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A re-examination of thortveitite

RICCARDO BIANCHI, TULLIO PILATI
C.N.R., Centro per lo Studio delle Relazioni tra Struttura e Reattività Chimica, via Golgi, 19 I-20133, Milan, Italy
VALERIA DIELLA
C.N.R., Centro di Studio per la Stratigrafia e Petrografia delle Alpi Centrali, via Botticelli, 23 I-20133, Milan, Italy
CARLO MARIA GRAMACCIOLI, GREGORIO MANNUCCI
Dipartimento di Scienze della Terra, Università degli Studi di Milano, via Botticelli, 23 I-20133, Milan, Italy

ABSTRACT

Four different natural crystals of thortveitite $(Sc,Y)_2Si_2O_7$ have been analyzed by electron microprobe, and the structure has been determined from single-crystal data using Mo*Kα* radiation up to at least $\theta = 40°$. The form factor of the metal has been derived from the chemical analysis of each crystal. The final disagreement factor $R = \Sigma| \; |F_o| - |F_c| \; |/\Sigma|F_o|$ is around 0.02; the standard deviations of the bond distances are between 0.001 and 0.002 Å, and those of the angles are around 0.1°. The Si–O–Si angle is indeed 180°; the crystal symmetry is $C2/m$, and there is no evidence for disorder involving the Si_2O_7 group; the analytical data indicate extensive substitution of Y and REE for Sc, as well as nonnegligible amounts of Zr and Hf; the charge balance is maintained by multiple substitution of Ca, Mg, and Mn in the metal position and of Al for Si.

INTRODUCTION

Thortveitite, essentially $(Sc,Y)_2Si_2O_7$, is one of the few scandium minerals, and it is one of the simplest silicates with isolated Si_2O_7 groups (sorosilicates). The Si–O–Si angle in thortveitite is reported to be 180°; this value is, however, unusual with respect to most other sorosilicates, where the corresponding angles are definitely smaller (130–140°) (Liebau, 1961). The preference of a nonlinear structure for the Si–O–Si bridge is supported by quantum-mechanical calculations (Meagher et al., 1979; Gibbs et al., 1981): in fact, the energy of a bent Si–O–Si link is shown to be smaller than for the linear (180°) counterpart. Thortveitite is also very interesting in that it is used for calibrating a general force field for silicates in Raman and infrared spectroscopy. This is especially true in connection with the bridge-stretching frequencies in the Si_2O_7 group (Ross, 1971).

The crystallographic results that have been obtained so far on the natural material (Zachariasen, 1930; Cruickshank et al., 1962) are not sufficiently accurate; this low accuracy is due on one hand to a limited collection of data and even more to the uncertainty of the scattering factor of the metal, since no chemical analyses are available for all the natural samples from which X-ray data were collected. This inconvenience is particularly serious, because even for the same group of natural occurrences, e.g., those of the Setesdalen district (see also below), there is a wide variability of composition: in most samples a considerable portion of Sc is replaced by Y or by the heaviest REEs such as Yb or Lu. The substitution of the heaviest REEs for Sc is not surprising, in line with the well-known lanthanide contraction of the ionic radii. However, the scattering factor is very strongly affected, owing to the substantial difference in the atomic numbers ($Z = 21$ against about 70). Although the difference in Z between Sc and Y ($Z = 39$) is less than that between Sc and the heavy REEs, the effect on the scattering factor of replacing Sc by Y is also very strong because the substitution is more extensive. Even the cell dimensions appear to vary considerably, depending on the presence of large amounts of Y (see below). Other difficulties include absorption and anomalous dispersion, which have not been considered previously in working out the crystal structure of natural samples. With respect to the chemical composition, a possible substitution of Sc by Zr and Hf should also be taken into account and is supported by most chemical data that have been published on the natural material. The corresponding mechanism of charge balance seems to imply a concomitant substitution of Al for Si (and also by Be). A more recent crystal-structure determination was performed on synthetic pure $Sc_2Si_2O_7$ (Smolin et al., 1973); the linear conformation for the Si_2O_7 group has been confirmed, but such a "conformation" might be the average of a distribution of bent disiloxy groups. For this purpose, a thermal-vibration and peak-distribution analysis would be interesting to obtain; however, such data and consequent discussion about the possible existence of disordered models are lacking.

For all these reasons, accurate crystal-structure analyses of natural samples whose compositions have been exactly determined were considered to be useful.

