Be}_2\text{Si}_8\text{O}_{24}]\text{Cl}_2$. *Canadian Mineralogist*, 29, 385–390.
- Hassan, I., Antao, S.M., and Parise, J.B. (2004) Sodalite: high-temperature structures obtained from synchrotron radiation and Rietveld refinements. *American Mineralogist*, 89, 359–364.
- Henderson, C.M.B. and Taylor, D. (1977) The thermal expansion of tugtupite. *Mineralogical Magazine*, 41, 130–131.
- Larson, A.C. and Von Dreele, R.B. (2000) General Structure Analysis System (GSAS). Los Alamos National Laboratory Report, LAUR 86–748.
- Toby, B.R. (2001) EXPGUI, a graphical user interface for GSAS. *Journal of Applied Crystallography*, 34, 210–221.

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