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The thermal expansion of tugtupite

TUGTUPITE (Danø, 1966; Sørensen, Danø, and Petersen, 1971) has a distorted sodalite type of structure, tetragonal with space group $I\bar{4}$, and has almost the ideal composition $Na_8(Al_2Be_2Si_8O_{24})Cl_2$. The reduction from cubic symmetry results from the ordering of the framework cations (Danø, 1966). This note gives the results of a thermal expansion study of a red tugtupite from Kvanefjeld, Ilímaussaq, Greenland, kindly supplied by Professor H. Sørensen and O. V. Petersen, University of Copenhagen.

The experimental procedure has been described previously (Henderson and Taylor, 1975). Cell parameters, using the platinum plate as internal standard, were calculated by the method of least squares from more than 14 diffraction peaks, generally 18, which were indexed by reference to Danø (1966).

The cell parameters, volumes, and *c*/*a* ratios are given for room temperature and elevated temperatures in Table I. When plotted these data yield smooth expansion curves without discontinuities. No change from tetragonal symmetry was detected in the temperature range examined. The cell parameters and volume were fitted by least squares to quadratic functions of the temperature, and the quadratic equations obtained then modified to the form $Y = Y_0(1 + BT + CT^2)$, where Y_0 is the parameter at 0 °C and Y the parameter at T °C. The values of Y_0 and the coefficients B and C are given in Table II with the standard errors of the coefficients, the multiple correlation coefficients, and the standard errors of the estimates, SE.

TABLE I. *Cell parameters, volumes, and c/a ratios for tugtupite at room temperature and elevated temperatures*

T°C	*a*, Å	*c*, Å	vol., Å³	*c*/*a*	*T*°C	*a*, Å	*c*, Å	vol., Å³	*c*/*a*
20	8·6384(6)	8·8674(8)	661·70(7)	1·0265(1)	405	8·6846(5)	8·9025(5)	671·45(7)	1·0251(1)
20*	8·6367(6)	8·8694(8)	661·59(8)	1·0269(1)	495	8·6967(5)	8·9125(8)	674·07(8)	1·0248(1)
20†	8·6381(4)	8·8703(5)	661·87(6)	1·0269(1)	600	8·7127(7)	8·9258(8)	677·56(10)	1·0245(2)
20‡	8·6397(5)	8·8658(6)	661·78(5)	1·0262(1)	700	8·7283(5)	8·9407(6)	681·12(7)	1·0243(1)
110	8·6471(5)	8·8755(6)	663·64(7)	1·0264(1)	795	8·7468(5)	8·9558(6)	685·18(7)	1·0239(1)
205	8·6574(6)	8·8835(7)	665·82(9)	1·0261(1)	905	8·7686(9)	8·9758(11)	690·14(11)	1·0236(2)
315	8·6713(6)	8·8937(7)	668·73(8)	1·0257(1)					

The figures in brackets are standard errors referring to the last digit.
* silicon internal standard.
†, ‡ after heating to 495 and 905 °C respectively.

TABLE II. *Constants and coefficients for the fitted thermal expansion curves*

Y	Y_0	10^6B	10^9C	R	SE
a	8·6368	10·49±0·32	6·95±0·37	0·9998	0·0008 Å
c	8·8671	6·91±0·54	7·18±0·61	0·9994	0·0014 Å
Vol.	661·45	27·58±0·77	22·12±0·88	0·9999	0·15 Å³

The expansion is anisotropic, being higher at right angles to the *c* axis than parallel to it, as shown by the decrease in the *c*/*a* ratio with increasing temperature (Table I) and the lower B coefficient for the *c* parameter (Table II). The combination of tilting of the framework tetrahedra, the presence of BeO_4, AlO_4, and SiO_4 tetrahedra in the framework and the distortion of the SiO_4 tetrahedra do not lend themselves to an unambiguous interpretation of the thermal expansion and its anisotropy in terms of the crystal structure.

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Columbite from St. Austell, Cornwall

GUNHEATH PIT, 4½ km NNW of St. Austell, lies within the kaolinized part of the granite and the workings have exposed many pegmatite veins 5 to 20 cm thick in the north face. An investigation of these during 1972 and 1973 revealed columbite for the first time at this locality, in several vertical veins striking NNE. The mineralogical composition of these veins is variable, the columbite usually occurring as small subhedral platy crystals up to 5 mm across, either singly or as radiating aggregates, with microcline, quartz, and zinnwaldite. Accessory minerals are apatite, tourmaline, topaz, opal, arsenopyrite, and turquoise. The largest fragments of columbite, reaching 2 cm in size, occurred in a vertical lens of unusual composition, consisting entirely of quartz, 'gilbertite', and apatite, with rare accessory torbernite.

An electron-probe analysis was obtained from a 2 mm fragment of the columbite using the Geoscan instrument at the British Museum (Natural History). The elements were measured relative to pure metal standards, apart from tin, for which a pure specimen of cassiterite was used. After computer correction for matrix effects the analysis obtained was Nb_2O_5 55·91, Ta_2O_5 17·01, TiO_2 4·99, WO_3 3·65, FeO 14·98, MnO 3·60, Sc_2O_3 0·80, SnO_2 0·11, total 101·05%. The density, determined with a Berman balance, is 5·62 g. cm^{-3}. Recalculation of this analysis to a unit cell containing 24 oxygen atoms gives $(Fe_{2\cdot96}Mn_{0\cdot72}Sc_{0\cdot16}Sn_{0\cdot01})_{\Sigma3\cdot85}(Nb_{5\cdot97}Ta_{1\cdot09}Ti_{0\cdot89}W_{0\cdot21})_{\Sigma8\cdot16}O_{24}$. The mineral is noteworthy for the relatively high level of substitution of Ti and W for (Nb, Ta), and of Sc for (Fe, Mn). Scandium has been reported in a number of columbite–tantalites and ixiolites (Neumann, 1961; Haapala *et al.*, 1967; von Knorring *et al.*, 1969; Borisenko *et al.*, 1969) and we believe it to be a more widespread minor constituent of columbites than has hitherto been suspected. The X-ray powder pattern obtained from a sample of the mineral was in excellent agreement with those from other columbites and tantalites. In view of the close approach to site stoichiometry of the formula given above, cation disorder