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TABLE 1. Conditions and standards for microprobe analysis

Accelerating voltage	20 kV
Sample current on brass	0.02 μA
Objective aperture	200 μm
Beam spot diameter on periclase	about 5 μm
Counting times	20 s at peak position 2 s at both backgrounds
Analyzing crystals	LIF Mn*Kα*, Fe*Kα*, Dy*Lα*, Er*Lα*, Tm*Lα*, Yb*Lα*, Lu*Lα* PET Hf*Mα*, Y*Lα*, Zr*Lα*, Ca*Kα*, Sc*Kα* ADP Al*Kα*, Si*Kα*
Analytical standards	Mg, Ca, Al, Si, Fe ardennite, PSU-144 (Ingamells, 1978) Mn fayalite, USNM 85276 (Jarosewich et al., 1980) Dy, Er synthetic glass REE4 (Drake and Weill, 1972) Tm synthetic glass REE1 (Drake and Weill, 1972) Yb, Lu synthetic glass REE2 (Drake and Weill, 1972) Y synthetic glass, 12.75 wt% Y_2O_3 Sc synthetic glass, 34.19 wt% Sc_2O_3 Zr synthetic glass, 5.80 wt% ZrO_2 Hf synthetic glass, 5.78 wt% HfO_2
Correction method	MAGIC IV (Colby, 1968)

CHEMICAL COMPOSITION

In this work, four different samples of thortveitite have been examined. The first three are in the private collection of one author (C.M.G.) and come from the Setesdalen district in Norway; they were not obtained from the same source and were probably found in different localities at different times; the fourth one is from the Malagasy Republic ("Madagascar," very probably Befanamo) and comes from the collection of the Earth Science Department of the University of Milan.

Electron-microprobe analyses were performed on polished grain mounts by using the ARL-SEMQ instrument of the Italian National Research Council (C.N.R.) at Centro di Studi per la Stratigrafia e la Petrografia delle Alpi Centrali, Milan.

To determine the content of Si, Al, Mn, Fe, Mg, and Ca, a series of natural standards was employed (see Table 1). For the REEs, the synthetic glasses REE1, REE2, and REE4 were used as standards (Drake and Weill, 1972). For Y, Sc, Zr, and Hf, suitable synthetic glasses were used as standards: these glasses were prepared by us, by melting high-purity (99.9%) commercial oxides at high temperature in an oxygen-rich atmosphere. Such oxides were provided to us in the form of fine powders, and before melting they were mixed in a vibrating device and stirred for about 2 h to ensure homogeneity even before melting. After melting, the glasses were ground in a silica mortar and then remelted. The Zr-Hf standard glass contains SiO_2 27.60 wt%, Al_2O_3 31.09, CaO 25.81, ZrO_2 5.80, HfO_2 5.78, and Sc_2O_3 3.93. The Y-Sc glass approaches thortveitite in composition and contains SiO_2 39.83 wt%, Sc_2O_3 34.19, Y_2O_3 12.75, and Yb_2O_3 13.23; such a composition was selected in order to minimize the errors due to inadequate knowledge of some data concerning Sc in the MAGIC IV program. For instance, the mass absorption coefficient of Sc is known only very approximately.

The X-ray lines of the various elements used and details of our analytical procedure are also reported in Table 1.

To examine the possibility of interference in the X-ray spectra between the various elements contained in thortveitite, a series of measurements of standards of known composition was carried out. Nonnegligible interference effects resulted only for Zr (overlap of the *Kα* line with a Sc line, probably Sc*Lβ*).

In order to provide for an appropriate correction of the errors due to such interference, a series of four standard glasses with an increasing Sc content was prepared (3.92, 15.50, 34.19, and 50.07 wt% Sc_2O_3); moreover, a lump

TABLE 2. Analytical results on different samples of thortveitite

	1			2			3a		
	Wt%	Range	Stoic.*	Wt%	Range	Stoic.*	Wt%	Range	Stoic.*
MnO	0.67	(0.49–0.77)	0.030	1.33	(1.00–1.79)	0.054	0.26	(0.13–0.42)	0.018
Dy_2O_3	1.38	(1.23–1.66)	0.023	0.96	(0.36–1.21)	0.015	0.45	(0.13–0.71)	0.007
Er_2O_3	1.65	(1.12–1.78)	0.027	0.55	(0.29–0.72)	0.008	0.97	(0.83–1.05)	0.014
Tm_2O_3	0.54	(0.44–0.82)	0.009	0.06	(0.04–0.12)	0.001	0.19	(0.13–0.29)	0.003
Yb_2O_3	7.01	(6.67–7.23)	0.111	2.58	(2.11–3.01)	0.038	4.52	(4.24–4.74)	0.066
Lu_2O_3	1.68	(1.23–1.94)	0.026	0.49	(0.19–0.71)	0.007	1.03	(0.89–1.15)	0.015
HfO_2	0.55	(0.41–0.71)	0.008	0.99	(0.44–1.23)	0.014	0.11	(0.07–0.18)	0.001
Y_2O_3	17.73	(16.79–17.90)	0.490	8.67	(7.55–9.21)	0.223	8.41	(8.01–9.02)	0.213
ZrO_2	2.28	(2.01–2.42)	0.058	4.31	(4.02–4.69)	0.102	1.71	(1.40–1.90)	0.040
CaO	0.19	(0.08–0.22)	0.011	0.22	(0.11–0.40)	0.011	0.13	(0.02–0.26)	0.007
Sc_2O_3	25.01	(24.33–25.23)	1.132	32.83	(31.91–33.02)	1.385	37.13	(36.66–37.49)	1.548
MgO	0.26	(0.11–0.30)	0.020	0.33	(0.12–0.55)	0.024	0.07	(0.00–0.11)	0.005
Fe_2O_3	2.06	(1.94–2.34)	0.081	3.11	(3.00–3.29)	0.113	1.68	(1.33–2.04)	0.060
SiO_2	37.59	(36.94–37.88)	1.950	40.44	(39.99–41.21)	1.958	41.29	(40.80–42.60)	1.963
Al_2O_3	0.61	(0.21–0.89)	0.037	0.90	(0.76–1.44)	0.051	0.88	(0.49–1.12)	0.049
Total	99.21			97.77			98.83		
Formula		$R_{2.026}(Si,Al)_{1.987}O_7$			$R_{1.995}(Si,Al)_{2.009}O_7$			$R_{1.997}(Si,Al)_{2.012}O_7$	

Note: (1) 17 analyzed points; sample from Iveland (see Table 3). (2) 14 analyzed points; sample from Setesdalen. (3a) 12 analyzed points; sample from Flåt, Evje. (3b) 14 analyzed points; the same sample as 3a in a different part of the crystal. (4) 11 analyzed points; sample from "Madagascar."

* Stoichiometric ratios of elements based on seven oxygens.

TABLE 3. Unit-cell data on thortveitite-group minerals and related compounds

	1	2	3	4	5	6
a (Å)	6.650(1)	6.587(1)	6.582(1)	6.527(1)	6.503(2)	6.90
b (Å)	8.616(1)	8.547(1)	8.555(1)	8.507(1)	8.498(3)	8.98
c (Å)	4.686(1)	4.695(1)	4.693(1)	4.691(1)	4.682(2)	4.72
β (°)	102.20(1)	102.65(1)	102.59(1)	102.78(1)	102.77(7)	101.7
V (Å^3)	262.4	257.9	257.9	254.0	252.3	286.4

Note: (1) Thortveitite, Iveland, Setesdalen; (2) thortveitite, Setesdalen; (3) thortveitite, with zircon, Flåt, Evje, Setesdalen; (4) thortveitite, Malagasy Republic (Befanamo ?); (5) synthetic $Sc_2Si_2O_7$, data from Smolin et al., 1973; (6) synthetic β-$Y_2Si_2O_7$, data from Ito and Johnson, 1968.

of pure scandium oxide was obtained by melting the powder at very high temperature (3000 °C). From measurement of such standards on our microprobe, the following correction formula was derived from a least-squares fit: $E_{0,\mathrm{Zr}}$, = $E_{\mathrm{a,Zr}}$ − K$E_{0,\mathrm{Sc}}$ where $E_{0,\mathrm{Zr}}$, $E_{0,\mathrm{Sc}}$, and $E_{\mathrm{a,Zr}}$ are the true content of Zr and Sc and the apparent content of Zr, respectively, and *K* is a constant equal to 0.06 (±0.02). The procedure is similar to our previous experience with monazite (Mannucci et al., 1986); owing to the very low Sc content of the "usual" minerals and to the low value of the constant *K*, such an interference was probably overlooked in previous works. Of the other elements that are likely to occur in thortveitite, those REEs not mentioned in Table 2 and U, Th, Nb, Ta, Sn, Pb, Ti, Cl, Cu, P, Na, K, and W are below the limit of detection with our instrument.

Of the elements that are not detectable by electron microprobe, Be seems to be present in minor amounts in thortveitite (Lacroix, 1923); atomic absorption analysis was performed on one sample (no. 3; see below).

The analytical results (see Table 2) are essentially satisfactory, especially in view of the number of elements that are present in nonnegligible amounts. The metal/(Si + Al) ratio (except Al) is close to unity in all the samples. Zr and Hf are present; in agreement with the analytical data already reported in the literature; however, in all our specimens the Hf/Zr ratio is not as high as found in other samples from the Setesdalen district and Madagascar (Levinson and Borup, 1960). Only in samples 1 and 2 are observed marked enrichments of Hf with respect to the general average for minerals. The presence of Zr and Hf implies a problem of charge balance. In most cases, charge balance is substantially achieved by the simultaneous presence of divalent cations, such as Mn, Ca, and Mg; the rest can be accounted for by the replacement of Si by Al. From Table 2, the extent of such replacements appears to be more than sufficient for this purpose. Also, replacement of Sc by Al in octahedral coordination cannot be excluded. However, our interpretation of the analytical results cannot be pushed beyond their expected significance.

TABLE 2—*Continued*

3b			4		
Wt%	Range	Stoic*	Wt%	Range	Stoic.*
0.21	(0.12–0.39)	0.015	0.30	(0.08–0.40)	0.011
0.22	(0.12–0.27)	0.003	0.00	—	0.000
0.54	(0.39–0.66)	0.008	0.00	—	0.000
0.05	(0.00–0.13)	0.001	0.00	—	0.000
3.33	(2.99–3.49)	0.048	0.18	(0.00–0.25)	0.002
0.78	(0.60–0.99)	0.011	0.00	—	0.000
0.07	(0.01–0.20)	0.001	0.15	(0.02–0.21)	0.002
5.79	(5.21–5.93)	0.144	2.31	(2.09–2.42)	0.054
1.84	(1.70–2.03)	0.042	1.65	(1.13–1.79)	0.035
0.14	(0.09–0.21)	0.007	0.09	(0.01–0.14)	0.004
40.41	(39.23–41.47)	1.658	47.81	(46.26–48.01)	1.836
0.14	(0.07–0.33)	0.010	0.05	(0.00–0.09)	0.003
1.39	(0.97–1.46)	0.049	1.39	(1.20–1.61)	0.046
41.90	(39.92–42.30)	1.960	44.63	(43.19–45.00)	1.967
0.96	(0.50–1.22)	0.053	1.05	(0.93–1.71)	0.055
97.77			99.61		
	$R_{1.997}(Si,Al)_{2.013}O_7$			$R_{1.993}(Si,Al)_{2.022}O_7$	

In sample 3, atomic absorption spectroscopy shows the presence of significant amounts of BeO (above 2000 ppm), in agreement with similar results obtained by other authors (Urbain analysis in Lacroix, 1923). On analyzing sample 3, a particularly wide variation of the content in Sc, Y, and REE was also observed; the results relative to two representative parts of the same sample are reported in columns 3a and 3b, respectively, of Table 2.

CRYSTAL-STRUCTURE ANALYSIS

The unit-cell data of four different samples are given in Table 3; the numbering of such samples is the same as in Table 2. For each crystal, the unit-cell parameters were derived from a least-squares fit of 25 independent reflections with θ ranging from 30° to 38° with the Mo*Kα* radiation (λ = 0.71069 Å) at room temperature.

From inspection of Table 3, a wide variation of the unit-cell parameters is observed, especially of *a* and *b*. Such a variation is clearly linked to the chemical composition, the largest parameters (and therefore the largest unit-cell volume) corresponding to the highest content of Y. The unit-cell parameters of the "Madagascar" sample (no. 4), which is the richest in Sc, are reasonably close to the corresponding ones reported by Smolin et al. (1973) relative to the synthetic pure $Sc_2Si_2O_7$: these data are also reported in column 5 of Table 3 for comparison. This is completely in line with the larger ionic radius of Y with respect to Sc and the heaviest REEs.

For crystal-structure refinement, reflections up to a value of θ of at least 40° with the Mo*Kα* radiation were collected with a NONIUS CAD-4 diffractometer from pure

TABLE 4. X-ray data–collecting details for thortveitite

Sample no.:	1	2	3	4
$R(I)$ (%)*	2.1(8.4)	1.8(1.8)	1.8(1.8)	1.8(2.0)
$R(F)$ (%)*	1.3(4.5)	1.2(1.2)	1.3(1.1)	1.2(1.3)
Reflections measured	1757	1691	1688	2856
Independent reflections	849	837	835	1387
Maximum Bragg angle (°)	40	40	40	50
Final R value (%)	2.1	2.5	2.9	2.3
Final R_w value (%)	2.9	2.4	3.6	2.8

* Disagreement indices between symmetrically related reflections; the number within parentheses corresponds to data not corrected for absorption.

fragments of four crystals, whose diameters range from 0.1 to 0.2 mm; detailed data about such collections are reported in Table 4. For all crystals, empirical absorption corrections were derived according to the ψ-scan technique of Walker and Stuart (1983); an additional correction corresponding to a spherical crystal whose diameter is equal to the smallest diameter of the fragment was also applied. After correcting for absorption, the agreement between the F values corresponding to symmetrically equivalent reflections in the same crystal improved considerably for samples 1 and 4 (see Table 4; the values between parentheses correspond to neglecting the absorption correction). For crystals 2 and 3, whose diameter is nearly constant and which are smaller, the effect of the anisotropic absorption correction is almost zero.

Scattering factors according to the *International Tables* (1974) for the neutral atoms were used, including the real and the imaginary parts of the anomalous scattering; for each crystal, a weighted average of the scattering factors of the different elements corresponding to the analytical data was assigned to the Sc position.

TABLE 5a. Atomic coordinates (× 10^5) for thortveitite

	x/a	y/b	z/c
M	0	30503(3)	50000
	0	30670(3)	50000
	0	30666(5)	50000
	0	30881(2)	50000
Si	22108(11)	0	−8762(15)
	22179(8)	0	−8941(11)
	22221(13)	0	−8977(18)
	22319(5)	0	−9105(8)
O(1)	0	0	0
	0	0	0
	0	0	0
	0	0	0
O(2)	38654(28)	0	22171(38)
	38887(21)	0	22133(29)
	38959(32)	0	22099(45)
	39182(14)	0	22124(20)
O(3)	23655(26)	15499(17)	−28174(30)
	23544(18)	15622(12)	−28405(22)
	23522(27)	15615(19)	−28407(34)
	23532(11)	15709(8)	−28576(15)

Note: For each atom, each row corresponds to samples 1 to 4, in sequence.

TABLE 5b. Temperature factors (Å^2 × 10^4) for thortveitite

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
M	74(1)	82(1)	82(1)	0	3(1)	0
	87(1)	88(1)	109(1)	0	7(1)	0
	75(1)	74(2)	84(1)	0	6(1)	0
	51(1)	54(1)	68(1)	0	5(1)	0
Si	79(3)	86(3)	56(2)	0	−7(2)	0
	94(2)	101(2)	82(2)	0	1(2)	0
	87(3)	85(3)	63(3)	0	−2(2)	0
	51(1)	63(1)	48(1)	0	3(1)	0
O(1)	75(13)	777(38)	426(25)	0	83(15)	0
	116(11)	706(25)	416(18)	0	117(11)	0
	141(17)	557(33)	328(24)	0	86(16)	0
	74(5)	369(11)	224(8)	0	74(5)	0
O(2)	95(7)	106(7)	62(6)	0	−16(5)	0
	114(5)	113(6)	86(5)	0	0(4)	0
	99(8)	97(9)	70(8)	0	−12(6)	0
	75(3)	74(3)	55(3)	0	−9(2)	0
O(3)	262(7)	86(5)	95(5)	23(5)	22(5)	21(4)
	231(5)	103(4)	127(4)	28(4)	34(4)	21(3)
	208(7)	91(6)	104(6)	22(5)	46(5)	22(5)
	112(2)	74(2)	84(2)	22(2)	24(2)	24(2)

Note: The temperature factors are in the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 \cdots + 2U_{12}a^*b^*hk \cdots +)]$. For each atom, each row corresponds to samples 1 to 4, in sequence.

The refinement of the structures of the four different crystals was carried out by full-matrix least-squares, using the program VALRAY (Stewart and Spackman, 1981), by minimizing the quantity $\Sigma w(|F_o| - |F_c|)^2$. The parameters of the starting model are those of $C2/m$ symmetry of Cruickshank et al. (1962). The final weights were assigned equal to $1/\sigma^2(F) = 4I/\sigma^2(I)$; the variance of each reflection $\sigma^2(I)$ was assigned according to the formula $\sigma^2(I) = \sigma^2_{c.s.}(I) + (0.03I)^2$, where $\sigma^2_{c.s.}(I)$ is the variance derived from counting statistics. The final values of the R index $= \Sigma| \, |F_o| - |F_c| \, |/\Sigma|F_o|$ and of the corresponding weighted index R_w are reported in Table 4; the atomic coordinates and the anisotropic temperature factors for the four different crystals are reported in Tables 5a and 5b, respectively, with their esd's. In the final difference Fourier syntheses of sample 4, no peak exceeding 0.4 e/Å^3 was found. A table of observed and calculated structure factors for all the crystals here studied has been deposited.[1] The conformation of the disilicate group in the four cases is given in Figure 1, together with the thermal-vibration ellipsoids of the Si and O atoms. In the four different crystals, the respective Si–O bond distances (see Table 6) are the same within the limits of our experimental accuracy; there is, however, a significant difference in the bond angles O(1)–Si–O(2) and O(2)–Si–O(3): for a high Y content, the former angle tends to be larger, whereas the latter becomes smaller.

A considerable difference occurs between the temper-

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[1] A copy of the observed and calculated structure factors may be ordered as Document AM-88-377 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.

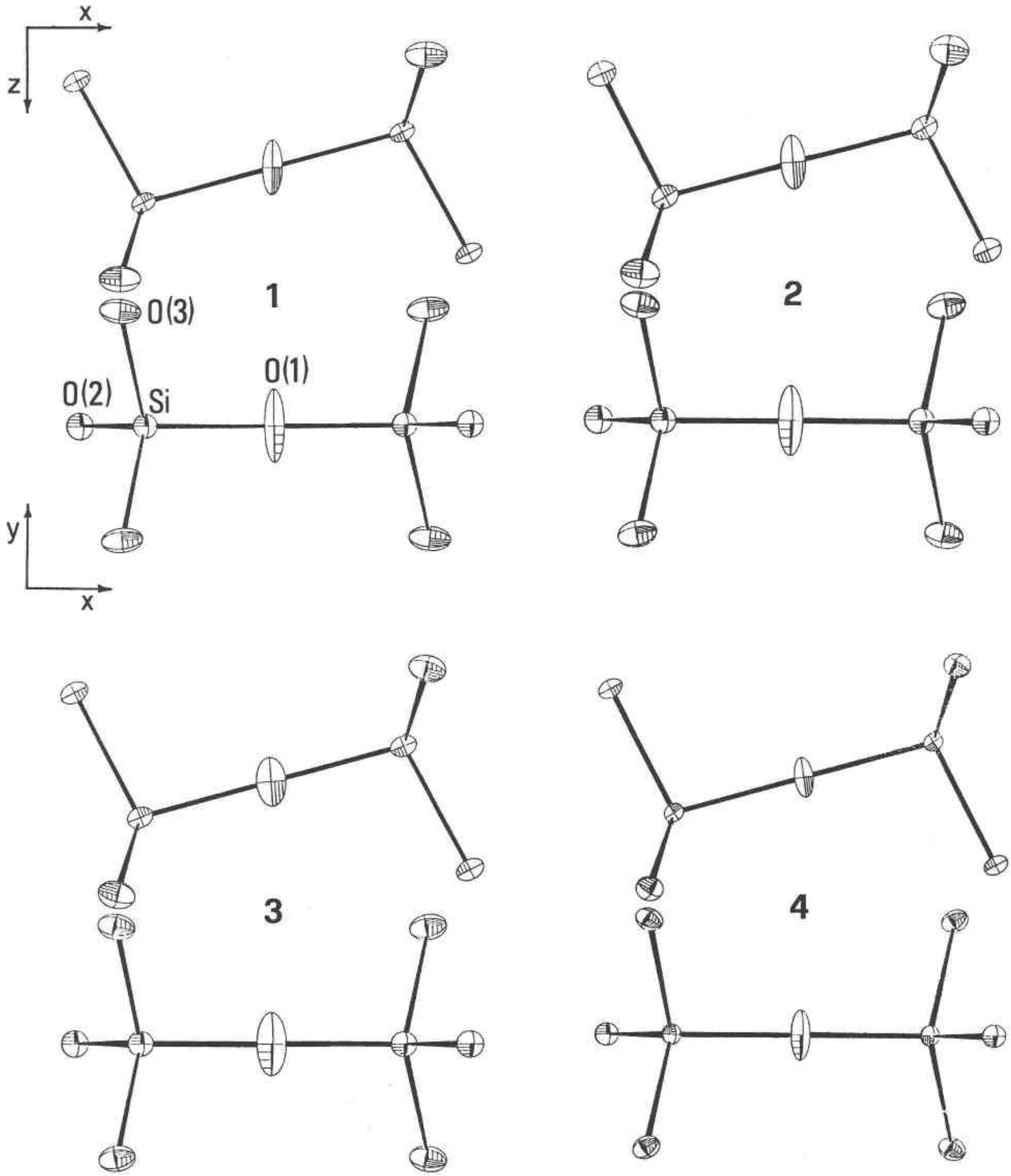

Fig. 1. An ORTEP plot (Johnson, 1976) of thermal-vibration ellipsoids (drawn at 20% probability contour) of the Si_2O_7 group in thortveitite (crystals 1 to 4, respectively).

ature factors of the corresponding O atoms in the four crystals; this difference is the most salient detail on Figure 1; a smaller difference occurs between the Si atoms.

On the whole, with respect to the temperature factors, two main effects can be easily noticed: first, these factors tend to be larger upon replacing Sc by Y, second, there is a relatively strong component of the motion of O(1) along the *y* axis, perpendicular to the Si–O bond.

The increase of temperature factors for Y-containing thortveitite can be accounted for, at least in part, on con-

TABLE 6. Bond distances (Å) and angles (°) for thortveitite

	1	2	3	4	1 − 4*
			T1 tetrahedron		
Si–O(1)	1.608(1)	1.606(1)	1.608(1)	1.606(1)	0.002
–O(2)	1.624(2)	1.624(1)	1.625(1)	6.626(1)	−0.002
–O(3) × 2	1.631(2)	1.632(1)	1.630(2)	1.630(1)	0.001
Mean	1.623	1.623	1.623	1.623	
O(1)–Si–O(2)	104.81(8)	103.98(6)	104.00(10)	103.50(4)	1.31
O(1)–Si–O(3) × 2	108.13(6)	108.14(4)	107.95(6)	107.95(2)	0.18
O(2)–Si–O(3) × 2	112.77(6)	113.18(4)	113.21(6)	113.43(2)	−0.66
O(3)–Si–O(3)^A	109.90(10)	109.85(8)	110.10(10)	110.09(5)	−0.20
O(1)–O(2)	2.561(2)	2.545(1)	2.548(2)	2.538(1)	0.023
O(1)–O(3) × 2	2.623(2)	2.622(1)	2.619(2)	2.618(1)	0.005
O(2)–O(3) × 2	2.711(2)	2.717(2)	2.718(2)	2.722(1)	−0.011
O(3)–O(3)^A	2.670(2)	2.670(2)	2.679(2)	2.673(1)	−0.003
			Oc1 octahedron		
M–O(2)^B × 2	2.162(1)	2.135(1)	2.136(1)	2.108(1)	0.054
–O(3)^C × 2	2.124(2)	2.097(1)	2.097(2)	2.086(1)	0.040
–O(3)^D × 2	2.234(2)	2.222(2)	2.222(2)	2.201(1)	0.033
Mean	2.173	2.151	2.152	2.132	
O(2)^B–M–O(2)^E	78.05(6)	78.59(5)	78.53(8)	79.04(3)	−0.99
O(2)^B–M–O(3)^C × 2	93.09(5)	93.46(3)	93.58(6)	93.93(2)	0.84
O(2)^B–M–O(3)^D × 2	87.07(6)	88.36(4)	88.44(7)	89.57(3)	−2.50
O(2)^B–M–O(3)^F × 2	79.14(6)	79.93(4)	78.78(7)	78.71(3)	0.43
O(3)^C–M–O(3)^G × 2	105.02(8)	104.35(5)	104.25(9)	103.56(3)	1.46
O(3)^C–M–O(3)^F × 2	116.49(6)	115.96(4)	115.94(7)	115.47(3)	1.02
O(3)^C–M–O(3)^D	75.03(6)	74.77(4)	74.84(7)	74.51(3)	0.52
O(2)^B–O(2)^E	2.723(2)	2.704(3)	2.703(3)	2.683(1)	0.040
O(2)^B–O(3)^C × 2	3.112(2)	3.082(1)	3.086(2)	3.066(1)	0.046
O(2)^B–O(3)^D × 2	3.029(2)	3.037(2)	3.040(3)	3.037(1)	−0.008
O(2)^B–O(3)^F × 2	2.081(2)	2.770(2)	2.780(3)	2.757(1)	0.044
O(3)^C–O(3)^G × 2	3.371(2)	3.313(2)	3.311(2)	3.280(1)	0.091
O(3)^C–O(3)^F × 2	3.706(2)	3.663(2)	3.662(2)	3.626(1)	0.080
O(3)^C–O(3)^D	2.655(2)	2.625(2)	2.626(2)	2.597(1)	0.058

Note: Column numbers correspond to sample numbers. Symmetry transformations are as follows: (*A*) *x*, *y*, *z*; (*B*) −½ + *x*, ½ + *y*, *z*; (*C*) −*x*, *y*, −*z*; (*D*) −½ + *x*, ½ − *y*, 1 + *z*; (*E*) ½ − *x*, ½ − *y*, 1 − *z*; (*F*) ½ − *x*, ½ − *y*, −*z*; (*G*) *x*, *y*, 1 + *z*.

* Difference between columns 1 and 4.

sidering the large unit-cell difference between the pure Sc compound and the pure Y compound (corresponding to β-$Y_2Si_2O_7$: see columns 5 and 6, respectively, in Table 3).

Such increase with Y content, however, is not regular; strangely enough, the highest temperature factors occur in crystal 2, not in crystal 1, which is the richest in Y. Discordant values are also obtained for temperature factors concerning oxygen: here again crystal 2 seems to show abnormally high values of temperature factors with respect to a possible uniform trend between samples 1 and 4. Such a discordance perhaps suggests the presence of systematic errors due to an unsatisfactory absorption correction. This is particularly likely for crystal 1, which is larger than the others and more irregular and contains relatively large amounts of heavy elements; Table 4 shows the definite improvement of the agreement between equivalent reflections after applying the Walker and Stuart (1983) technique. In spite of all these difficulties, however, the increase of temperature factors on increasing the Y content seems to be evident. Moreover, in all the crystals here examined, the motion of O(1) appears to be increased mainly perpendicularly to the Si–O bonds. According to various authors (Hirshfeld, 1976; Rosenfield et al., 1978), for a "true" thermal motion, the components of temperature factors should be smaller along the chemical bonds and larger perpendicularly to the bonds, just as here. Therefore, a larger amplitude of motion results on replacing Sc by Y. Only a theoretical calculation of temperature factors via lattice dynamics would exhaustively explain this phenomenon, but this calculation is at the border of feasibility at the present; however, if the increase of the unit cell is considered, the available space for atomic motion also increases.

In short, the "compactness" of the thortveitite structure, and in particular that of the pure Sc compound with a smaller unit cell, is probably also the reason for the "linear" or nearly linear conformation for the Si_2O_7 group, despite the minimum-energy requirement that would indicate a "bent" conformation (Meagher et al., 1979; Gibbs et al., 1981). Since the interactions between the various atoms are strong in thortveitite owing to the considerably covalent character of all the X–O bonds and since the difference in energy between all the more or less "bent" disiloxy group conformations is relatively small, here the Si–O–Si angle is easily constrained from its minimum-energy value to linearity. This is probably the most surprising feature in such a structure. At the beginning of our study, the possibility of statistical disorder simulating high thermal motion, with a Si–O–Si angle significantly different from 180°, was considered by us as likely. In the "pure" crystal (no. 4), however, although some temperature factors are relatively high (with a maximum of U_{22} for O(1) = 0.0369 Å^2), such values are in the same range as values relative to oxygen atoms of other silicates, which are regarded as ordered (see, for instance, hemimorphite as determined by McDonald and Cruickshank, 1966).

Consequently, with the present data, which do not show any resolution of possible double peaks, we cannot ascertain whether the relatively high value of U_{22} is due to disorder (involving a nonlinear conformation of the disiloxy group), or rather to a "soft" mode of vibration. In any case, however, the situation in thortveitite is not significantly different from a number of other compounds, where terminal vibration cannot be distinguished from disorder, even theoretically.

In spite of the value close to 180° for the bridging Si–O–Si angle, the corresponding value of the Si–O bond length (1.607 Å) practically corresponds to the "absolute" minimum-energy value for the most energetically favorable "bent" conformation of the disiloxy group.

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